

## Supplementary Information

# Estimation of Rate Constants for Reactions of Organic Compounds Under Atmospheric Conditions

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## S1. Additional Discussion

### S1.1. Database

The derivation of estimation methods such as those discussed in this work requires as large and comprehensive a database as possible. We used a total of 1911 different rate constants, or 853 for OH, 421 for Cl, 331 for NO<sub>3</sub>, and 40 for O<sup>3</sup>P. The numbers of the various types of compounds, and how the data were used in this study, are shown graphically in Figure S1. The rate constants for reactions with OH, NO<sub>3</sub>, O<sub>3</sub>, and Cl atoms were taken from the compilation of McGillen et al (2020), which was constructed for the purpose of SAR development as part of the work of the Structure-Reactivity Evaluation panel discussed by Vereecken et al (2018). This is probably the largest database of experimental data for rate constants for reactions of organics with these oxidants available in computer readable form, and incorporates evaluated and summarized rate constants in the reviews of Calvert et al (2000, 2002, 2011, 2015) and the IUPAC (2019) and JPL (2015), and results from a number of publications that were omitted or too recent for these reviews. Note that the database includes a recommended 298K rate constant and (if available) a set of Arrhenius parameters for each compound for which sufficient data are available. Rate constants for O<sup>3</sup>P reactions were not included in the McGillen et al (2020) compilation, so the O<sup>3</sup>P rate constants and temperature dependences used previously when developing the estimates for the SAPRC-07 mechanism (Carter, 2010a,b) were used in this work with some updates. The sources of these rate constants are given in footnotes to Table S25. Although McGillen et al (2020) included uncertainty estimates for most of the rate constants, measurement uncertainty weighting was not used when deriving best fit parameters for this study, and each of the 1197 rate constants used for parameter derivation were weighted equally.

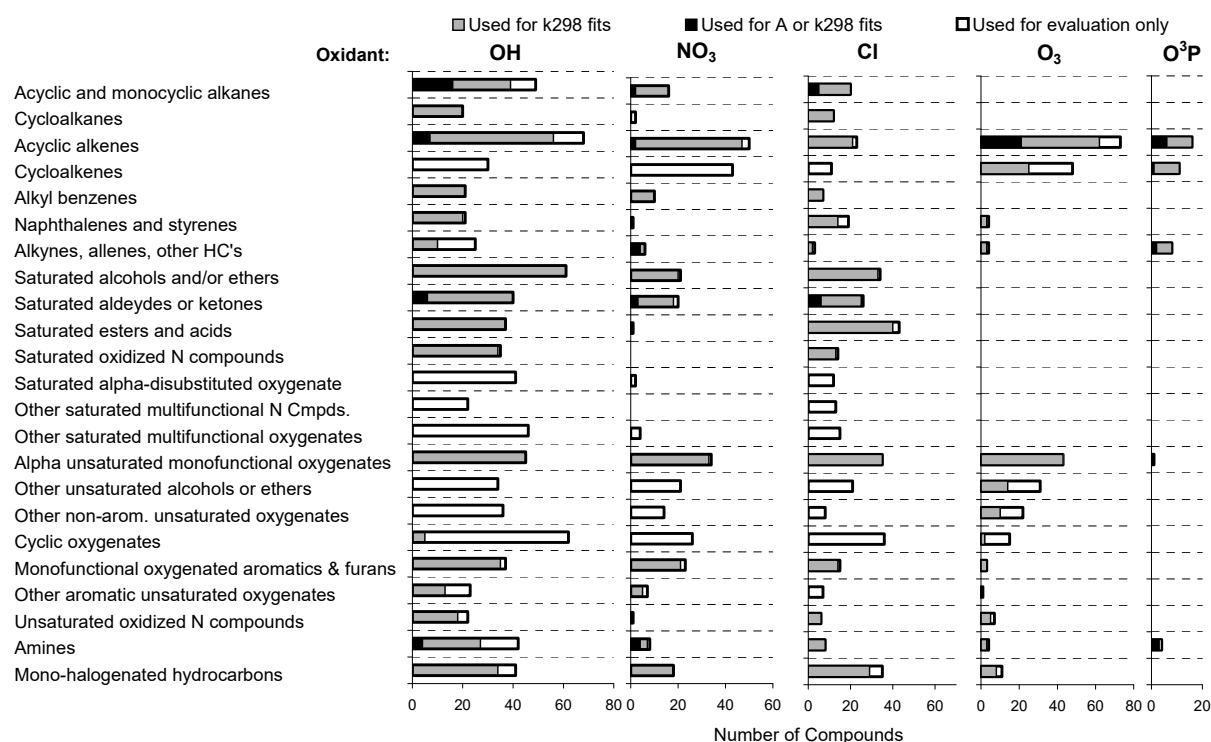


Figure S1. Numbers of compounds of various types whose rate constant with rate constant data for various oxidants used in this work.

## S1.2. Implementation and Optimization Procedures

The structure-reactivity estimation procedures discussed in this work were implemented and tested using the SAPRC mechanism generation system (MechGen), which is accessible online (Carter, 2021) and described by Carter (2020). Given the structure of the compound and the type of reaction to generate, MechGen incorporates the various estimation procedures and parameters discussed in this work to derive estimated rate constants for the various possible reaction routes as the first step of generating a mechanism for the compound (Carter, 2020). For this purpose, molecules are broken down into "groups" that consist of portions of the molecules for which the structure-reactivity parameters are defined. The groups supported by this work are listed in Table 1 in the main text, and these group designations are used where applicable in the tables of parameters given in Section 0. Note that MechGen also supports specifications of structures of molecules with other groups and atoms other than C, H, O, or N, such as halogens, but does not yet estimate rate constants or generate reactions for them.

The various parameters used in the estimation methods are maintained and organized in an Excel spreadsheet file, which is also used to organize and analyze the results and quantify and summarize how well the estimates agree with the experimental data. Macros in this Excel file are used to produce a text file that can be input into MechGen, giving not only the parameter values, but also information about where these parameters are contained within the spreadsheet file. In addition, separate sheets in the Excel file have lists of compounds with their measured rate constants for the various reactions, and these lists can be input into MechGen in order to obtain rate constant estimates for the full set of compounds in batch mode. MechGen then outputs a file containing not only the estimated rate constants for the selected type of

reaction, but also Excel calculation information that can be used to calculate the rate constants within Excel, using the current parameter values in the spreadsheet. Once this is loaded into the Excel file, this calculation information allows the effects of changing any of the parameters on the estimated rate constants to be readily determined. This allows parameters to be optimized to improve agreements with the experimental rate constants contained within the spreadsheet. In most cases Excel's Solver function was used for the optimization, though in some cases the parameters could be derived from a single rate constant. The rate constant values that are provided by MechGen along with the calculation information are used to verify that the calculations within Excel agree with those derived by MechGen when the same parameter values are used.

The quality of the fits of estimated to experimental rate constants are measured by the sum of squares of the differences of the logs of the rate constants,

$$\text{Total Error} = \sum_{\text{compounds}} \{ \ln [k(\text{estimated})] - \ln [k(\text{experimental})] \}^2$$

where "compounds" refers to sets of rate constants used in the optimizations. This is the quantity that is minimized during the optimization procedures. This optimization is carried out in a stepwise manner by grouping compounds and parameters according to the types of reactions they may undergo and parameters required, and by uncertainty considerations. The sets of parameters involving the least uncertainty and that can be derived independently of other parameters using an appropriate set of compounds are derived first, and these are held at the optimized values when the other parameters are optimized in subsequent steps, using rate constants that may also require parameters that were previously optimized as well as an appropriate set of additional parameters. Some sets of parameters can be determined independently using appropriate compounds, but optimizations of others are affected by values used by other types of parameters. Compounds where estimates are particularly uncertain (e.g., multifunctional or polycyclic compounds, compounds with separated double bonds or reactive substituents, cyclic compounds with substituents for which data are insufficient to derive ring corrections, etc.) were not used in the optimizations unless sufficient data were available for unambiguous optimizations of the parameters involved.

The groups of parameters, and the compounds whose data were used to derive these parameters, are listed on Table S1 through Table S5. The tables also indicate the order that the parameters were optimized. Table S6 gives the designations, types, and descriptions of the parameters that are summarized on these tables, and also indicates the equations in the main text where they are used. Note that the parameters listed there are the only parameters derived by optimization, which are only a subset of all the parameters required. Most of the other parameters are assumed to be the same as or are derived from values derived for the optimized parameters, though a few are estimated or derived separately. The methods used to derive values for the other parameters are indicated in footnotes to the tables of parameters given in Section 0, where the parameter values are summarized.

The individual compounds used in the parameter optimizations, and the categories assigned to them, are given on the tables of estimated and experimental rate constants in Section S3, in the sections titled "Used for parameter derivations". The compounds not used for optimizations are given in the sections of these tables "Used for evaluations only". In most cases, these are compounds whose rate constants depend on multiple parameters and groups or and/or on structural characteristics whose interactions are too uncertain to use for optimizations, as discussed in the main text.

A few additional rate constants in the McGillen et al (2020) database were also excluded from the optimizations because they were judged to be unrepresentative of compounds for which estimates are of interest, or because discrepancies between experimental and estimated rate constants suggest steric effects or other factors that are not being taken into account, or because the experimental measurements are questionable. Examples of the unique simple compounds that are not, or may not be, representative of the larger compounds where estimates are needed include formaldehyde, glyoxal, formic acid and glyoxalic acid. Examples of unsubstituted compounds where inclusion in the optimization sets results in poorer predictions for the substituted compounds that are of greater interest for estimates include furan for Cl and NO<sub>3</sub> estimates and naphthalene for Cl estimates. Compounds where unaccounted-for steric effects may be affecting the rate constant, resulting in underpredictions of rate constants for the estimates, were t-butyl formate and t-butyl acetate in the case of Cl estimates and 3,4-diethyl hexane in the case of O<sub>3</sub>.

In addition, a small number of rate constants were excluded from the optimizations because of possible measurement errors. The rate constants for NO<sub>3</sub> + eugenol and 4-ethylguaicol reported by Zhang et al (2016) were excluded from the optimizations because they were significantly lower than rate constants for similar compounds reported in other studies, and could be affected experimental difficulties. That study used the same method that was used by to obtain a rate constant for guaicol (Yang et al, 2016) that was significantly lower than measured by Lauraguais et al (2016), who discussed possible problems with the with the method employed by the other group. In addition, the rate constant for NO<sub>3</sub> + isopropenyl acetate was excluded from the optimization because it was inconsistent with estimates for other compounds for reasons that are unknown. Note that only these few compounds were excluded from the optimizations based on poor performance of the estimation methods; most were excluded based on decisions made before the optimization results were known.

Table S1. List of optimized parameters and groups of compounds used to derive them for estimation of reactions with OH.

Compounds and Parameters [a]	Compounds and Parameters	Compounds and Parameters
1. Acyclic alkanes Abs[CH3] Abs[CH2] Abs[CH] AbsF[-CH2-] / CH3 AbsF[>CH-] / CH3 AbsF[>C<] / CH3	6. (continued) AbsF[-O-] / CH2 AbsF[-O-] / CH AbsF[-CH2-CO-] / CH3 AbsF[-O-CO-] / CH3 AbsF[-O-CHO] / CH3 AbsF[-CHO] / CHO AbsF[-CO-CO] / CHO AbsF[-CO-] / CHO AbsF[-CO-O-] / CH3 AbsF[-O-CO-O-] / CH3 AbsF[-CH2-OH] / CH3	11. Substituted aromatics AddF[-OH] / M AddF[-OH] / P AddF[-OH] / Ip Add[aC(OH)] Add[aC(aCOH)] Add[aCH(aCOH)] Abs[HO-aC<] AddF[-CHO] / O AbsF[aro] / CHO AddF[-OH] / O AddF[-O-] / O AddF[-NO2] / O
2. Cyclic alkanes Ring[3] / Alk Ring[4] / Alk Ring[5] / Alk	7. Acyclic Saturated nitrates AbsF[-NO2] / CH3 AbsF[-ONO2] / CH3 AbsF[-CH2-ONO2] / CH3 AbsF[-CH2-NO2] / CH3 AbsF[-ONO] / CH2 AbsF[>CH-NO2] / CH3	12. PAHs Add[aP]  AddF[aro] / O AddF[aro] / M AddF[aro] / P
3. Acyclic alkenes Add[C=(CH*)] Add[CH2=(CH)] Add[CH=(CH)]  Add[CH2=(C)] Add[CH=(C)] Add[C=(C)]  Add[CH2=(CH*)] Add[CH=(CH*)] Add[CH2=(C*)] Add[CH=(C*)] Add[C=(C*)]	8. Amines Add[-NH2] Add[-NH-] Add[-N<] Add[-NH2(CO)] Add[-NH(CO)-] Add[-N(CO)<]	13. Saturated monohalogenated AbsF[-CH2-Cl] / CH3 AbsF[-CH2-Br] / CH3 AbsF[-CH2-F] / CH3 AbsF[-F] / CH3 AbsF[-Cl] / CH3 AbsF[-BR] / CH3 AbsF[-I] / CH3
4. Allenes and alkynes Add[CH≡C] Add[C≡C]  Add[C=(CH2)(=CH)] Add[C=(CH2)(=C)] Add[C=(CH2)2]	9. Unsaturated oxygenates AbsF[=CH-] / CHO AddF[-CHO] / F1 AddF[-CO-O-ONO2] / F1 AddF[-CO-OH] / F1 AddF[-CO-O-] / F1 AddF[-CO-] / F1 AddF[-O-CO-] / F1 AddF[-CO-O-] / F2 AddF[-O-CO-] / F2 AddF[-O-] / F1 AddF[-O-] / F2 AddF[-O-(=CHx)] / F1 AddF[-NO2] / F1 AddF[-CH2-NO2] / F1 AddF[-CH2-ONO2] / F1 AddF[-CO-] / F2	14. Unsaturated monohalogenated AddF[-F] / F1 AddF[-F] / F2  AddF[-Cl] / F1 AddF[-Cl] / F2 AddF[-F] / O AddF[-Cl] / O  AddF[-BR] / O AddF[-BR] / F1 AddF[-CH2-F] / F1
5. Aromatic hydrocarbons Add[aC] AddF[-CH3] / O AbsF[aro] / CH2		15. Styrenes AddF[aro] / F2 AddF[aro] / F1
6. Acyclic Saturated oxygenates Abs[HCO-O] AbsF[-O-OH] / CH3 Abs[CHO] Abs[HO-CO-] Abs[HO-O-] AbsF[-CH2-] / CHO AbsF[>CH-] / CHO AbsF[>C<] / CHO AbsF[-OH] / CH2		16. Cyclic oxygenates Ring[4] / CO Ring[5] / CO Ring[6] / CO



AbsF[-OH] / CH	10. Unsaturated nitro	Ring[3] / O
AbsF[-CO-] / CH3	AddF[-CH2-ONO2] / F1	
AbsF[-CO-] / CHO	AddF[-CH2-NO2] / F1	
AbsF[-O-] / CH3	AddF[-NO2] / F1	

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[a] See Table S6 for a description of the parameter codes used on this table.

Table S2. List of optimized parameters and groups of compounds used to derive them for estimation of reactions with NO<sub>3</sub>.

Compounds and Parameters [a]	Compounds and Parameters	Compounds and Parameters
1. Acyclic alkanes AbsF[-CH <sub>2</sub> -] / CH <sub>3</sub> Abs[CH <sub>2</sub> ] Abs[CH] AbsF[>CH-] / CH <sub>3</sub> AbsF[>C<] / CH <sub>3</sub>	4. (continued) Abs[CH-O-] AbsF[-CH <sub>2</sub> -] / CHO AbsF[>C<] / CHO AbsF[-CHO] / CHO AbsF[-CO-] / CHO AbsF[-CH <sub>2</sub> -OH] / CH <sub>3</sub> AbsF[>CH-] / CHO	7. Aromatic aldehydes, phenols AddF[-OH] / O AddF[-OH] / P Abs[HO-aC<] AddF[-CHO] / O Add[aC(OH)] Add[aC(aCOH)] AddF[-O-] / O AddF[-CHO] / P AddF[-O-] / P
2. Acyclic alkenes AddSizeCorr Add[CH <sub>2</sub> =(CH)] Add[CH=(CH)] Add[CH <sub>2</sub> =(C)] Add[CH=(C)] Add[C=(C)] Add[CH <sub>2</sub> =(CH*)]  Add[CH=(CH*)] Add[CH <sub>2</sub> =(C*)]	5. Unsaturated oxygenates AddF[-CHO] / F1 AddF[-CHO] / F2 AddF[-O-(=CH <sub>x</sub> )] / F1 AbsF[=CH-] / CHO AddF[-CO-] / F1 AddF[-CO-O-ONO <sub>2</sub> ] / F1 AddF[-O-] / F2 AddF[-CO-O-] / F1 AddF[-O-CO-] / F2 AddF[-CO-O-] / F2 AddF[-CO-] / F2	8. Amines and amides Add[-N(CO)<] Add[-NH(CO)-]  9. Halogenated compounds AddF[-F] / F1 AddF[-Cl] / F1 AddF[-BR] / F1 AddF[-CH <sub>2</sub> -F] / F1 Add[I]
3. Alkynes Add[CH≡(C)] Add[C≡(CH)] Add[C≡(C)]		
4. Acyclic Saturated oxygenates Abs[CH <sub>3</sub> -C-O-] Abs[CH <sub>2</sub> -C-O-] Abs[CH <sub>2</sub> -OH] Abs[CH-OH] Abs[CH <sub>3</sub> -O-] Abs[CH <sub>2</sub> -O-]	6. Alkylbenzenes and styrene Add[aC] AddF[-CH <sub>3</sub> ] / O AddF[aro] / F2 AddF[-CH <sub>3</sub> ] / P Add[aCH]	AddF[-CH <sub>2</sub> -Cl] / F1 AddF[-CH <sub>2</sub> -Cl] / F2 AddF[-CH <sub>2</sub> -Br] / F1

[a] See Table S6 for a description of the parameter codes used on this table.

Table S3. List of optimized parameters and groups of compounds used to derive them for estimation of reactions with Cl.

Compounds and Parameters	Compounds and Parameters	Compounds and Parameters
1. Acyclic alkanes Abs[CH3] Abs[CH2] Abs[CHF2] Abs[CH]	7. Halogenated formates Abs[HCO-O]	11. Substituted aromatics AddF[-OH] / O AddF[-CHO] / O AddF[-NO2] / O
2. Cyclic alkanes Ring[3] / Alk Ring[4] / Alk Ring[5] / Alk	8. Acyclic Saturated CO, O AbsF[-CO-CO] / CHO Abs[CHO] AbsF[-CHO] / CH3 AbsF[-CHO] / CH2 AbsF[-CO-] / CH3 AbsF[-CO-] / CH2 AbsF[-CHO] / CHO AbsF[-CO-CO] / CH3 AbsF[-CO-CO] / CH2 AbsF[-O-CO-] / CH3	12. Furans AddF[-O-(=CHx)] / F1
3. Acyclic alkenes Add[CH2=(CH)] Add[CH=(CH)] Add[CH2=(C)]  Add[CH=(C)]	AbsF[-O-CHO] / CH3 AbsF[-O-OH] / CH2 AbsF[-O-CO-] / CH2 AbsF[-O-CHO] / CH2 AbsF[-CO-O-] / CH3 AbsF[-CH2-CO-] / CH3 AbsF[>CH-CO-] / CH3 AbsF[>C<CO-] / CH3 AbsF[-CH2-CO-] / CH2 AbsF[-O-CO-O-] / CH3	13. Amines Add[-NH2] Add[-NH2(CO)] Add[-NH(CO)-] Add[-N(CO)<] Add[-NH-] Add[-N<]
4. Aromatic hydrocarbons Add[aCH] Add[aC] AddF[-CH3] / O AbsF[aro] / CH3	9. Acyclic Saturated nitrates AbsF[-CH2-ONO2] / CH3 AbsF[>CH-ONO2] / CH3 AbsF[-ONO2] / CH2 AbsF[-CH2-NO2] / CH3	14. Allenes, alkynes, conj alkenes Add[C=(CH2)2] Add[CH≡(CH)] Add[CH2=(CH*)] Add[CH2=(C*)]
5. Naphthalenes Add[aP] AddF[aro] / O	10. Unsaturated oxygenates AddF[-CHO] / F1 AddF[-CO-] / F1 AddF[-O-CO-] / F1 AddF[-O-] / F1 AbsF[=CH-] / CHO	15. Monohaloalkanes AbsF[-CH2-Cl] / CH3 AbsF[-CH2-Br] / CH3 AbsF[-CH2-F] / CH3 AbsF[-F] / CH2 AbsF[-Cl] / CH2  AbsF[-BR] / CH3 AbsF[-I] / CH3
6. Acyclic Saturated O, OH AbsF[-OH] / CH3  AbsF[-OH] / CH2 AbsF[-OH] / CH AbsF[-O-OH] / CH3 AbsF[-O-] / CH3 AbsF[-O-OH] / CH2 AbsF[-O-] / CH2 AbsF[-CH2-OH] / CH3 AbsF[>CH-OH] / CH3 AbsF[>C<OH] / CH3		16. Saturated Halogenated AbsF[-CH2-Cl] / CHO
		17. Unsaturated halogenated AddF[-F] / F1 AddF[-CH2-Cl] / F1 AddF[-CH2-F] / F1 AddF[-Cl] / F1

[a] See Table S6 for a description of the parameter codes used on this table.

Table S4. List of optimized parameters and groups of compounds used to derive them for estimation of reactions with O<sub>3</sub>.

Compounds and Parameters	Compounds and Parameters	Compounds and Parameters
1. Acyclic alkenes Add[CH <sub>2</sub> =CH-CH=CH] Add[CH <sub>2</sub> =C-CH=CH <sub>2</sub> ] Add[CH <sub>2</sub> =C-CH=CH] Add[CH <sub>2</sub> =C-C=CH <sub>2</sub> ] Add[CH=CH-CH=CH] Add[C=CH-CH=C] Add[CH <sub>2</sub> =CH] Add[CH <sub>2</sub> =C] Add[cis-CH=CH] Add[trans-CH=CH] Add[CH=C] Add[C=C] BrCorr	2. (continued) Add[C=CH-CO-O-] Add[CH <sub>2</sub> =CH-CO-] Add[CH <sub>2</sub> =C-CO-] Add[CH=CH-CO-] Add[CH=C-CO-] Add[C=CH-CO-] Add[CH <sub>2</sub> =CH-O-CO-] Add[CH <sub>2</sub> =C-O-CO-] Add[CH <sub>2</sub> =CH-O-] Add[CH <sub>2</sub> =C-O-] Add[CH <sub>2</sub> =CH-CO-OH] 3. Cycloalkenes Ring[6] / Add-S Ring[5] / Add-S Ring[6] / Add-C Ring[7] / Add-S Ring[8] / Add-S Ring[7] / Add-C 4. Beta-substituted oxy, nitro alkenes AddF(CH <sub>x</sub> -OH) AddF(CH <sub>x</sub> -ONO <sub>2</sub> ) AddFo(O) AddFc(CO) AddF(CH <sub>x</sub> -OH)	4. (continued) AddF(CH <sub>x</sub> -O-) AddF(CH <sub>x</sub> -CHO) AddF(CH <sub>x</sub> -CO-) AddF[-NO <sub>2</sub> ] 5. Furans Furan Furan(1sub) Furan(2sub) 6. Alkynes Add[CH≡CH] Add[CH≡C] 7. Styrenes AddF[aro] 8. Amines Add[-NH <sub>2</sub> ] Add[-NH-] Add[-N<] 9. Monohalogenated AddF[-F] AddF[-Cl]
2. Unsaturated oxygenates and nitrates Add[CO <sub>x</sub> -CH <sub>x</sub> =CH <sub>x</sub> -CO <sub>x</sub> ] Add[CH <sub>2</sub> =CH-CHO] Add[CH <sub>2</sub> =C-CHO] Add[CH=CH-CHO] Add[C=CH-CHO] Add[CH=C-CHO] Add[CH <sub>2</sub> =C-CO-OH] Add[CH <sub>2</sub> =CH-CO-O-] Add[CH <sub>2</sub> =C-CO-O-] Add[CH=CH-CO-O-]		

[a] See Table S6 for a description of the parameter codes used on this table.

Table S5. List of optimized parameters and groups of compounds used to derive them for estimation of reactions with O<sup>3</sup>P.

Compounds and Parameters	Compounds and Parameters	Compounds and Parameters
1. Acyclic alkenes Add[CH <sub>2</sub> =CH-CH=CH <sub>2</sub> ] Add[CH <sub>2</sub> =CH] Add[CH <sub>2</sub> =C] Add[CH=CH]  Add[CH=C] Add[C=C] Add[CH <sub>2</sub> =C-CH=CH <sub>2</sub> ]	2. Allenes Add[CH <sub>2</sub> =C=CH <sub>2</sub> ] Add[CH <sub>2</sub> =C=CH] Add[CH <sub>2</sub> =C=C] Add[CH=C=CH] 3. Acyclic unsaturated oxygenates Add[CH <sub>2</sub> =CH-CHO]	4. Monoalkynes Add[CH≡CH] Add[CH≡C] Add[C≡C] 5. Alkyl amines Add[-NH <sub>2</sub> ] Add[-NH-] Add[-N<] 6. Cycloalkenes Add[cyc-CH=CH]

[a] See Table S6 for a description of the parameter codes used on this table.

Table S6. Descriptions and types of parameters listed in Table S1 through Table S5 and the equations in the main text where they are used.

Designation	Type	Description	Equation
Abs[G <sub>1</sub> ]	kH <sup>base</sup>	Base rate constant for H-abstraction from group G <sub>1</sub>	(1)
AbsF[G <sub>1</sub> ] / G <sub>2</sub>	FH <sup>nhr</sup>	Substituent correction factor for substituent group G <sub>1</sub> for H-abstractions from group G <sub>2</sub>	(2-3)
Ring[n] / type	FH <sup>struct</sup>	Correction factor for abstraction from a group in an n-member ring. Types are "CO" for addition to a ring with a CO group, "O" for a ring with an ether group, or "alk" for rings not containing these groups (or any ring for Cl)	(1)
Add[G <sub>1</sub> =(G <sub>2</sub> )] Add[G <sub>1</sub> ≡(G <sub>2</sub> )]	kA <sup>base</sup>	Base rate constant for addition of a radical to group G <sub>1</sub> when bonded to group G <sub>2</sub> by a double (=) or triple (≡) bond	(4)
Add[G <sub>1</sub> =(G <sub>2</sub> *)]	kA <sup>base</sup>	Base rate constant for addition of a radical to group G <sub>1</sub> when bonded to group G <sub>2</sub> by a double bond, where the radical formed on group G <sub>2</sub> is allylic	(4)
AddF[G <sub>1</sub> ] /F1 AddF[G <sub>1</sub> -G <sub>2</sub> ]	FA <sub>1</sub> <sup>nbr</sup>	Addition correction factor for substituent G <sub>1</sub> bonded to the group where the addition occurs. The presence of a second group bonded to G <sub>1</sub> indicates a β-substituent effect.	(4)
AddF[G <sub>2</sub> ] /F2	FA <sub>2</sub> <sup>nbr</sup>	Addition correction factor for substituent G <sub>2</sub> on the other side of the bond where the addition occurs	(4)
Add[C(=G <sub>1</sub> )(=G <sub>2</sub> )]	kCA	Base rate constant for addition to G <sub>2</sub> in an G <sub>1</sub> =G <sub>2</sub> =G <sub>3</sub> allene system	(5)
AddSizeCorr	FS <sup>NO3</sup>	Size correction parameter used when estimating additions of NO <sub>3</sub> to double bonds	(6)
Add[G <sub>1</sub> =G <sub>2</sub> ] Add[G <sub>1</sub> =G <sub>2</sub> -G <sub>3</sub> =G <sub>4</sub> ] Add[G <sub>1</sub> =G <sub>2</sub> -X] Add[G <sub>1</sub> ≡G <sub>2</sub> ]	kA' <sup>base</sup>	Base rate constant for addition of O <sub>3</sub> or O <sup>3</sup> P to the indicated double (=) or triple (≡) bond structure. Note that "X" is an oxygenated group or sequence of oxygenated groups bonded to G <sub>2</sub> .	(7)
AddF[G <sub>1</sub> ] AddF[G <sub>1</sub> -G <sub>2</sub> ]	FA' <sup>nbr</sup>	Addition correction factor for group G <sub>1</sub> bonded to a double or triple bond structure. The presence of a second group bonded to G <sub>1</sub> indicates a β-substituent effect.	(7)
Ring[n] / Add-S Ring[n] / Add-C	FA' <sup>struct</sup>	Ring correction factor for addition to a double bond structure in a ring. "Add-S" and "Add-C" indicate additions to a separated or conjugated double bond structure.	(7)
BrCorr	Fβ <sup>O3</sup>	Branched structure correction for O <sub>3</sub> additions	(8)
Add[G <sub>1</sub> ]	kAro <sup>base</sup>	Base rate constant for addition to aromatic rings. Note that the designation "aP" refers to a group in more than one aromatic ring in a polycyclic aromatic compound.	(9)
AddF[G <sub>1</sub> ] /O AddF[G <sub>1</sub> ] /M AddF[G <sub>1</sub> ] /P AddF[G <sub>1</sub> ] /Ip	FA <sup>ortho</sup> FA <sup>meta</sup> FA <sup>para</sup> FA <sup>ipso</sup>	Substituent correction factor for the presence of group G <sub>1</sub> in the ortho, meta, para, or ipso positions, respectively, of an aromatic ring relative to the group where the addition occurs	(9)

Add[NH <sub>x</sub> ]	kA	Rate constant for addition to an amino, amide or iodo group	(10)
Add[NH <sub>x</sub> (CO)]		(no correction factors used)	
Add(I)			

### S1.3. Abstraction Substituent Corrections for Multiple $\alpha$ Substituents

Some groups where abstraction reactions can occur can have two or three substituents, and multiplying the factors for the different groups may overestimate effects of multiple substituents that have both very high or very low factors. In a few cases there are sufficient data available to derive correction factors for pairs of substituents, as is the case for reactions of OH with carbonyl and hydroxyl nitrates,  $\alpha$ -hydroxy ketones, and  $\alpha$ -diethers, as shown on Table S7. Figure S2 shows plots of the pair factors estimated in different ways from the factors for the individual substituents against those that were directly derived by optimization. The results indicate that the products of the factors for the individual substituents best predict the pair optimized values when the product is less than one but that the average performs better when the product is greater than one. In other words, the product of the factors appear to perform better when the substituents inhibit the reaction, while the average is better if they both enhance the estimated rate constant. The data are ambiguous as to the best approach if one enhances and the other inhibits.

Based on these results in and other considerations, the following method is used to estimate correction factors for abstraction from groups with multiple substituents: Hydrocarbon groups and groups with single-group correction factors of 1 (i.e., no correction) are classified as "type 1" and all others are classified as "type 2". If there is no more than one type 1 substituent, the overall correction factor for all substituents is derived by just multiplying the single-group factors for the substituents as given on Table S12 through Table S14. If there are more than one type 2 substituent next to the reaction site, a single correction factor is derived for these two or three type 2 substituents, which is used in Equation (4) in the main text along with correction factors for any type 1 substituents that may also be present. If there are two or more type 2 substituents, the maximum of the single substituent factors are used for the pair if they are both  $>1$ , the minimum is used if they are both  $<1$ , and the average is used if one is  $>1$  and one is  $<1$ . If there is a third type 2 substituent, then the minimum or maximum is used if they are all  $<1$  or  $>1$ , respectively, or the average of the minimum and maximum is used otherwise. This approach gives the best fits to the pair factors listed on Table S7 in most (though not all) cases, as shown on Figure S2.

Table S7. Abstraction correction factors for pairs of groups that best fit the data for  $\alpha$ -disubstituted bifunctional compounds, and estimated pair factors derived from the correction factors of the two groups.

Reaction with	Group 1		Group 2		Pair Factor			
	Group	F1	Group	F2	Best Fit	F1 * F2	Average	Est. Used
OH	-O-	9.5	-O-	9.5	4.3	90	9.5	9.5
OH	-OH	3.9	-CO-	1.0	5.7	3.8	2.4	2.4
OH	-CH <sub>x</sub> - (ONO <sub>2</sub> )	3.9	-OH	0.4	2.9	1.42	2.2	2.2
Cl	-OH	1.31	-CO-	0.64	0.78	0.83	0.97	0.83
OH	-CO-	0.95	-ONO <sub>2</sub>	0.14	0.38	0.13	0.55	0.13
OH	-Cl	0.27	-Cl	0.27	0.118	0.075	0.27	0.075

OH	-Br	0.25	-Br	0.25	0.130	0.061	0.25	0.061
OH	-F	0.163	-F	0.163	0.013	0.027	0.163	0.027
Cl	-Cl	0.081	-Cl	0.081	0.005	0.007	0.081	0.007

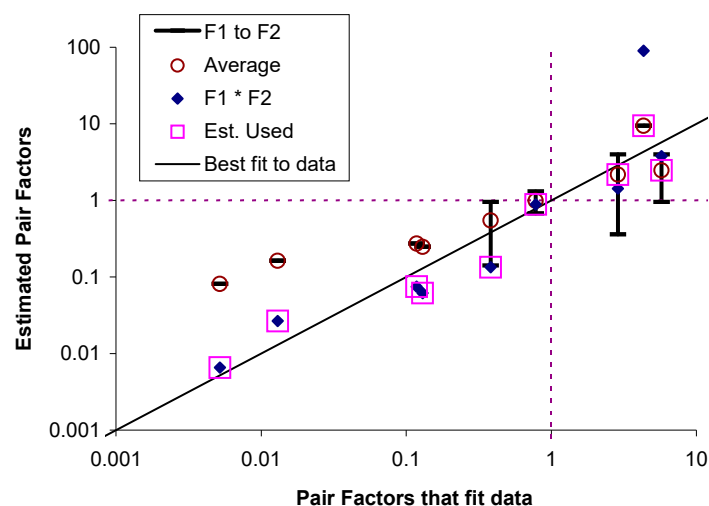


Figure S2. Plots of estimated abstraction correction factors for pairs of groups derived using different methods against pair factors that gave best fits to the data for reactions of OH and Cl with  $\alpha$ -disubstituted bifunctional compounds.

#### S1.4. Estimation of Parameters for NO<sub>3</sub> Reactions from those Derived for OH or Cl

Because of insufficient data or insensitivity of data to parameters, it was necessary to estimate a relatively large number of base rate constants or correction factors for NO<sub>3</sub> reactions, compared to those for OH or Cl reactions, where the kinetic database is more extensive or more sensitive to some of the parameters. However, many of these parameters for NO<sub>3</sub> reactions can be estimated using empirical relationships between the NO<sub>3</sub> parameters that could be derived, and those derived for the other reactions. The parameters that were estimated in this way included the base rate constants for H-abstraction from -CH<sub>3</sub> groups, rate constants for additions to certain separate conjugated and separate double bond groups, base rate constants for additions to certain amine or amide groups, and a number of substituent factors for H abstractions. These were derived as discussed below.

Base rate constants. The following linear free energy relationship was used to estimate base rate constants for NO<sub>3</sub> reactions from those derived for OH,

$$\text{Log}_{10} k^{\text{base}}(\text{NO}_3) = A + B \text{Log}_{10} k^{\text{base}}(\text{OH}) \quad (\text{S1})$$

where the rate constants are in cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> and A and B are empirical parameters derived to fit the data for the NO<sub>3</sub> parameters that could be derived from the kinetic data. The parameters that fit the data for the various types of reactions are as follows.

Reaction	A	B
H-abstractions from alkyl groups	11.79	2.39
Additions to separated double bonds	39.9	5.04
Additions to conjugated double bonds	36.58	4.77
Additions to amine or amide groups	7.66	0.59

Figure S3 shows the derived and estimated parameters and the various fit lines based on Equation (S1) that were used for base rate constants for H abstractions and additions to double bonds that were used in this work. In the case of additions amine or amide groups, the kinetic data for NO<sub>3</sub> reactions were insufficient to derive the "B" parameter needed for Equation (S1), so that was derived based on use of an analogue to Equation (S1) for Cl vs OH reactions, and assuming that the slope for the NO<sub>3</sub> reaction is the same. The derived and estimated parameters and fit parameters used in this case are shown on Figure S4.

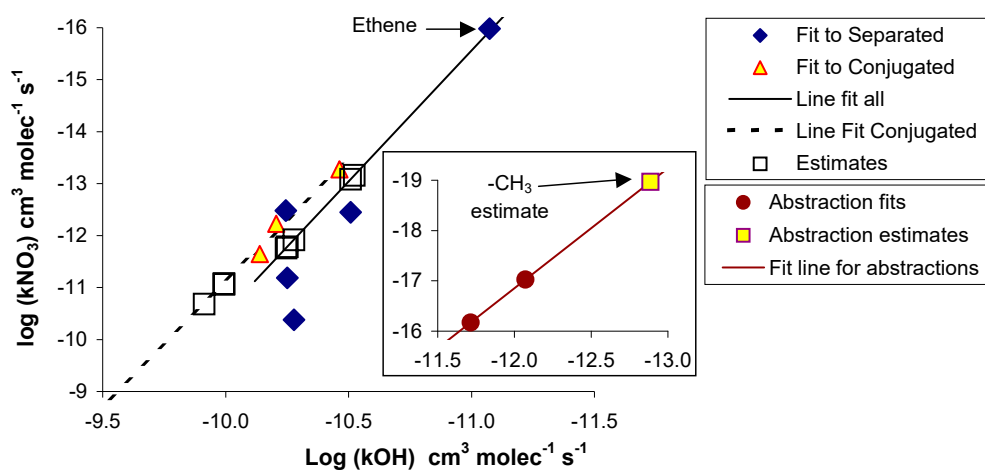


Figure S3. Plots of logs of base group addition rate constant parameters derived from the data for OH radical reactions against those derived or estimated for NO<sub>3</sub> radical reactions.



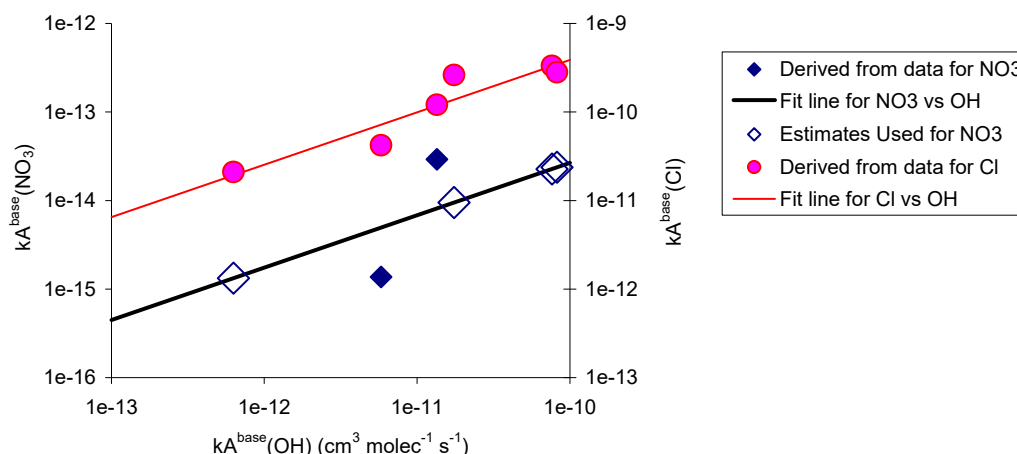


Figure S4. Plots of derived or estimated base rate constants for additions of Cl or NO<sub>3</sub> to amine or amide groups against the corresponding rate constants for OH.

Correction factors for H abstractions. The kinetic data were sufficient to derive substituent correction factors for H abstractions by NO<sub>3</sub> for only 5 types of substituents (see Table S14), while parameters for almost 50 types of substituents are required for comprehensive estimates. The data for the parameters that could be derived were reasonably well fit by the following equation

$$FH^{nbr}(\text{NO}_3) = 1.61 \times FH^{nbr}(\text{OH})^{0.81} \quad (\text{S2})$$

Where 1.61 and 0.81 are parameters derived to fit the data. This was then used to estimate substituent parameters for NO<sub>3</sub> abstractions that could not be derived from the kinetic data. The derived and estimated parameters and a plot of Equation (S2) are shown on Figure S5, and the resulting estimated parameter values are included on Table S14.

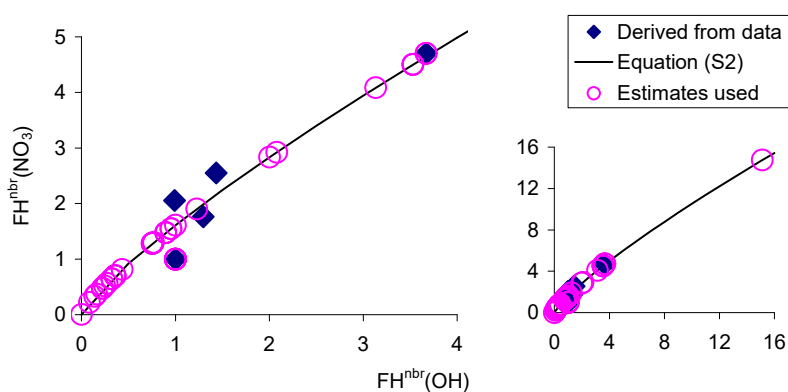


Figure S5. Plots of derived or estimated correction factors for H-abstractions by NO<sub>3</sub> against those derived for H-abstractions from OH.

### **S1.5. Ratios of Base Rate Constants for Radical Additions to Unsymmetrical Double Bonds**

As discussed in Section 3.2 of the main text, the kinetic data on the additions of radicals to double bonds of alkenes are insufficient to derive rate constant ratios for additions on different sides of unsymmetrical double bonds, so these have to be estimated. The estimates used to derive site-specific rate constants for mechanism generation purposes are listed on Table S8, along with footnotes indicating how they were derived. As indicated there, the ratios for OH reactions were derived by assuming the base rate constants for isolated bonds depended on the radical formed by the addition rather than the number of hydrogens on the group where the addition occurred, and those for conjugated double bonds are estimated based on and the ~5% yields of furan products from isoprene and 2,3-butadiene (Calvert et al, 2000). 100% addition to the most favorable position was assumed for NO<sub>3</sub> additions and equal addition to both positions was assumed for Cl additions, based on considerations of expected selectivity.

### **S1.6. Ring Corrections for O<sub>3</sub> Additions**

Table S19 shows ring corrections that were derived to fit the available rate constant data for reactions of O<sub>3</sub> with isolated, conjugated, and  $\alpha$ -substituted double bond structures. These factors are plotted against ring size on Figure S6. The data suggest no ring correction may be the least bad estimate for additions to separated bonds in 6-member rings, though there is variability by almost a factor of 10 if we include separated dienes, terpenes, and sesquiterpenes. The presence of the separated double bond in

Table S8. Derivation of ratios of base rate constants for additions of radicals to different types of double bonds.

Groups about bond [a]		$k^{\text{base}}(G_1, G_2) / [k^{\text{base}}(G_1, G_2) + k^{\text{base}}(G_2, G_1)]$ (%) [b]					
G <sub>1</sub>	G <sub>2</sub>	kOH		kNO <sub>3</sub>		kCl	
		Ratio	Notes	Ratio	Notes	Ratio	Notes
=CH <sub>2</sub>	=CH-	85%	1	100%	2	50%	3
=CH <sub>2</sub>	=C<	93%	1	100%	2	50%	3
=CH-	=C<	64%	4	100%	2	50%	3
=CH <sub>x</sub>	=CH <sub>x</sub> -*	95%	5	100%	2	90%	6
=CH-*	=C<*	50%	7	100%	2	50%	3

[a] "\*" indicates the group in conjugated alkenes that is bonded to another double bonded group.

[b] Footnotes indicating the derivation of the ratios used are as follows:

- 1 Derived by assuming that the base rate constant for OH addition to CH=(CH<sub>2</sub>) or C=(CH<sub>2</sub>) groups is the same as half the high pressure rate constant for OH addition to ethene at the high pressure limit, since -CH<sub>2</sub>· radicals are formed in both cases.
- 2 Addition by NO<sub>3</sub> radicals is expected to be more selective because of the lower rate constants compared to additions by OH or Cl, so it is assumed that all of the addition occurs at the most favorable, least substituted position.
- 3 Addition by Cl radicals is expected to be relatively fast and unselective, so it is assumed that addition to each side of the double bond occurs at equal rates.
- 4 Derived by assuming that the base rate constant for OH addition to C=(CH) groups is the same the base rate constant for addition to CH=(CH). since -CH(-)· radicals are formed in both cases.
- 5 Although most of the reaction is expected at the least substituted double bond because it forms an allylic radical, it is assumed that approximately 5% of the addition occurs on the other end in order to account for the observation and yields of furan products in the reactions of OH with 1,3-butadiene and isoprene (Calvert et al, 2000). Because of insufficient information, this ratio is used regardless of the number of hydrogens on the groups.
- 6 Because Cl addition is less selective than OH addition, the addition to the least favorable group is arbitrarily increased by a factor of 2 compared to the estimate used for OH.
- 7 Group rate constants for addition radicals forming allylic radicals are assumed to be the same regardless of the numbers of hydrogens on the group where the addition occurs (see Table S16).

a 5-, 7-, or 8-member ring appears to enhance the rate constant, though again there is significant variability. There are fewer data but less variability in the case of ring corrections for conjugated bonds, with significant enhancements for 6 member rings but reductions for 7 member rings. No data are available for other ring sizes, and the data are too variable for reliable extrapolations, so no corrections are used for such rings, and insufficient data are available for non-hydrocarbons, the estimates for such compounds must be considered to be highly uncertain. But given the variability, the estimates of O<sub>3</sub> addition rate constants even to

hydrocarbons with double bonds in 5-, 6- or 7-member rings must be considered to be uncertain by at least a factor of 10.

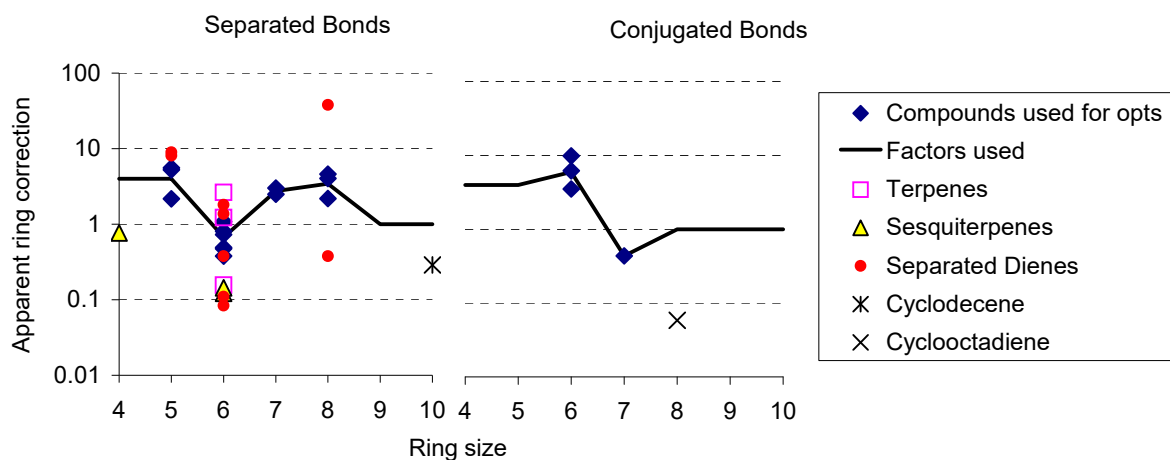


Figure S6. Plots of ratios of measured rate constants for O<sub>3</sub> addition to cyclic compounds relative to estimated rate constants without ring correction factors.

### S1.7. Estimation of Base Rate Constants for O<sub>3</sub> and O<sup>3</sup>P Additions

Estimates for O<sub>3</sub> + conjugated dialkenes. There are a total of 20 possible combinations of the three possible end groups (CH<sub>2</sub>=, -CH= and >C=) and two middle groups (-CH=, >C=) for conjugated dialkene systems, but available are sufficient to derive group parameters for only 7 of them; so estimates need to be made for the remaining 13. As shown on Figure S7, the base rate constants that can be derived from the data could be fit reasonably well with the empirically-derived formula

$$kA'^{\text{base}}(\text{CH}_w=\text{CH}_x-\text{CH}_y=\text{CH}_z) = 10^{-17.05 + 0.667 \{(2-w) + 0.27 [(1-x) + (1-y)] + (2-z)\}} \quad (\text{S3})$$

where the units of  $kA'^{\text{base}}$  are cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>,  $w$ ,  $x$ ,  $y$ , and  $z$  are the numbers of non-hydrogen substituents on the groups, and range from 0 to 2 for end groups and 0 to 1 for middle groups, and the numbers 29.25, 1.54, and 0.27 are parameters adjusted to fit the data for the 7 groups with data. Equation (S3)

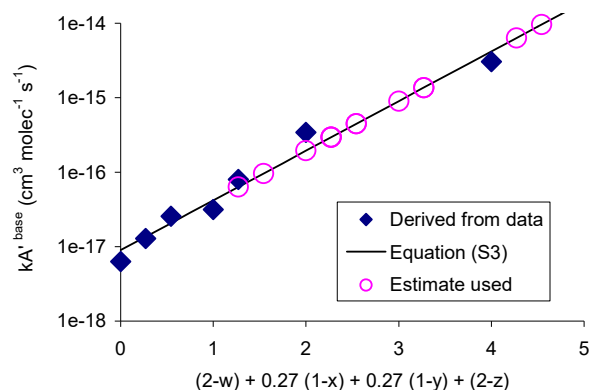


Figure S7. Plot of derived or estimated base rate constant for the additions of O<sub>3</sub> to conjugated double bond systems against parameters used to fit rate constant data according to Equation (S3).

was then used to estimate the base addition rate constants for the other 13 groups, as shown on the figure. Except for 1,3-butadiene, where a rate constant of  $6.3 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  (Calvert et al, 2015) was used, the derived and estimated base rate constants are included in Table S18.

Estimates for base addition rate constants for O<sub>3</sub> +  $\alpha$ -substituted double bonds. Separate base rate constants are assigned for double bond groups with  $\alpha$  aldehyde, ketone, ester, or acid substituents, and in each case separate estimates for the numbers of alkyl substituents around the double bonds, where there are 6 possibilities for each. The data are sufficient to derive base rate constants for 19 of these 36 cases, meaning that 17 have to be estimated (See Table S18). The available data for the substituents with sufficient data, including alkyl substituents, were reasonably well fit by

$$kA'_{\text{base}}(\text{CH}_x=\text{CH}_y\text{-X}) = 10^{-\text{Int}(\text{X}) + \text{Slope}(\text{X}) \{ \alpha + fB(\text{X}) \beta \}} \quad (\text{S4})$$

where

$$\alpha = 1-y; \quad \beta = 2-x$$

and X refers to an oxygenated substituent, Int(X), Slope(X), and fB(X) are parameters that are derived separately for each, as summarized on Table S9. As indicated on the "Notes" column, the data were insufficient to optimize all these parameters and all cases, and assumptions or estimates were made for some of the Slope or fB parameters for substituents for insufficient data. Figure S8 shows plots of derived and estimated base rate constants and Equation (S4) for monoalkenes and the six type of  $\alpha$ -oxygenated substituents for which base rate constants are derived. The estimated base rate constants are included in Table S18 in Section S3.

Estimates for O<sup>3</sup>P additions to double bonds. There are sufficient rate constant data to derive base rate constants for only 12 of the 68 types of double bond systems where base rate constants are estimated. The remainder were estimated by assuming linear relationships between the base rate constants for OH and O<sup>3</sup>P additions to the same double bond system, i.e.,

$$kA'_{\text{base}}(\text{O}^3\text{P}) = A + B \times kA'_{\text{base}}(\text{OH}) \quad (\text{S5})$$

where A and B are sets of fitting parameters derived separately for separated, conjugated, oxygenated, and cumulated double bonds from the base rate constants adjusted to fit available rate constant data. Note

Table S9. Parameters used in Equation (S2) to estimate base rate constants for  $\alpha$ -substituted double bond systems. Parameters derived for monoalkenes are also shown for comparison.

Substituent (X)	Parameters			Notes
	Int	Slope	fB	
Alkenes	-16.90	0.283	2.96	All parameters optimized to fit the data.
-CHO	-18.43	0.540	0.806	
-CO-O-	-17.81	0.770	0.578	Data too scattered to derive all the parameters for X = -CO-. The fB parameter for -CO-O- and -CO- forced to be the same during the fits to the data, but slopes and intercepts optimized separately. Best fit fB primarily determined by the data for X = -CO-O-.
-CO-	-17.10	0.344	0.578	
-O-CO-	-18.05	0.557	0.578	Data insufficient to derive all the parameters. Use same fB parameter as derived from X = -CO-O- and -CO- data as indicated above; forced the slope to the the average of those derived for X = -CO-O- and -CO-; and adjusted only the intercept to fit the data.
-O-	-16.45	0.557	0.578	
-CO-OH	-18.00	0.557	0.578	

that our standard methods for estimating rate constants for OH additions are based on assignments for groups around the double bonds (as discussed in Section 3.2 of the main text), while those for O<sub>3</sub> and O<sup>3</sup>P addition are assigned for each double bond structure (Section 3.3), so the base OH addition rate constants given in Table S16 do not correspond directly with those used for O<sup>3</sup>P additions, as given in Table S18. Therefore, base rate constants were derived separately for OH additions to the double bond structures, analogous to the derivations for O<sub>3</sub> and O<sup>3</sup>P additions discussed in Section 3.3, were used to derive best fit values for  $kA'^{\text{base}}(\text{OH})$  in Equation (S5). The A and B parameters so derived for the various types of double bonds are given in Table S10. Note that the A and B parameters derived for separated bonds were not needed for O<sup>3</sup>P estimates because all could be derived from the experimental data, though the B parameter so derived had to be used for conjugated and  $\alpha$ -oxygenated substituted bonds because of limited data for these types of reactions. Plots of the experimentally-derived and estimated base rate constants for O<sup>3</sup>P and OH reactions are shown on Figure S9.

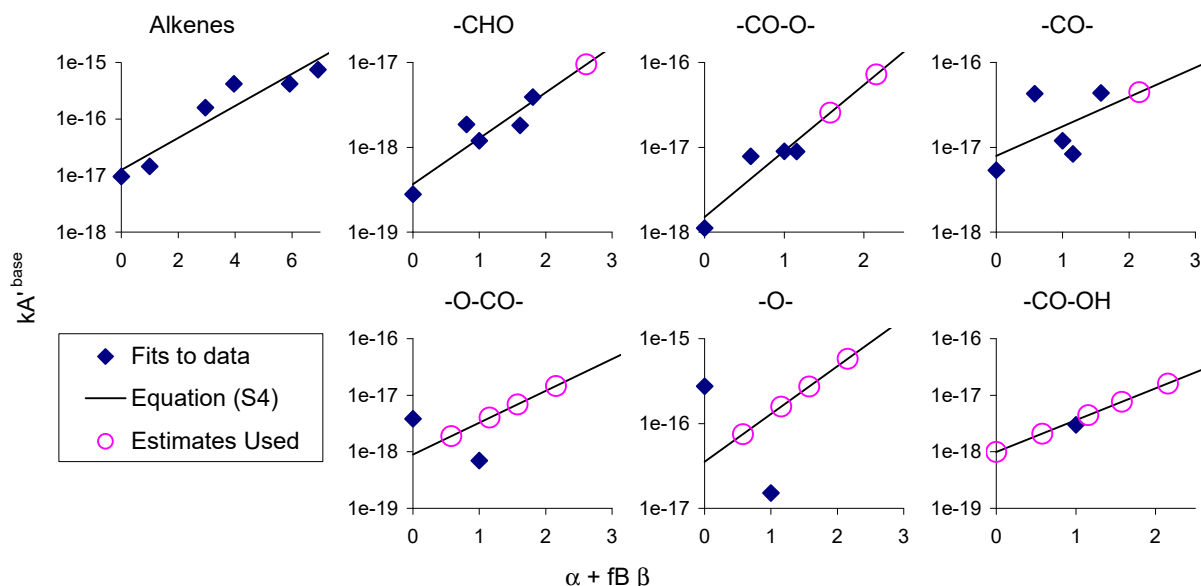


Figure S8. Plots of derived and estimated base rate constants for O<sub>3</sub> additions to alkenes and  $\alpha$ -substituted double bond systems against parameter used to fit rate constant data according to Equation (S2).

Table S10. Parameters used in Equation (S5) to estimate base rate constants for O<sup>3</sup>P additions to various double bond systems from those derived for OH additions.

Double bond system	Parameters		Derivation of parameters
	A	B	
Separated	13.06	2.33	Least squares fit to the available data
Conjugated	12.89	2.33	Insufficient data to derive slope, so the B parameter derived for separated bonds used, with the A parameter (intercept) adjusted to fit the available data.
$\alpha$ -Oxygenate Substituted	12.95	2.33	
Cumulated	8.71	1.89	Least squares fit to the available data.

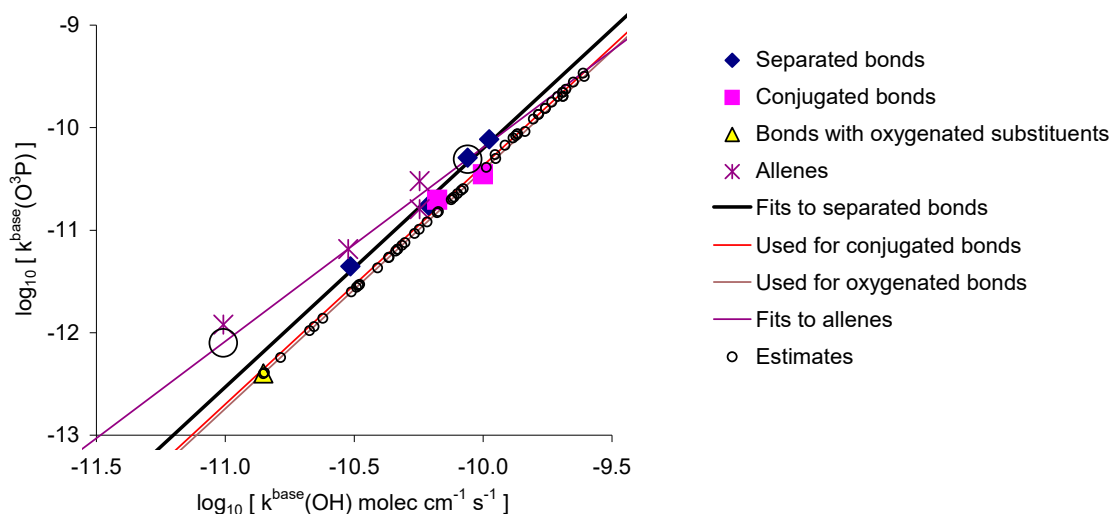
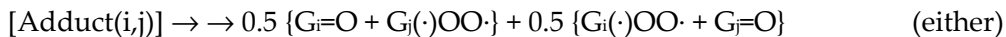
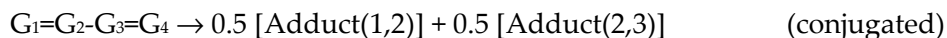


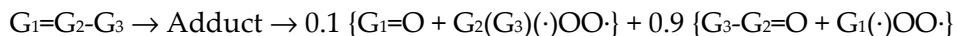
Figure S9. Plots of derived and estimated rate constants for O<sup>3</sup>P additions to various double bond systems against those derived for OH additions for the same double bond systems.

### S1.8. Estimated branching ratios for initial reactions of O<sub>3</sub> or O<sup>3</sup>P with alkenes

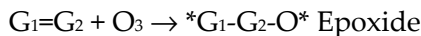
The equations in Section 3.3 of the main text provide a means for estimating total rate constants for reactions of O<sub>3</sub> or O<sup>3</sup>P at a double bond structure, but do not provide a means of estimating branching ratios for the purposes of mechanism generation if more than one reaction is possible. In the case of O<sub>3</sub> additions, the net result of the reaction is believed to be conversion of one group to the corresponding carbonyl compound and the other to a Criegee intermediate, so there are two possible modes of reaction for addition to separated bonds and four for conjugated bond systems. In the case of hydrocarbon groups, we assume for mechanism estimation purposes that each mode is equally likely, i.e.



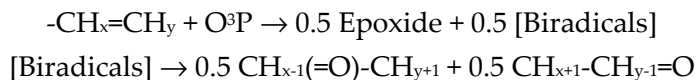
Following the estimates of Jenkin et al (2020), for reactions at double structures with non-hydrocarbon  $\alpha$ -substituents with base rate constant assignments, we assume that the  $\alpha$  substituent group goes on the carbonyl product 90% of the time, i.e.



In the case of O<sup>3</sup>P reactions, the possible reactions are assumed to be epoxide formation and (if at least one group has an  $\alpha$  hydrogen) carbonyl formation after an H shift by from the  $\alpha$  hydrogen to the O adduct, with equal probability for these routes







If neither group has an  $\alpha$  hydrogen then only epoxide formation is assumed, and if only one has one then there is only one biradical reaction. Note that formation of radicals in  $\text{O}^3\text{P}$  reactions with  $\text{C}_{3+}$  alkenes are assumed to be negligible based on results of modeling environmental chamber experiments (e.g., Carter, 2010a,b).

These assumptions need to be evaluated and refined by a comprehensive analysis of available product data for  $\text{O}_3$  reactions, but this is beyond the scope of the present study because it does not affect predictions of total rate constants.

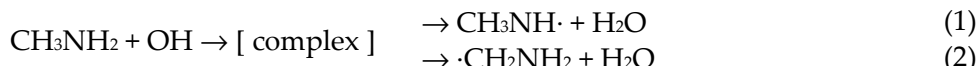
### S1.9. Reactions with Amines

Reactions with radicals. Amines can react with atmospheric radicals such as OH and  $\text{NO}_3$  by H-atom abstraction from the amino group or from another H-containing group in the molecule. In principle, the rate constants for these reactions can be estimated by assigning base rate constants for abstractions from  $-\text{NH}_2$ - or  $-\text{NH}-$  groups and by assigning substitution correction factors for amino groups, as discussed in Section 3.1 of the main text. However, this does not give acceptable fits to the available rate constant data. For example, our rate constant dataset includes the following rate constants for the reactions of OH radicals with representative amines, with the base rate constant for abstraction from  $-\text{CH}_3$  shown for comparison (rate constants in units of  $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ):

<u>Compound</u>	<u>kOH</u>	<u>Comment</u>
$\text{kH}^{\text{base}}(\text{CH}_3)$	$1.30 \times 10^{-13}$	Table S11
$\text{CH}_3\text{-NH}_2$	$1.97 \times 10^{-11}$	
$\text{CH}_3\text{-NH-CH}_3$	$6.52 \times 10^{-11}$	
$\text{CH}_3\text{-N(CH}_3\text{)-CH}_3$	$4.84 \times 10^{-11}$	Abstraction from the amino group not possible, so it must be from $-\text{CH}_3$ . This requires using $F(>\text{N-}) \approx 120$ .
$(\text{CH}_3)_3\text{C-NH}_2$	$1.18 \times 10^{-11}$	The amino group is not adjacent to the $-\text{CH}_3$ so abstraction from there is not expected to be significant contributor, so most of the reaction must be at $-\text{NH}_2$ .

These rate constants suggest that the presence of the amino group significantly enhances the reaction rate regardless of whether the amino group or the group next to the amino group has a hydrogen. The high rate constant for trimethylamine indicates that the reaction cannot be at the amino group for this compound, so if the approach discussed in Section 3.1 of the main text were used to estimate the rate constant for reaction at the methyl group, then a high amino substituent factor of  $\sim 120$  would have to be used. However, extreme enhancement of rates of abstraction from C-H bonds on adjacent groups is not sufficient to account for the relatively high rate constant for t-butyl amine, which has no C-H bonds on groups adjacent to the amino group.

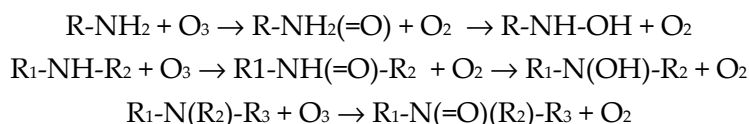
Rather than treating reactions of OH and the other radicals with amines as simple abstractions, better estimates are obtained by assuming that the reaction involves an initial formation of an amine-radical complex, which can be treated as an addition for estimation purposes. The adduct is assumed to subsequently react by H-atom transfer either from the amino group or an adjacent C-H bond, depending on what is available. For example,



If the formation of the complex is the rate determining step, the rate constant should depend only on the amino group and not, to a first approximation at least, on the substituents. Although this does not give perfect fits to the data, it performs much better than attempting to fit the data using H-abstraction estimates, so this is the approach used in this work. No correction factors are used in this case.

The rate constant data are not sufficient to determine the branching ratios between abstraction from the amino group (Reaction 1 in the example above) or the adjacent C-H group in compounds (Reaction 2) where both is possible. For the purpose of mechanism derivation, we roughly that abstraction from the amino group dominates whenever it is possible. However, we have not comprehensively evaluated whether this is consistent with available product data. Note, however, that this uncertainty does not affect estimates of total rate constants.

Reactions with O<sub>3</sub> Amines also react with O<sub>3</sub> under atmospheric conditions, though rate constant data are available for only a limited number of compounds. We assume that the initial reaction is transfer of an O atom from O<sub>3</sub> to the amino group, forming O<sub>2</sub> and an amine oxide. Primary and secondary amine oxides are assumed to decompose, while tertiary amine oxides are assumed to be stable. The net reactions assumed are as follows:



The rate determining step is assumed to be the initial O-transfer reaction, so it is reasonable to assume the rate constant would depend primarily on the nature of the amino group, as was assumed for the reactions of amines with radicals. This also is treated as an addition reaction, and the base rate constants used are included in Table S18. Because of lack of data, no correction factor is used.

#### S1.10. Estimating temperature dependences

All temperature dependence estimates in this work are based on the assumption that, at least for temperatures relevant to the lower atmosphere, the temperature dependence can be approximated by the 2-parameter Arrhenius expression

$$k^{\text{base}}(\text{type}, T) = A^{\text{base}}(\text{type}) \times \exp(-E_a^{\text{base}}(\text{type}) / T) \quad (\text{S6})$$

where  $k^{\text{base}}(\text{type})$  is the rate constant for a type of reaction at temperature  $T$ ,  $A^{\text{base}}$  is the base rate constant at the high temperature limit, and  $E_a^{\text{base}}$  is an overall activation energy for the base rate constant in temperature units. Because of insufficient data, the various types of substituent or structure correction factors are treated as being temperature-independent, though this probably not the case in most instances. The values of  $A^{\text{base}}$  were either derived to fit the measured  $A$  factors for selected compounds, or were estimated from  $A$  factors derived for similar types of reactions. The activation energies were derived from the base  $A$  factors and 298K base rate constants by

$$E_a^{\text{base}} = 298 \times \ln [A^{\text{base}} / k^{\text{base}}(298)] \quad (\text{S7})$$

where the units of  $E_a$  are deg K.

Because in general the rate constants reflect sums of rate constants for reactions at different positions in the molecule, the mechanism generation system was used to estimate total rate constants for reactions from those given for the base rate constants. The procedure employed to derive estimated A factors for total reactions using the various estimation parameters. The base A factors were among the parameters stored in the spreadsheet file and input to MechGen, and in addition outputting values and calculations of rate constants at 298K, MechGen also output values and calculations for rate constants at 279K and 330K, using the temperature-dependent base rate constants derived from the base A factors that were input and the corresponding activation energies calculated using Equation S6. The estimated A factor for the individual reactions were then derived using

$$\ln (A^{\text{est}}) = \{330 \times \ln [k^{\text{est}}(330)] - 270 \times \ln [k^{\text{est}}(270)]\} / (330 - 270) \quad (\text{S8})$$

The base A factors used to derive  $k^{\text{est}}(270)$  and  $k^{\text{est}}(330)$  are then adjusted to minimize

$$\text{Error} = \{ \ln (A^{\text{est}}) - \ln (A^{\text{expt}}) \}^2 \quad (\text{S9})$$

if suitable data are available.

Figure S10 shows a plot of the estimated vs experimental A factors for all the compounds in our experimental database that have temperature dependence data in 2-parameter Arrhenius form. It can be seen that there is a large degree of scatter for many classes of compounds, especially for OH reactions where the most data are available. However, reasonably consistent results are available for a number of classes of compounds, allowing reasonable optimizations to be carried out if outliers are excluded from the optimizations. The specific groups of compounds used to derive the A factors where the data are sufficient for optimizations are indicated in the footnotes to the tables in Section 0 where the A factors derived for the various base rate constants are given. Those tables also give the estimated A factors, along with how they are estimated. The tables in Section S3 that give the estimated and experimental rate constants for all compounds in the database also include the estimated and experimental

A

factors

for

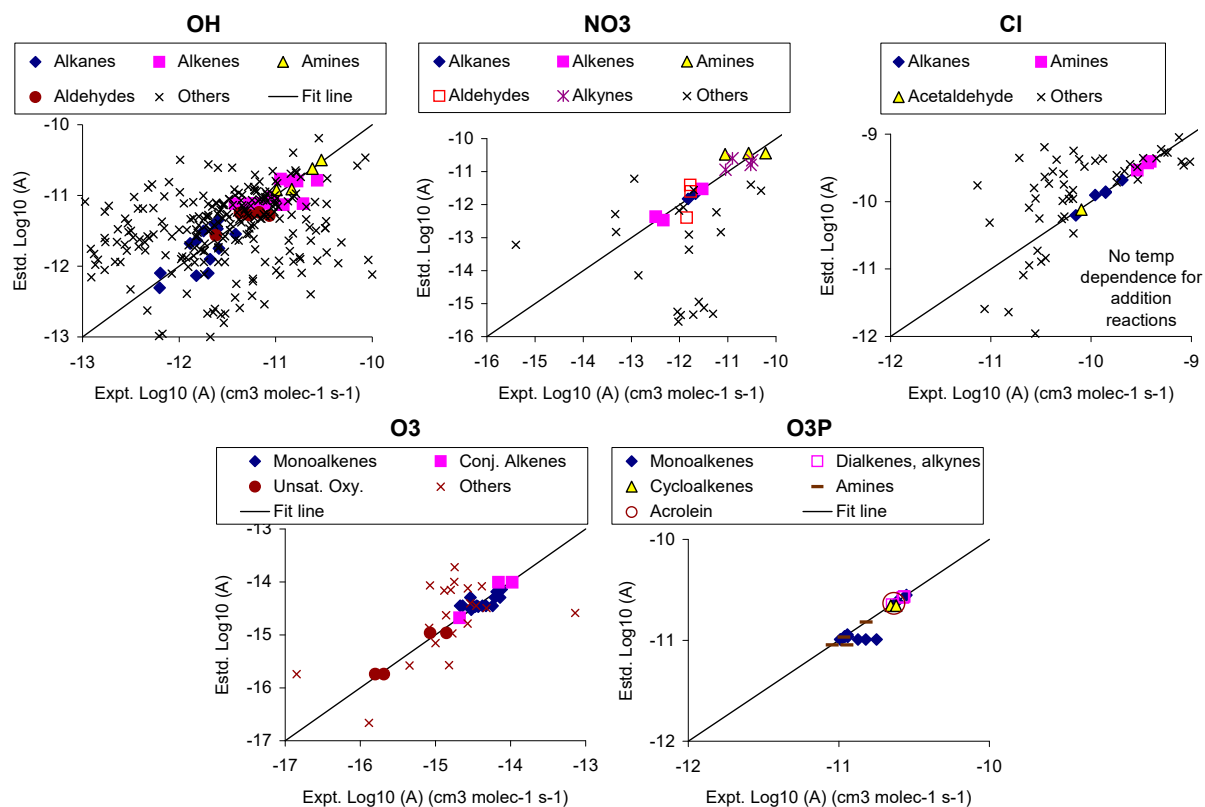


Figure S10. Plots of estimated vs. experimental A factors for the compounds in the database that had A factor data.

those compounds whose experimental A factors were used to derive the estimates. However, for clarity the tables do not include the estimated or experimental A factors not used in the derivations. The latter are shown as "others" on the plots on Figure S10.

#### **S1.11. Additional comparisons with previous work**

Figure S11 has additional plots comparing distributions of factor errors using estimates developed in this work with those developed previously by Jenkin et al (2019a,b) for OH reactions, Kedouchi et al (2014) for NO<sub>3</sub>, and Jenkin et al (2020) for O<sub>3</sub>. The figure has three rows -- the top row for OH, the middle for NO<sub>3</sub>, and the bottom for O<sub>3</sub> estimates. The figure also has three columns giving different comparisons. Columns (a) and (b) show the distribution plots for compounds estimated in this work where estimates are also tabulated in the previous works, with Column (a) showing distributions for the compounds used for parameter derivations in this work, and column (b) showing distributions for compounds used for evaluation only. Note that there are a number of rate constants that were estimated in this work but not in the previous work. To assess the extent to which this may affect the comparisons of the estimation methods, Column (c) shows distribution plots for all rate constants estimated in this work, with one curve being for compounds that were estimated in both this and the previous works, and the other for compounds estimated in this work alone. It can be seen that the numbers of rate constants that are well estimated in this work are only slightly less for the compounds estimated in this work alone compared to those estimated in the previous work.

## **S2. Tables of Parameters**

The tables giving the parameters that are used in all the estimates discussed in this work are given in this section. Table S11 through Table S15 show parameters for estimating H-abstraction rate constants and Table S16 through Table S20 show parameters for estimating the various types of addition rate constants. Footnotes indicate which of the parameters are derived by adjustments to fit the data and which are estimated, and how they were derived or estimated. The tables showing base rate constants (Table S11, Table S16, and Table S18) also give the estimated A factors used for approximate temperature dependences and indicate how they are derived.

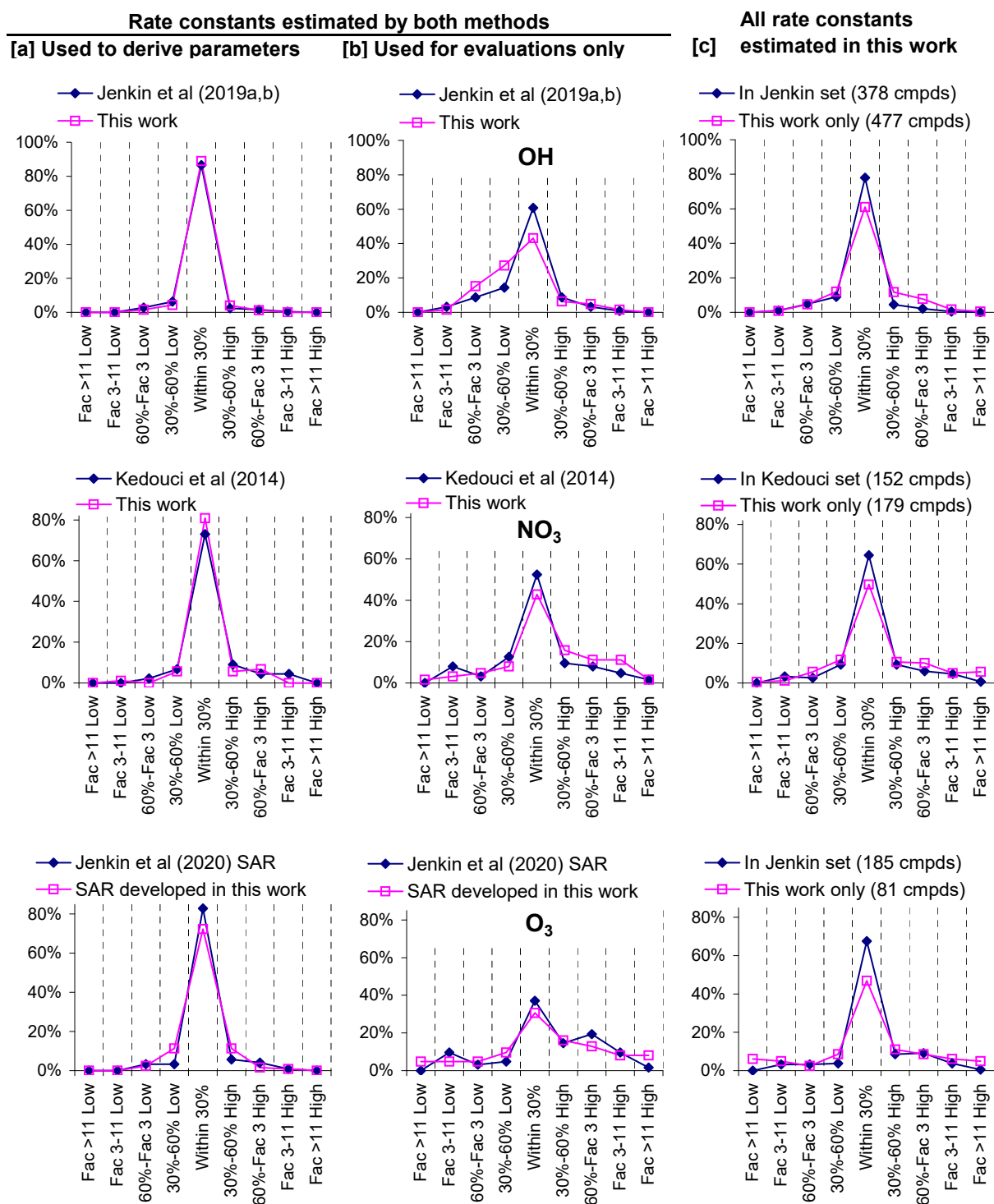


Figure S11. Comparison of distribution plots for factor errors in the SARs developed by Jenkin et al (2019a,b, 2020) and Kedouchi et al (2014) with those developed in this work.

Table S11. Base group rate constant parameters for estimating H-atom abstraction rate constants.

Group [a]	OH					NO <sub>3</sub>					Cl	
	k(298) [b]		A [c]	Ea (K)		k(298) [b]		A [c]	Ea	k(298) [b,d]		
Correction factors used for abstractions from these groups												
CH <sub>3</sub>	1.30e-13	1	3.66e-13	1	309	1.07e-19	(1)	2.83e-16	(1)	2347	2.89e-11	1
CH <sub>2</sub>	8.47e-13	1	3.21e-13	1	-290	9.45e-18	1	1.89e-16	2	893	6.54e-11	1
CH	1.93e-12	1	2.44e-13	1	-616	6.72e-17	1	2.17e-12	2	3095	5.18e-11	1
CHO	1.48e-11	2	2.65e-12	3	-513	2.66e-15	(2)	4.04e-13	4	1497	5.72e-11	2
Correction factors not used for abstractions from these groups												
OH	1.31e-13	(3)	2.65e-12	(2)	896	0	(4)				0	(4)
CHO-O	8.46e-14	2	2.65e-12	(2)	1026	0	(4)				1.27e-14	4
HO-O-	5.45e-12	2	2.65e-12	(2)	-216	0	(4)				0	(4)
HO-CO-	6.22e-13	2	2.65e-12	(2)	432	0	(4)				0	(4)
HO-O-CO-	1.00e-14	(5)	2.65e-12	(2)	1662							
HO-aro	9.20e-13	3	2.65e-12	(2)	315	4.62e-12	3				0	(4)
The following substituent effects are only used for NO <sub>3</sub> reactions. Correction factors are not used												
CH <sub>2</sub> -OH						1.83e-15	2	1.89e-16	(3)	-677		
CH-OH						2.13e-15	2	2.17e-12	(3)	2065		
CH <sub>3</sub> -O						1.02e-16	2	2.83e-16	(3)	304		
CH <sub>2</sub> -O						1.55e-15	2	1.89e-16	(3)	-628		
CH-O						2.03e-15	2	2.17e-12	(3)	2079		
CH <sub>3</sub> -CH <sub>x</sub> -O						1.01e-16	2	2.83e-16	(3)	307		
CH <sub>2</sub> -CH <sub>x</sub> -O						1.09e-15	2	1.89e-16	(3)	-521		
CH-CH <sub>x</sub> -O						2.03e-15	(6)	2.17e-12	(3)	2079		

[a] If more than one group is shown, the abstraction is from the first of the groups listed.

[b] Base rate constants at 298K are in units of cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>, and are derived as indicated according to the footnote given to the left of the value. The following are used to indicate parameters adjusted to fit rate constant data, with the group of compounds used indicated below.

- 1 Acyclic alkanes
- 2 Acyclic Saturated oxygenates
- 3 Substituted aromatics
- 4 Halogenated formates

The following indicates derivations for estimated parameters, parameters dependent on adjusted parameters, or parameters derived by other mean, as indicated below.

- (1) Total alkane rate constants are too insensitive to this parameter to derive by optimization. Rate constants estimated by assuming a linear relationship between ln(k<sub>Base</sub>) for OH and NO<sub>3</sub> for abstraction from CH<sub>3</sub>, CH<sub>2</sub>, and CH. See Section S1.4.
- (2) Derived from the rate constant for acetaldehyde.
- (3) Rate constant derived from total rate constant and branching ratios for reactions of methanol as recommended by IUPAC (2019).
- (4) H atom abstractions from -OH or formate groups are assumed to be negligible compared to competing processes unless data are sufficient to derive estimated base rate constants.
- (5) Estimated to be low based on low rate constant for peroxyacetic acid. Base rate constant assignment is arbitrary and highly uncertain.
- (6) No data are available concerning effects of beta-O substitution on abstraction from tertiary hydrogens. The group rate constant used is estimated to be approximately the same as that for alpha-O substituted tertiary hydrogens, based on similarities between alpha- and beta-O substitutions for abstractions of primary and secondary hydrogens.

[c] A factors as used to estimate temperature dependences according to  $k(T) = A \exp(-E_a/T)$ . A factors are

Table S11 (continued)

in units of  $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  and are estimated based on measured A factors for the following compounds, as indicated in notes to the left of the tabulated A factors. These A factors, and how well they correspond to the estimated values, are given in Table S21 through Table S23. The estimated activation energies are in deg K and are derived from the A factor and the 298K rate constant. The following are used to indicate compounds used to derive the A factors.

- 1 n-alkanes through n-decane, 2,2-dimethyl propane, 2,2,3,3-tetramethyl butane, 2,3-dimethyl butane and 2-methyl propane
- 2 isobutane and 2-methylbutane
- 3 acetaldehyde, n-pentanal, n-hexanal, and 2-methylpropanal and 2,2-dimethylpropanal
- 4 acetaldehyde, n-butanal, and 2-methylpropanal

The following are used for estimates.

- (1) Estimated to be 3/2 the value derived for abstraction from  $-\text{CH}_2-$ .
- (2) Insufficient data to derive an unambiguous estimate. Roughly estimated to be the same as the A factor derived for abstraction from  $-\text{HCO}$ .
- (3) Used the same A factor as for the unsubstituted group.

[d] The temperature dependence is expected to be small, so A factors are not estimated for Cl reactions.



Table S12. Substituent correction factors for H-atom abstractions by OH.

Group	Corrections [a] for OH Abstractions From ...							
	CH3		CH2		CH		CHO	
Hydrocarbon substituents								
-CH2-	1.30	2	1.30	(1)	1.30	(1)	1.46	3
>CH-	0.99	2	0.99	(1)	0.99	(1)	2.02	3
>C<	1.43	2	1.43	(1)	1.43	(1)	1.84	3
=CH-	1	(2)	1	(2)	1	(2)	0.52	4
=C<	1	(2)	1	(2)	1	(2)	0.52	(3)
≡C-	1	(2)	1	(2)	1	(2)	1	(4)
-aro	3.13	(5)	1.27	5	1.27	(6)	0.91	6
Non-hydrocarbon substituents								
-OH	5.75	(7)	3.95	3	2.70	3	-	-
-CHO	1	(2)	1	(2)	1	(2)	0.31	3
-CO-	0.95	3	0.95	(1)	0.95	(1)	0.86	3
-ONO	2.08	(7)	0.71	7	0.71	(6)	-	-
-O-	15.1	3	9.48	3	2.68	3	-	-
-NO2	0.086	7	0.086	(1)	0.086	(1)	-	-
-ONO2	0.141	7	0.141	(1)	0.141	(1)	-	-
-F	0.163	8	0.163	(1)	0.163	(1)	-	-
-Cl	0.27	8	0.27	(1)	0.27	(1)	-	-
-BR	0.25	8	0.25	(1)	0.25	(1)	-	-
-I	0.43	8	0.43	(1)	0.43	(1)	-	-
-NH2	1	(2)	1	(2)	1	(2)	-	-
-NH-	1	(2)	1	(2)	1	(2)	1	(4)
-N<	1	(2)	1	(2)	1	(2)	1	(4)
Non-hydrocarbon substituents								
-O-OH	1.23	3	1.23	(1)	1.23	(1)	-	-
-O-CO-	2.00	3	2.00	(1)	2.00	(1)	1	(4)
-O-CO-O-	1.19	3	1.19	(1)	1.19	(1)	1	(4)
-O-CHO	0.77	3	0.77	(1)	0.77	(1)	-	-
-CO-OH	0.22	(7)	0.22	(1)	0.22	(1)	-	-
-CO-O-	0.22	3	0.22	(1)	0.22	(1)	1	(4)
-CO-CO	0.95	(8)	0.95	(1)	0.95	(1)	0.79	3
Non-hydrocarbon substituents								
-CH2-OH	3.66	3	3.66	(1)	3.66	(1)	1.46	(8)
>CH-OH	3.66	(9)	3.66	(1)	3.66	(1)	2.02	(8)
>C(-)-OH	3.66	(9)	3.66	(1)	3.66	(1)	1.84	(8)
-CH2-CO-	3.55	3	3.55	(1)	3.55	(1)	1.46	(8)
>CH-CO-	3.55	(9)	3.55	(1)	3.55	(1)	2.02	(8)
>C(-)-CO-	3.55	(9)	3.55	(1)	3.55	(1)	1.84	(8)
-CH2-NO2	0.001	7	0.001	(1)	0.001	(1)	1.46	(8)
>CH-NO2	0.32	7	0.32	(1)	0.32	(1)	2.02	(8)
>C(-)-NO2	0.32	(10)	0.32	(1)	0.32	(1)	1.84	(8)
-CH2-ONO2	0.36	7	0.36	(1)	0.36	(1)	1.46	(8)
>CH-ONO2	0.36	(9)	0.36	(1)	0.36	(1)	2.02	(8)
>C(-)-ONO2	0.36	(9)	0.36	(1)	0.36	(1)	1.84	(8)
-CH2-F	0.75	8	0.75	(1)	0.75	(1)	1.46	(8)
>CH-F	0.75	(9)	0.75	(1)	0.75	(1)	2.02	(8)
>C(-)-F	0.75	(9)	0.75	(1)	0.75	(1)	1.84	(8)
-CH2-Cl	0.89	8	0.89	(1)	0.89	(1)	1.46	(8)

Table S11 (continued)

Group	Corrections [a] for OH Abstractions From ...							
	CH3		CH2		CH		CHO	
>CH-Cl	0.89	(9)	0.89	(1)	0.89	(1)	2.02	(8)
>C(-)-Cl	0.89	(9)	0.89	(1)	0.89	(1)	1.84	(8)
-CH2-Br	0.76	8	0.76	(1)	0.76	(1)	1.46	(8)
>CH-Br	0.76	(9)	0.76	(1)	0.76	(1)	2.02	(8)
>C(-)-Br	0.76	(9)	0.76	(1)	0.76	(1)	1.84	(8)

[a] The derivations of the correction factors are as indicated in the following notes, given to the left of the tabulated factors. The following are used to indicate parameters adjusted to fit rate constant data, with the group of compounds used indicated below.

- 1 Acyclic alkanes
- 2 Acyclic saturated oxygenates
- 3 Unsaturated oxygenates
- 4 Aromatic hydrocarbons
- 5 Substituted aromatics
- 6 Acyclic saturated nitrates
- 7 Halogenated compounds

The following are used to estimated parameters, parameters dependent on adjusted parameters, or parameters derived by other mean, as indicated below.

- (1) The correction factors for reactions at -CH<sub>3</sub>, -CH<sub>2</sub>- and -CH< are assumed to be the same and are adjusted together. See the note for -CH<sub>3</sub> for the optimization set used.
- (2) No correction used because total rate constants are too insensitive to this parameter for it to be derived by adjustment.
- (3) Assumed to have the same correction factor as the similar group given above on the list. See the note for that factor for how the factor for these groups were derived.
- (4) No correction factor is used for the effect of this substituent because insufficient data are available. The rate constant estimate is highly uncertain.
- (5) Derived from the benzaldehyde yield from toluene and the total OH + toluene rate constant, using estimated nitrate yields in peroxy + NO reactions.
- (6) The correction factors for reactions at -CH<sub>2</sub>- and -CH< are assumed to be the same and are adjusted together. See the note for -CH<sub>2</sub>- for the optimization set used.
- (7) Derived from the rate constant for CH<sub>3</sub>-X, where X is the group in question.
- (8) Use the same substituent correction factor as derived for substitution by the  $\alpha$  group by itself.
- (9) The substituent factors are adjusted assuming that the beta substituent effects are the same regardless of the type of a hydrocarbon group. See comment for the  $\beta$  substituent on -CH<sub>2</sub>-.
- (10) Although the data are fit better using a separate factor for the  $\beta$  substituent on a secondary carbon the factors for the substituent on tertiary and quaternary carbons are assumed to be the same, and are adjusted together.

Table S13. Substituent correction factors for H-atom abstractions by Cl.

Group	Corrections for Cl Abstractions From ...							
	CH3		CH2		CH		CHO	
Hydrocarbon substituents								
-CH2-	1	(1)	1	(1)	1	(1)	1	(1)
>CH-	1	(1)	1	(1)	1	(1)	1	(1)
>C<	1	(1)	1	(1)	1	(1)	1	(1)
=CH-	1	(2)	1	(2)	1	(2)	2.77	1
=C<	1	(2)	1	(2)	1	(2)	2.77	(3)
≡C-	1	(2)	1	(2)	1	(2)	1	(2)
-aro	0.94	2	0.94	(4)	0.94	(4)	1	(2)
Non-hydrocarbon substituents								
-OH [c]	1.77	3	1.31	3	0.91	3	-	-
-CHO	0.79	4	0.40	4	0.40	'(6)	0.31	4
-CO-	0.037	4	0.60	4	0.60	'(6)	0.87	4
-ONO	0.073	(5)	0.073	(4)	0.073	(4)	-	-
-O- [c]	3.08	3	1.17	3	1.17	(6)	-	-
-NO2	0.001	(5)	0.001	(4)	0.001	(4)	-	-
-ONO2	0.008	(5)	0.067	5	0.067	(6)	-	-
-F	0.012	(5)	0.005	6	0.005	(6)	-	-
-Cl	0.017	(5)	0.081	6	0.081	(6)	-	-
-BR	0.015	6	0.015	(4)	0.015	(4)	-	-
-I	0.035	6	0.035	(4)	0.035	(4)	-	-
-NH2	1	(2)	1	(2)	1	(2)	-	-
-NH-	1	(2)	1	(2)	1	(2)	1	(2)
-N<	1	(2)	1	(2)	1	(2)	1	(2)
Non-hydrocarbon substituents								
-O-OH	2.04	3	1.24	3	1.24	(6)	-	-
-O-CO-	0.005	4	0.001	4	0.001	(6)	1	(2)
-O-CO-O	0.048	4	0.048	(9)	0.048	(4)	-	-
-O-CHO	0.048	4	0.001	4	0.001	(6)	-	-
-CO-OH	~0	(5)	~0	(4)	~0	(4)	-	-
-CO-O-	0.097	4	0.097	(4)	0.097	(6)	0.87	(7)
-CO-CO	0.008	4	0.184	4	0.184	(6)	0.87	(7)
Non-hydrocarbon substituents								
-CH2-OH	0.44	3	0.44	(4)	0.44	(4)	1	(7)
>CH-OH	0.55	3	0.55	(4)	0.55	(4)	1	(7)
>C(-)-OH	0.39	3	0.39	(4)	0.39	(4)	1	(7)
-CH2-CO-	0.20	4	0.27	4	0.27	(6)	1	(7)
>CH-CO-	0.54	4	0.54	(4)	0.54	(4)	1	(7)
>C(-)-CO-	0.46	4	0.46	(4)	0.46	(4)	1	(7)
-CH2-NO2	0.004	4	0.004	(4)	0.004	(4)	1	(7)
>CH-NO2	0.004	(3)	0.004	(4)	0.004	(4)	1	(7)
>C(-)-NO2	0.004	(3)	0.004	(4)	0.004	(4)	1	(7)
-CH2-ONO2	0.001	5	0.001	(4)	0.001	(4)	1	(7)
>CH-ONO2	0.006	5	0.006	(4)	0.006	(4)	1	(7)
>C(-)-ONO2	0.006	(3)	0.006	(4)	0.006	(4)	1	(7)
-CH2-F	0.25	6	0.25	(4)	0.25	(4)	1	(7)
>CH-F	0.25	(3)	0.25	(4)	0.25	(4)	1	(7)
>C(-)-F	0.25	(3)	0.25	(4)	0.25	(4)	1	(7)
-CH2-Cl	0.173	6	0.173	(4)	0.173	(4)	0.143	7

Table S11 (continued)

Group	Corrections for Cl Abstractions From ...							
	CH <sub>3</sub>		CH <sub>2</sub>		CH		CHO	
>CH-Cl	0.173	(3)	0.173	(4)	0.173	(4)	0.143	(3)
>C(-)-Cl	0.173	(3)	0.173	(4)	0.173	(4)	0.143	(3)
-CH <sub>2</sub> -Br	0.37	6	0.37	(4)	0.37	(4)	1	(7)
>CH-Br	0.37	(3)	0.37	(4)	0.37	(4)	1	(7)
>C(-)-Br	0.37	(3)	0.37	(4)	0.37	(4)	1	(7)

[a] The derivations of the correction factors are as indicated in the following notes, given to the left of the tabulated factors. The following are used to indicate parameters adjusted to fit rate constant data, with the group of compounds used indicated below.

- 1 Unsaturated oxygenates
- 2 Acyclic Saturated O, OH
- 3 Acyclic Saturated CO, O
- 4 Acyclic Saturated nitrates
- 5 Monohalo alkanes
- 7 Saturated halogenated compounds

The following are used to estimated parameters, parameters dependent on adjusted parameters, or parameters derived by other mean, as indicated below.

- (1) The data are consistent with assuming that no corrections are needed for substitution by these groups, with optimizations giving factors close to 1.
- (2) No correction factor is used for the effect of this substituent because insufficient data are available. The rate constant estimate is highly uncertain.
- (3) Assumed to have the same correction factor as the similar group given above on the list. See the note for that factor for how the factor for these groups were derived.
- (4) The correction factors for reactions at -CH<sub>3</sub>, -CH<sub>2</sub>- and -CH< are assumed to be the same and are adjusted together. See the note for -CH<sub>3</sub> for the optimization set used.
- (5) Derived from the rate constant for CH<sub>3</sub>-X, where X is the group in question.
- (6) The correction factors for reactions at -CH<sub>2</sub>- and -CH< are assumed to be the same and are adjusted together. See the note for -CH<sub>2</sub>- for the optimization set used.
- (7) Use the same substituent correction factor as derived for substitution by the  $\alpha$  group by itself.

Table S14. Substituent correction factors for H-atom abstractions by NO<sub>3</sub>.

Group	Corrections [a,b] for NO3 Abstractions From ...							
	CH3		CH2		CH		CHO	
Hydrocarbon substituents								
-CH2-	1.76	1	1.76	(1)	1.76	(1)	6.23	2
>CH-	2.06	1	2.06	(1)	2.06	(1)	9.54	2
>C<	2.55	1	2.55	(1)	2.55	(1)	9.03	2
=CH-	1	(2)	1	(2)	1	(2)	0.39	3
=C<	1	(2)	1	(2)	1	(2)	0.39	(3)
≡C-	1	(2)	1	(2)	1	(2)	1	(6)
-aro	4.09	(4)	4.09	(2)	4.09	(2)	1	(2)
Non-hydrocarbon substituents								
-OH [c]	1	(5)	1	(5)	1	(5)	-	-
-CHO	1.61	(4)	1.61	(4)	1.61	(4)	0.075	2
-CO-	1.55	(4)	1.55	(4)	1.55	(4)	0.188	2
-ONO	2.92	(4)	2.92	(4)	2.92	(4)	-	-
-O- [c]	14.7	(4)	14.7	(4)	14.7	(4)	-	-
-NO2	0.22	(4)	0.22	(4)	0.22	(4)	-	-
-ONO2	0.33	(4)	0.33	(4)	0.33	(4)	-	-
-F	0.37	(4)	0.37	(4)	0.37	(4)	-	-
-Cl	0.56	(4)	0.56	(4)	0.56	(4)	-	-
-BR	0.52	(4)	0.52	(4)	0.52	(4)	-	-
-I	0.81	(4)	0.81	(4)	0.81	(4)	-	-
-NH2	1	(2)	1	(2)	1	(2)	-	-
-NH-	1	(2)	1	(2)	1	(2)	1	(6)
-N<	1	(2)	1	(2)	1	(2)	1	(6)
Non-hydrocarbon substituents								
-O-OH	1.90	(4)	1.90	(1)	1.90	(1)	-	-
-O-CO-	2.84	(4)	2.84	(1)	2.84	(1)	-	-
-O-CHO	1.30	(4)	1.30	(1)	1.30	(1)	-	-
-CO-OH	0.47	(4)	0.47	(1)	0.47	(1)	-	-
-CO-O-	0.47	(4)	0.47	(1)	0.47	(1)	0.188	(7)
-CO-CO	1.55	(4)	1.55	(1)	1.55	(1)	0.188	(7)
Non-hydrocarbon substituents								
-CH2-OH	4.70	2	4.70	(1)	4.70	(1)	6.23	(7)
>CH-OH	4.70	(8)	4.70	(1)	4.70	(1)	9.54	(7)
>C(-)-OH	4.70	(8)	4.70	(1)	4.70	(1)	9.03	(7)
-CH2-CO-	4.52	(4)	4.52	(1)	4.52	(1)	6.23	(7)
>CH-CO-	4.52	(4)	4.52	(1)	4.52	(1)	9.54	(7)
>C(-)-CO-	4.52	(4)	4.52	(1)	4.52	(1)	9.03	(7)
-CH2-NO2	0.006	(4)	0.006	(1)	0.006	(1)	6.23	(7)
>CH-NO2	0.64	(4)	0.64	(1)	0.64	(1)	9.54	(7)
>C(-)-NO2	0.64	(4)	0.64	(1)	0.64	(1)	9.03	(7)
-CH2-ONO2	0.70	(4)	0.70	(1)	0.70	(1)	6.23	(7)
>CH-ONO2	0.70	(4)	0.70	(1)	0.70	(1)	9.54	(7)
>C(-)-ONO2	0.70	(4)	0.70	(1)	0.70	(1)	9.03	(7)
-CH2-F	1.28	(4)	1.28	(1)	1.28	(1)	6.23	(7)
>CH-F	1.28	(4)	1.28	(1)	1.28	(1)	9.54	(7)
>C(-)-F	1.28	(4)	1.28	(1)	1.28	(1)	9.03	(7)
-CH2-Cl	1.47	(4)	1.47	(1)	1.47	(1)	6.23	(7)
>CH-Cl	1.47	(4)	1.47	(1)	CH	(1)	9.54	(7)

Table S12 (continued)

Group	Corrections [a,b] for NO <sub>3</sub> Abstractions From ...							
	CH <sub>3</sub>		CH <sub>2</sub>		CH		CHO	
>C(-)-Cl	1.47	(4)	1.47	(1)	1.47	(1)	9.03	(7)
-CH <sub>2</sub> -Br	1.29	(4)	1.29	(1)	1.29	(1)	6.23	(7)
>CH-Br	1.29	(4)	1.29	(1)	1.29	(1)	9.54	(7)
>C(-)-Br	1.29	(4)	1.29	(1)	1.29	(1)	9.03	(7)

[a] The derivations of the correction factors are as indicated in the following notes, given to the left of the tabulated factors. The following are used to indicate parameters adjusted to fit rate constant data, with the group of compounds used indicated below.

- 1 Acyclic alkanes
- 2 Acyclic unsaturated oxygenates
- 3 Acyclic saturated oxygenates

The following are used to estimated parameters, parameters dependent on adjusted parameters, or parameters derived by other mean, as indicated below.

- (1) The correction factors for reactions at -CH<sub>3</sub>, -CH<sub>2</sub>- and -CH< are assumed to be the same and are adjusted together. See the note for -CH<sub>3</sub> for the optimization set used.
- (2) No correction used because total rate constants are too insensitive to this parameter for it to be derived by adjustment.
- (3) Assumed to be the same as the related group with fewer substituents.
- (4) Insufficient information is available to estimate a substitution correction factor for this group for abstractions by NO<sub>3</sub>. It is estimated based on factors for abstractions by OH and the relationship between these and those factors for abstraction by NO<sub>3</sub> that could be derived from the data. See Section S1.4.
- (5) This correction is not used because the effect of this substituent is incorporated in the base rate constant.
- (6) No correction factor is used for the effect of this substituent because insufficient data are available. The rate constant estimate is highly uncertain.
- (7) Use the same substituent correction factor as derived for substitution by the  $\alpha$  group by itself.
- (8) The substituent factors are adjusted assuming that the beta substituent effects are the same regardless of the type of a hydrocarbon group. See comment for the  $\beta$  substituent on -CH<sub>2</sub>-.

Table S15 Ring strain correction factors used for H-abstraction reaction for OH, NO<sub>3</sub>, and Cl.

Ring Size	Default (alkyl)				-CO- or CO-O in ring				-O- in ring			
	OH or NO <sub>3</sub>		Cl [a]		OH or NO <sub>3</sub>		Cl [a]		OH and NO <sub>3</sub>		Cl [a]	
3	0.018	1	7.1e-4	2	0.018	2	7.1e-4	2	0.0044	3	7.1e-4	2
4	0.352	1	0.841	2	0.169	4	0.841	2	0.352	2	0.841	2
5	0.775	1	0.887	2	0.310	4	0.887	2	0.775	2	0.887	2
6	1	5	1	5	0.558	4	1	5	1	5	1	5
7+	1	5	1	5	1	5	1	5	1	5	1	5

[a] Ring correction factors were derived as indicated in the footnotes below. Note that because of lack of sufficient data, factors derived for abstractions by NO<sub>3</sub> are estimated to be the same as those derived for OH.

- 1 Derived to fit rate constant data for OH + cycloalkanes. Assuming same correction factor for NO<sub>3</sub> reactions gives acceptable fits to the limited available data.
- 2 Because of insufficient or inconsistent data, assume same factor as derived for cycloalkanes.
- 3 Derived from the rate constant for various cyclic ethers.
- 4 Adjusted to fit rate constant data for various cyclic carbonyl compounds.
- 5 Assume no ring correction factor needed for 6-member or larger rings, unless available data indicate otherwise.

Table S16. Base group rate parameters for estimating addition rate constants for OH, NO<sub>3</sub>, and Cl.

Group Added to	OH [a,b]				NO <sub>3</sub> [a,b]				Cl [a,c]	
	k(298)	A	Ea (K)		k(298)	A	Ea		k(298)	
Additions to single or separated C=C double bonds [d]										
CH <sub>2</sub> =(CH)	2.61e-11	1	6.19e-12	a1 -428	1.16e-14	1	4.31e-13	a2 1079	1.07e-10	1
CH=(CH <sub>2</sub> )	4.50e-12	(1)	1.07e-12	a1 -428	0	(2)			1.07e-10	(3)
CH=(CH)	3.10e-11	1	3.74e-12	a1 -630	1.78e-13	1	2.16e-13	a2 57	1.37e-10	1
CH <sub>2</sub> =(C)	5.69e-11	1	8.57e-12	a1 -564	3.31e-13	1	4.31e-13	a2 79	1.22e-10	1
C=(CH <sub>2</sub> )	4.50e-12	(1)	6.78e-13	a1 -564	0	(2)			1.22e-10	(3)
CH=(C)	5.61e-11	1	4.82e-12	a1 -732	6.52e-12	1	4.31e-13	a2 -809	1.47e-10	1
C=(CH)	3.10e-11	(1)	2.66e-12	a1 -732	0	(2)			1.47e-10	(3)
C=(C)	5.27e-11	1	3.74e-12	a1 -789	2.08e-11	1	2.16e-13	a2 -1362	1.47e-10	(4)
Additions to conjugated double bonds [d,e]										
CH <sub>2</sub> =(CH*)	3.27e-11	2	8.07e-12	a3 -417	5.30e-14	2	1.87e-12	a4 1062	1.95e-10	2
*CH=(CH <sub>2</sub> )	1.72e-12	(5)	4.25e-13	a3 -417	0	(6)			2.16e-11	(7)
CH=(CH*)	6.90e-11	2	8.07e-12	a3 -640	2.26e-12	2	1.87e-12	a4 -57	1.95e-10	(9)
*CH=(CH)	3.63e-12	(5)	4.25e-13	a3 -640	0	(6)			2.16e-11	(9)
CH <sub>2</sub> =(C*)	5.92e-11	2	8.07e-12	a3 -594	5.94e-13	2	1.87e-12	a4 342	1.60e-10	2
*C=(CH <sub>2</sub> )	3.11e-12	(5)	4.25e-13	a3 -594	0	(6)			1.78e-11	(7)
CH=(C*)	9.66e-11	2	8.07e-12	a3 -740	8.59e-12	(8)	1.87e-12	a4 -454	1.60e-10	(9)
*C=(CH)	5.08e-12	(5)	4.25e-13	a3 -740	0	(8)			1.78e-11	(9)
C=(CH*)	9.66e-11	(5)	8.07e-12	a3 -740	8.59e-12	(8)	1.87e-12	a4 -454	1.95e-10	(9)
*CH=(C)	5.08e-12	(5)	4.25e-13	a3 -740	0	(8)			2.16e-11	(9)
C=(C*)	1.16e-10	2	8.07e-12	(a1) -795	2.08e-11	(8)	1.87e-12	(a1) -718	1.60e-10	(9)
*C=(C)	6.12e-12	(5)	4.25e-13	(a1) -795	0	(8)			1.78e-11	(9)
*CH=(CH*)	6.90e-11	(10)	8.07e-12	(a1) -640	2.26e-12	(10)	1.87e-12	(a1) -57	1.95e-10	(10)
*CH=(C*)	9.66e-11	(10)	8.07e-12	(a1) -740	8.59e-12	(10)	1.87e-12	(a1) -454	1.60e-10	(10)
*C=(CH*)	9.66e-11	(10)	8.07e-12	(a1) -740	8.59e-12	(10)			1.95e-10	(10)
*C=(C*)	1.16e-10	(10)	8.07e-12	(a1) -795	2.08e-11	(10)	1.87e-12	(a1) -718	1.60e-10	(10)
Additions to cumulated double bonds [f]										
C(=CH <sub>2</sub> )(=CH)	3.00e-11	3	7.66e-12	a5 -406	6.96e-14	(11)	8.98e-13	a5	4.38e-10	(12)
C(=CH <sub>2</sub> )(=C)	5.67e-11	3	7.66e-12	a5 -597	1.74e-12	(11)	8.98e-13	a5 -197	4.38e-10	(12)
C(=CH)(=CH)	3.10e-11	(13)	7.66e-12	a5 -417	8.28e-14	(11)	8.98e-13	a5 711	4.38e-10	(12)
C(=CH)(=C)	5.61e-11	(13)	7.66e-12	a5 -593	1.64e-12	(11)	8.98e-13	a5 -180	4.38e-10	(12)
C(=C) <sub>2</sub>	5.27e-11	(13)	7.66e-12	a5 -575	1.21e-12	(11)	8.98e-13	a5 -88	4.38e-10	(12)
Additions to triple bonds [d]										
CH≡(C)	5.35e-12	4	7.31e-12	(a2) 93	5.06e-16	4	2.55e-11	a6 3227	2.60e-11	(14)
C≡(CH)	5.00e-13	(15)	6.83e-13	(a2) 93	0	4			2.60e-11	(14)
C≡(C)	1.34e-11	4	4.00e-12	(a2) -360	2.20e-14	4	2.55e-11	a6 2103	2.60e-11	(14)
Additions to aromatic groups [g]										
aCH	2.04e-13	(16)			1.47e-18	5			2.57e-12	5
aC	2.85e-13	5			3.78e-17	5			7.07e-16	5
aP	7.95e-13	5			3.78e-17	(17)			1.19e-11	5
Additions to aromatic groups in phenols [g]										
aCH (ortho OH)					1.44e-13	6				
aC (ortho OH)					1.60e-18	6				
aC(ipso OH)					1.18e-12	6				



Table S17 (continued)

Group	OH [a,b]					NO <sub>3</sub> [a,b]					Cl [a,c]	
Added to	k(298)		A		Ea (K)	k(298)		A		Ea	k(298)	
Addition to amino N [h]												
NH <sub>2</sub>	1.75e-11	7	1.17e-11	a7	-118	9.47e-15	(18)	3.66e-11	(a4)	2462	2.61e-10	7
NH	7.63e-11	7	3.14e-11	a7	-265	2.27e-14	(18)	3.66e-11	(a4)	2202	3.31e-10	7
N	8.24e-11	7	2.36e-11	a7	-373	2.37e-14	(18)	3.66e-11	(a4)	2188	2.81e-10	7
NH <sub>2</sub> (CO)	6.30e-13	7	1.17e-11	(a3)	872	1.32e-15	(18)	3.66e-11	(a4)	3048	2.09e-11	7
NH(CO)	5.82e-12	7	3.14e-11	(a3)	502	1.37e-15	7	3.66e-11	(a4)	3037	4.20e-11	7
N(CO)	1.35e-11	7	2.36e-11	(a3)	167	2.92e-14	7	3.66e-11	a8	2126	1.21e-10	7
Addition to I atoms (NO <sub>3</sub> reactions only) [h]												
-I						3.14e-13	8					

[a] Base rate constants at 298K are in units of cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>, and are derived as indicated according to the footnote given to the left of the value. The following are used to indicate parameters adjusted to fit rate constant data, with the group of compounds used indicated below.

- 1 Acyclic monoalkenes
- 2 Acyclic conjugated dialkenes
- 3 Allenes
- 4 Alkynes
- 5 Aromatic hydrocarbons
- 6 Phenols
- 7 Amines and/or amides
- 8 Methyl and ethyl iodides

The following indicates derivations for estimated parameters, parameters dependent on adjusted parameters, or parameters derived by other mean, as indicated below.

- (1) In order to estimate branching ratios for additions to unsymmetrical double bonds, base rate constants for the most substituted (least favorable) position are assumed to half of the base rate constant for symmetrical double bonds between the least substituted group, using the high pressure limit if the rate constant is in the falloff regime at atmospheric pressure. This is based on the assumption that the substituents about the radical formed are the major factor affecting the base rate constant. These estimates affect predictions of branching ratios only.
- (2) It is assumed that all addition occurs on the least substituted position, where applicable. Using the approach used for OH reactions also estimates that reactions at the more substituted position occur no more than ~1% of the time.
- (3) It is assumed that addition at either position is equally likely, regardless of substitution about the bond. Using the approach used for OH reactions also estimates that reactions at the two positions occur at comparable rates.
- (4) Insufficient data are available to estimate the base rate constant for addition to a double bond with 4 substituents. It is estimated to be similar to the maximum of the group rate constants derived for additions to bonds with 3 substituents.
- (5) Addition to the side that yields the non-allylic stabilized radical is assumed to occur about ~5% of the time, based roughly on the yields of furans from isoprene and 1,3-butadiene.
- (6) It is assumed that the addition occurs only at the position that yields an allylic stabilized radical.
- (7) It is roughly estimated that 90% of the reaction involves addition to form the allylic stabilized radical.
- (8) No data could be found to derive best fit estimates for rate constants of additions of NO<sub>3</sub> to this conjugated diene group. The base group rate constants are estimated assuming a linear relationship between the log of the base rate constant for OH additions to conjugated double bond groups and the base rate constants that were derived for NO<sub>3</sub> additions where data was available. See Section S1.4. Addition is assumed to occur entirely at the position yielding the

Table S17 (continued)

- allylic radical, where applicable.
- (9) Information is not available to derive rate constants for reactions of Cl with conjugated dialkenes with these structures. We estimate the rate constants for addition at each group to be approximately the same as those derived for reactions with isoprene and 1,3-butadiene, which were similar. It is roughly estimated that 90% of the reaction involves addition to form the allylic stabilized radical.
  - (10) Insufficient rate constant data are available for deriving rate constants for conjugated trienes. The total rate constant for formation of an allylic radical is estimated to be the same as that derived for reactions of conjugated dienes forming a similar allylic radical.
  - (11) No data could be found to derive best fit estimates for rate constants of additions of NO<sub>3</sub> to allenes. The base group rate constant for the NO<sub>3</sub> addition is estimated from the estimated rate constant derived for OH addition and from assuming a linear relationship between the log of the base rate constant for OH additions to various types of double bonds and the base rate constants that were derived for NO<sub>3</sub> additions where data was available. See Section S1.4.
  - (12) The only available rate constant for Cl + cumulated alkenes is for allene itself. The rate constant is relatively high, suggesting that the rate constants for addition to substituted allene systems are probably not much higher. Therefore, we assume that the rate constant for Cl addition to cumulated double bonds is not affected by the presence of alkyl substituents.
  - (13) No rate constant data found for allenes with this substituent configuration. However, rate constants for allene, 1,2-butadiene and 1,2-pentadiene are not too different from those for ethene, propene, and 1-butene, respectively. Based on this, it is assumed that rate constants for these allenes are the same as the analogous alkene with one double bond removed.
  - (14) Acetylene is the only compound in our evaluation dataset with a rate constant for reaction with Cl atoms, but it is pressure dependent and therefore not representative of higher acetylenes. Based on lack of information, we assume that the rate constant for addition to all triple bonds for alkyl acetylenes is the same as the high pressure limit for Cl + acetylene, as recommended by IUPAC (2019).
  - (15) Assumed to be the same as 1/2 of the high pressure limit rate constant for acetylene.
  - (16) Derived from the rate constant for benzene.
  - (17) Insufficient reliable data to derive rate constants for reactions of NO<sub>3</sub> with PAH compounds because of possible interference with N<sub>2</sub>O<sub>5</sub> reactions. Roughly estimate that the group rate constant is the same as for substituted non-PAH (-aC<) groups.
  - (18) Data are available only for reduced N compounds with -N(CO)< and -NH-CO-O- groups, so it is assumed that rate constants for addition at -any -N< groups are the same as derived for -N(CO)<, and that addition at any -NH- or -NH<sub>2</sub> groups are the same as that derived for addition at NH-CO-O-.
- [b] A factors as used to estimate temperature dependences according to  $k(T) = A \exp(-E_a/T)$ . A factors are in units of cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> and are estimated based on measured A factors for the following compounds, as indicated in notes to the left of the tabulated A factors. These A factors, and how well they correspond to the estimated values, are given in the tables in Section S3. The estimated activation energies are in deg K and are derived from the A factor and the 298K rate constant. The following are used to indicate compounds used to derive the A factors.
- a1 propene, 1-butene, 2-butenes, 2-methyl-1-butene, and 2-methyl-2-butene
  - a2 propene and 1-butene
  - a3 1,3-butadiene, 2-methyl-1,3-butadiene, and 1,3-pentadienes (used for total additions per bond for all conjugated alkenes)
  - a4 isoprene
  - a5 allene
  - a6 propyne, 1-butyne, 1-pentyne and 1-hexyne
  - a7 methyl and ethyl amine, dimethylamine and trimethylamine
  - a8 N,N-dimethylformamide, N,N-dimethylacetamide, and N,N-dimethylpropanamide.

Table S17 (continued)

The following are used for estimates.

- (a1) Same A factor per bond as derived for conjugated dialkenes.
  - (a2) Because of insufficient consistent data, total A factor for addition to alkyne bonds roughly estimated to be the same as the average of those derived for alkenes. Rate constant for addition at each group derived from estimated branching ratios.
  - (a3) A factors assumed to be the same as that derived for the corresponding amine.
  - (a4) Estimated to be the same as those derived for addition to  $\text{-N(CO)<}$ .
- [c] The temperature dependence is expected to be small, so A factors are not estimated for Cl reactions.
- [d] Addition is to the group on the left side of the bond. However, the group on the other side, which is where the radical center is formed, is generally the more important factor affecting the group rate constant.
- [e] A "\*" indicates that this group is bonded to the group by the other double bond in the conjugated bond system.
- [f] Addition is to the central carbon only.
- [g] Addition to the indicated group in the aromatic ring. Temperature dependence is expected to be complex and is not estimated. Correction factors are applied if there are substituents in the ortho, meta, para, or ipso positions. If "(ipso OH)" or "(ortho OH)" are indicated, then the base rate constant assignment is used if an OH is in the ipso or ortho position, and correction factors for ipso or ortho positions are not used if they are used to determine the base rate constant.
- [h] As discussed in the text, more reasonable results are obtained if reaction is assumed to occur via addition to the N or (for  $\text{NO}_3$ ) I atom, rather than using substituent correction factors.

Table S17. Substituent correction factors for additions of OH, NO<sub>3</sub>, and Cl to double bonds.

Substituent Group	kOH			kNO <sub>3</sub>			kCl		
	FA <sub>1</sub> <sup>sub</sup>	FA <sub>2</sub> <sup>sub</sup>	[a]	FA <sub>1</sub> <sup>sub</sup>	FA <sub>2</sub> <sup>sub</sup>	[a]	FA <sub>1</sub> <sup>sub</sup>	FA <sub>2</sub> <sup>sub</sup>	[a]
-CH <sub>3</sub>	1	1	(1)	1	1	(1)	1	1	(1)
-CH <sub>2</sub> -	1	1	(2)	1	1	(2)	1	1	(2)
>CH-	1	1	(2)	1	1	(2)	1	1	(2)
>C<	1	1	(2)	1	1	(2)	1	1	(2)
=CH-	1	1	(3)	1	1	(3)	1	1	(3)
=C<	1	1	(3)	1	1	(3)	1	1	(3)
#CH	1	1	(3)	1	1	(3)	1	1	(3)
#C-	1	1	(3)	1	1	(3)	1	1	(3)
aro	0.001	1.36	2	1	78	2	1	1	(3)
-OH	1	1	(3)	1	1	(3)	1	1	(3)
-O-	9.82	1.19	1	1	124	1	1.28	1.28	1
-NO <sub>2</sub>	0.039	0.039	1				1	1	(3)
-ONO <sub>2</sub>	0.039	0.039	(5)				1	1	(3)
-ONO	1	1	(3)				1	1	(3)
-F	0.001	0.23	3	0.030	0.030	3	0.72	0.72	3
-Cl	0.157	0.26	3	0.030	0.030	3	0.59	0.59	3
-BR	0.22	0.22	3	0.020	0.020	3	1	1	(3)
-I	1	1	(3)				1	1	(3)
-NH <sub>2</sub>	1	1	(3)	1	1	(3)	1	1	(3)
-NH-	1	1	(3)	1	1	(3)	1	1	(3)
>N-	1	1	(3)	1	1	(3)	1	1	(3)
=N-	1	1	(3)	1	1	(3)	1	1	(3)
-O-OH	1	1	(3)	1	1	(3)	1	1	(3)
-O-CHO	0.001	0.98	(4)	1	0.78	(4)	1.16	1.16	(4)
-O-CO-	0.001	0.98	1	1	0.78	1	1.16	1.16	1
-O-(=CH <sub>x</sub> )	0.47	0	1	1.62	1.62	1	0.92	0.92	4
-CHO	0.46	0.46	1	0.033	0.007	1	0.001	0.001	1
-CO-	1.43	0.68	1	0.020	0.014	1	0.86	0.86	1
-CO-OH	0.54	0.54	1	0.002	0.009	(6)	0.86	0.86	(7)
-CO-O-	0.60	0.66	1	0.002	0.009	1	0.86	0.86	(7)
-CO-O- ONO <sub>2</sub>	0.47	0.47	1	~0	~0	1	0.86	0.86	(7)
-CH <sub>2</sub> -NO <sub>2</sub>	0.40	0.40	1				1	1	(3)
>CH-NO <sub>2</sub>	0.40	0.40	(8)				1	1	(3)
>C<NO <sub>2</sub>	0.40	0.40	(8)				1	1	(3)
-CH <sub>2</sub> -ONO <sub>2</sub>	0.54	0.54	1				1	1	(3)
>CH-ONO <sub>2</sub>	0.54	0.54	(8)				1	1	(3)
>C<ONO <sub>2</sub>	0.54	0.54	(8)				1	1	(3)
-CH <sub>2</sub> -F	0.52	0.52	3	0.43	0.43	3	0.076	0.076	3
>CH-F	0.52	0.52	(8)	0.43	0.43	(8)	0.076	0.076	(8)
>C<F	0.52	0.52	(8)	0.43	0.43	(8)	0.076	0.076	(8)
-CH <sub>2</sub> -Cl	1	1	(3)	0.012	0.100	3	0.77	0.77	3
>CH-Cl	1	1	(3)	0.012	0.100	(8)	0.77	0.77	(8)
>C<Cl	1	1	(3)	0.012	0.100	(8)	0.77	0.77	(8)
-CH <sub>2</sub> -Br				0.36	0.36	3			
>CH-Br				0.36	0.36	(8)			
>C<Br				0.36	0.36	(8)			

Table S16 (continued)

[a] The derivations of the correction factors are as indicated in the following notes, given to the left of the tabulated factors. The following notes are used to indicate parameters adjusted to fit rate constant data, with the group of compounds used indicated below.

- 1 Unsaturated oxygenates and nitro or nitrato compounds
- 2 Styrenes
- 3 Unsaturated halogenated compounds
- 4 Furans

The following indicates derivations for estimated parameters, parameters dependent on adjusted parameters, or parameters derived by other mean, as indicated below.

- (1) Substituent adjustments not used for  $-\text{CH}_3$  substituents.
- (2) No substituent adjustments used for other alkyl substituents.
- (3) No correction factor is used for the effect of this substituent because insufficient data are available. The rate constant estimate is highly uncertain.
- (4) Because of lack of data, substitution by  $-\text{O}-\text{CHO}$  is assumed to have the same effect as substitution by  $-\text{O}-\text{CO}-$ .
- (5) No information available about substitution by nitrate groups. Assume approximately same correction as substitution by nitro groups.
- (6) Because of lack of data, substitution by  $-\text{CO}-\text{OH}$  is assumed to have the same effect as substitution by  $-\text{CO}-\text{O}-$ .
- (7) Use same factor as derived for  $-\text{CO}-$  substitution.
- (8) Assume effects of b substituents on alkyl groups are independent of the number of hydrogens on the alkyl group.

Table S18. Base group rate parameters for estimating addition rate constants for O<sub>3</sub> and O<sup>3</sup>P.

Groups	Reaction with O <sub>3</sub>					Reaction with O <sup>3</sup> P				
	k(298) [a]		A [b,c]		Ea (K)	k(298) [a]		A [b,d]		Ea (K)
Additions to single or separated C=C double bonds [e]										
CH <sub>2</sub> =CH	9.67e-18	1	3.55e-15	a1	1759	4.44e-12	1	1.02e-11	a1	248
CH <sub>2</sub> =C	1.45e-17	1	5.08e-15	a2	1745	1.74e-11	1	1.14e-11	a2	-127
CH=CH	1.59e-16	(1)	7.23e-15	a3	1138	1.88e-11	1	1.09e-11	a3	-163
cis-CH=CH	1.37e-16	1	3.42e-15	a5	959					
trans-CH=CH	1.84e-16	1	7.23e-15	a6	1094					
CH=C	4.20e-16	1	6.51e-15	a7	817	5.11e-11	1	2.44e-11	a5	-220
C=C	7.46e-16	1	3.00e-15	a8	415	7.69e-11	1	2.81e-11	a6	-300
Additions to conjugated double bond systems [e]										
CH <sub>2</sub> =CH-CH=CH	3.15e-17	1	2.10e-15	9	1251	5.45e-11	(3)	2.26e-11	(a1)	-262
CH <sub>2</sub> =CH-CH=C	1.94e-16	(2)	2.10e-15	(a2)	710	7.92e-11	(3)	2.26e-11	(a1)	-374
CH <sub>2</sub> =CH-C=CH	6.34e-17	(2)	2.10e-15	(a2)	1043	8.70e-11	(3)	2.26e-11	(a1)	-402
CH <sub>2</sub> =CH-C=C	2.94e-16	(2)	2.10e-15	(a2)	586	1.21e-10	(3)	2.26e-11	(a1)	-500
CH <sub>2</sub> =C-CH=CH <sub>2</sub>	1.28e-17	1	9.90e-15	(a3)	1982	3.50e-11	1	2.26e-11	(a1)	-130
CH <sub>2</sub> =C-CH=CH	8.00e-17	1	2.10e-15	(a2)	974	8.64e-11	(3)	2.26e-11	(a1)	-400
CH <sub>2</sub> =C-CH=C	2.94e-16	(2)	2.10e-15	(a2)	586	1.34e-10	(3)	2.26e-11	(a1)	-531
CH <sub>2</sub> =C-C=CH <sub>2</sub>	2.56e-17	1	9.90e-15	(a3)	1775	6.71e-11	(3)	2.26e-11	(a1)	-324
CH <sub>2</sub> =C-C=CH	9.61e-17	(2)	2.10e-15	(a2)	919	1.34e-10	(3)	2.26e-11	(a1)	-531
CH <sub>2</sub> =C-C=C	4.46e-16	(2)	2.10e-15	(a2)	462	1.77e-10	(3)	2.26e-11	(a1)	-613
CH=CH-CH=CH	3.43e-16	1	2.10e-15	(a2)	540	8.35e-11	(3)	2.26e-11	(a1)	-389
CH=CH-CH=C	9.01e-16	(2)	2.10e-15	(a2)	252	1.55e-10	(3)	2.26e-11	(a1)	-573
CH=CH-C=C	1.37e-15	(2)	2.10e-15	(a2)	128	2.01e-10	(3)	2.26e-11	(a1)	-651
CH=C-CH=CH	2.94e-16	(2)	2.10e-15	(a2)	586	1.55e-10	(3)	2.26e-11	(a1)	-573
CH=C-CH=C	1.37e-15	(2)	2.10e-15	(a2)	128	2.21e-10	(3)	2.26e-11	(a1)	-680
CH=C-C=CH	4.46e-16	(2)	2.10e-15	(a2)	462	2.21e-10	(3)	2.26e-11	(a1)	-680
C=CH-CH=C	3.06e-15	1	2.10e-15	(a2)	-112	2.37e-10	(3)	2.26e-11	(a1)	-701
C=C-CH=C	6.34e-15	(2)	2.10e-15	(a2)	-329	2.77e-10	(3)	2.26e-11	(a1)	-747
C=C-C=C	9.62e-15	(2)	2.10e-15	(a2)	-454	3.41e-10	(3)	2.26e-11	(a1)	-808
Additions to cumulated double bond systems										
CH <sub>2</sub> =C=CH	0	(4)				6.55e-12	3	2.72e-11	(a2)	424
CH <sub>2</sub> =C=C	0	(4)				3.00e-11	3	2.72e-11	(a2)	-29
CH=C=CH	0	(4)				1.60e-11	3	2.72e-11	(a2)	158
CH=C=C	0	(4)				8.71e-11	(3)	2.72e-11	(a2)	-347
C=C=C	0	(4)				9.82e-12	(3)	2.72e-11	(a2)	304
Additions to alpha-oxygenated double bond systems [f]										
CH <sub>2</sub> =CH-OH	2.76e-16	(5)	1.09e-15	(a4)	409					
CH <sub>2</sub> =C-OH	1.52e-17	(5)	1.09e-15	(a4)	1274					
CH=CH-OH	7.43e-17	(5)	1.81e-16	(a5)	265					
CH=C-OH	2.68e-16	(5)	1.81e-16	(a5)	-117					
C=CH-OH	1.56e-16	(5)	1.81e-16	(a5)	44					
C=C-OH	5.61e-16	(5)	1.81e-16	(a5)	-338					
CH <sub>2</sub> =CH-O-	2.76e-16	4	1.09e-15	(a4)	409	1.98e-11	(3)	2.32e-11	(a3)	47
CH <sub>2</sub> =C-O-	1.52e-17	4	1.09e-15	(a4)	1274	4.99e-11	(3)	2.32e-11	(a3)	-228
CH=CH-O-	7.43e-17	(6)	1.81e-16	(a5)	265	9.16e-11	(3)	2.32e-11	(a3)	-409
CH=C-O-	2.68e-16	(6)	1.81e-16	(a5)	-117	2.02e-10	(3)	2.32e-11	(a3)	-645
C=CH-O-	1.56e-16	(6)	1.81e-16	(a5)	44	2.02e-10	(3)	2.32e-11	(a3)	-645
C=C-O-	5.61e-16	(6)	1.81e-16	(a5)	-338	3.15e-10	(3)	2.32e-11	(a3)	-778

Table S17 (continued)

Groups	Reaction with O <sub>3</sub>			Reaction with O <sup>3</sup> P		
	k(298) [a]	A [b,c]	Ea (K)	k(298) [a]	A [b,d]	Ea (K)
CH <sub>2</sub> =CH-O-CHO	3.82e-18	(7)	1.09e-15 (a4)	1685		
C=CH-O-CHO	3.93e-18	(7)	1.81e-16 (a5)	1140		
CH=CH-O-CHO	1.88e-18	(7)	1.81e-16 (a5)	1361		
CH <sub>2</sub> =C-O-CHO	7.00e-19	(7)	1.09e-15 (a4)	2191		
CH=C-O-CHO	6.76e-18	(7)	1.81e-16 (a5)	979		
C=C-O-CHO	1.42e-17	(7)	1.81e-16 (a5)	758		
CH <sub>2</sub> =CH-O-CO-	3.82e-18	4	1.09e-15 (a4)	1685	1.38e-12 (3)	2.32e-11 (a3) 842
C=CH-O-CO-	3.93e-18	(6)	1.81e-16 (a5)	1140	2.77e-12 (3)	2.32e-11 (a3) 633
CH=CH-O-CO-	1.88e-18	(6)	1.81e-16 (a5)	1361	4.29e-12 (3)	2.32e-11 (a3) 503
CH <sub>2</sub> =C-O-CO-	7.00e-19	4	1.09e-15 (a4)	2191	1.52e-11 (3)	2.32e-11 (a3) 127
CH=C-O-CO-	6.76e-18	(6)	1.81e-16 (a5)	979	2.10e-11 (3)	2.32e-11 (a3) 29
C=C-O-CO-	1.42e-17	(6)	1.81e-16 (a5)	758	1.48e-11 (3)	2.32e-11 (a3) 134
CH <sub>2</sub> =CH-CHO	2.80e-19	4	1.09e-15 (a4)	2464	4.00e-13 4	2.32e-11 a9 1210
CH <sub>2</sub> =C-CHO	1.20e-18	4	1.09e-15 a11	2030	1.04e-12 (3)	2.32e-11 (a3) 924
CH=CH-CHO	1.86e-18	4	1.81e-16 a12	1363	2.49e-12 (3)	2.32e-11 (a3) 665
CH=C-CHO	3.91e-18	4	1.81e-16 (a5)	1142	2.89e-12 (3)	2.32e-11 (a3) 621
C=CH-CHO	1.82e-18	4	1.81e-16 (a5)	1370	9.24e-12 (3)	2.32e-11 (a3) 274
C=C-CHO	9.47e-18	(6)	1.81e-16 (a5)	879	7.12e-12 (3)	2.32e-11 (a3) 352
CH <sub>2</sub> =CH-CO-	5.40e-18	4	1.09e-15 (a4)	1582	1.15e-12 (3)	2.32e-11 (a3) 897
CH <sub>2</sub> =C-CO-	1.19e-17	4	1.09e-15 (a4)	1346	7.57e-12 (3)	2.32e-11 (a3) 334
CH=CH-CO-	4.18e-17	4	1.81e-16 (a5)	436	2.04e-11 (3)	2.32e-11 (a3) 39
CH=C-CO-	4.31e-17	4	1.81e-16 (a5)	427	2.26e-11 (3)	2.32e-11 (a3) 8
C=CH-CO-	8.29e-18	4	1.81e-16 (a5)	918	2.54e-11 (3)	2.32e-11 (a3) -27
C=C-CO-	4.38e-17	(6)	1.81e-16 (a5)	422	4.10e-11 (3)	2.32e-11 (a3) -169
CH <sub>2</sub> =CH-CO-OH	7.05e-19	4	1.09e-15 (a4)	2189	5.71e-13 (3)	2.32e-11 (a3) 1104
CH <sub>2</sub> =C-CO-OH	2.99e-18	4	1.09e-15 (a4)	1758	2.88e-12 (3)	2.32e-11 (a3) 621
CH=CH-CO-OH	2.07e-18	(6)	1.81e-16 (a5)	1331	2.95e-12 (3)	2.32e-11 (a3) 614
CH=C-CO-OH	7.47e-18	(6)	1.81e-16 (a5)	949	6.51e-12 (3)	2.32e-11 (a3) 379
C=CH-CO-OH	4.35e-18	(6)	1.81e-16 (a5)	1110	6.51e-12 (3)	2.32e-11 (a3) 379
C=C-CO-OH	1.57e-17	(6)	1.81e-16 (a5)	728	1.02e-11 (3)	2.32e-11 (a3) 246
CH <sub>2</sub> =CH-CO-O-	1.13e-18	4	1.09e-15 (a4)	2049	4.08e-13 (3)	2.32e-11 (a3) 1204
CH <sub>2</sub> =C-CO-O-	8.97e-18	4	1.09e-15 (a4)	1431	5.45e-12 (3)	2.32e-11 (a3) 432
CH=CH-CO-O-	7.88e-18	4	1.81e-16 (a5)	933	5.40e-12 (3)	2.32e-11 (a3) 434
C=CH-CO-O-	8.78e-18	4	1.81e-16 (a5)	901	6.24e-12 (3)	2.32e-11 (a3) 391
CH=C-CO-O-	2.51e-17	(6)	1.81e-16 (a5)	588	2.44e-11 (3)	2.32e-11 (a3) -15
C=C-CO-O-	6.99e-17	(6)	1.81e-16 (a5)	283	1.20e-11 (3)	2.32e-11 (a3) 196
CH <sub>2</sub> =CH-CO-CO <sub>x</sub>	5.40e-18	(8)	1.09e-15 (a4)	1582		
CH <sub>2</sub> =C-CO-CO <sub>x</sub>	1.19e-17	(8)	1.09e-15 (a4)	1346		
CH=CH-CO-CO <sub>x</sub>	4.18e-17	(8)	1.81e-16 (a5)	436		
CH=C-CO-CO <sub>x</sub>	4.31e-17	(8)	1.81e-16 (a5)	427		
C=CH-CO-CO <sub>x</sub>	8.29e-18	(8)	1.81e-16 (a5)	918		
C=C-CO-CO <sub>x</sub>	4.38e-17	(8)	1.81e-16 (a5)	422		
CO <sub>x</sub> -CH <sub>x</sub> =CH <sub>x</sub> -CO <sub>x</sub>	3.27e-18	4	1.81e-16 (a5)	1195	3.99e-13 (5)	2.32e-11 (a3) 1211
Additions to triple bonds [e]						
CH#CH	1.00e-20	5	(Not estimated)	1.40e-13	5	2.66e-11 (a4) 1563
CH#C	1.68e-20	5	(Not estimated)	8.97e-13	5	2.66e-11 a10 1010

Table S17 (continued)

Groups	Reaction with O <sub>3</sub>			Reaction with O <sup>3</sup> P		
	k(298) [a]	A [b,c]	Ea (K)	k(298) [a]	A [b,d]	Ea (K)
C#C	1.68e-20 (9)	(Not estimated)		8.60e-12 5	2.66e-11 (a4)	336
	Additions to amino groups					
-NH <sub>2</sub>	7.40e-21 6	(Not estimated)		8.54e-13 6	9.02e-12 a11	702
-NH-	1.67e-18 6	(Not estimated)		6.00e-12 6	1.52e-11 a12	277
-N<	7.84e-18 6	(Not estimated)		2.18e-11 6	1.08e-11 a13	-209

[a] Base rate constants at 298K are in units of cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>, and are derived as indicated according to the footnote given to the left of the value. The following are used to indicate parameters adjusted to fit rate constant data, with the group of compounds used indicated below.

- 1 Acyclic monoalkenes or conjugated dialkenes
- 2 Cyclic monoalkenes
- 3 Cumulated dialkenes
- 4 Unsaturated oxygenates
- 5 Monoalkynes
- 6 Acyclic alkyl amines

The following indicates derivations for estimated parameters, parameters dependent on adjusted parameters, or parameters derived by other mean, as indicated below.

- (1) Average of value derived for cis and trans isomers.
- (2) Estimated based on parameters adjusted to fit other types of conjugated alkenes, using a correlation between the number of substituents in the end and middle positions and the group rate constants derived to fit available data. See Section S1.7.
- (3) Estimated based on correlations between base rate constants for additions of O<sup>3</sup>P or OH to the same bond systems, as discussed in Section S1.7.
- (4) Additions of O<sub>3</sub> to cumulated double bonds are assumed to be slow.
- (5) No data available on effect of alpha -OH substitution. Assume same base rate constants as for unsaturated alpha ethers.
- (6) Estimated based on parameters adjusted to fit other types of unsaturated oxygenates, based on a correlation between the number of alpha and beta substituents around the double bond and the group rate constants derived to fit available data. See Section S1.7.
- (7) Assumed to have the same base rate constant as the structure substituted by -O-CO-.
- (8) Assumed to have the same base rate constant as the structure substituted by -CO- alone.
- (9) No data available. Assume the same group rate constant as derived to fit data for monosubstituted alkynes.

[b] A factors as used to estimate temperature dependences according to  $k(T)=A \exp(-E_a/T)$ . A factors are in units of cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> and are estimated based on measured A factors for the following compounds, as indicated in notes to the left of the tabulated A factors. These A factors, and how well they correspond to the estimated values, are given in Table S24 and Table S25. The estimated activation energies are in deg K and are derived from the A factor and the 298K rate constant.

[c] Notes for the derivations of A factors for O<sub>3</sub> reactions are as follows. The following are used to indicate compounds used to derive the A factors.

- 1 Propene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene and 1-heptene
- 2 2-methyl-1-propene, 2-methyl-1-butene and 2,4,4-trimethyl-1-pentene
- 4 cyclopentene, 3-methylcyclohexene, cycloheptene and cyclooctene
- 5 (Z)-2-hexene, (Z)-2-butene and (Z)-2-pentene
- 6 (E)-2-butene, (E)-2-pentene and (E)-2-hexene
- 7 2-methyl-2-butene
- 8 2,3-dimethyl-2-butene
- 9 (3E)-penta-1,3-diene
- 10 1,3-butadiene, isoprene and 2,3-dimethyl-1,3-butadiene
- 11 methacrolein and methyl vinyl ketone



Table S17 (continued)

12 (E)-2-pentenal and (E)-2-hexenal

The following are used to document estimates for A factors for O<sub>3</sub> reactions.

- (1) Assumed to be the same as that derived for 2-methyl-2-butene
- (2) Assumed to be the same as that derived for CH<sub>2</sub>=CH-CH=CH.
- (3) Assumed to be the same as that derived for CH<sub>2</sub>=CH-CH=CH<sub>2</sub>.
- (4) Assumed to be the same as that derived for CH<sub>2</sub>=C-CHO.
- (5) Assumed to be the same as that derived for CH=CH-CHO.

[d] Notes for the derivations of A factors for O<sup>3</sup>P reactions are as follows. The following are used to indicate compounds used to derive the A factors.

- a1 Propene
- a2 Isobutene
- a3 trans-2-Butene
- a4 Cyclohexene
- a5 2-Methyl-2-Butene
- a6 2,3-Dimethyl-2-Butene
- a7 1,3-Butadiene
- a8 1,2-propadiene (allene)
- a9 Acrolein
- a10 Methyl Acetylene
- a11 Methyl amine
- a12 Dimethyl amine
- a13 Trimethyl amine

The following are used to document estimates for A factors for O<sup>3</sup>P reactions.

- (a1) Use same A factor as derived for 1,3-Butadiene.
- (a2) Use same A factor as derived for 1,2-propadiene (allene).
- (a3) Use same A factor as derived for Acrolein.
- (a4) Use same A factor as derived for Methyl Acetylene.

[e] The various possible initial reaction routes forming Criegee intermediates are assumed to be equally probable in the case of O<sub>3</sub> additions.

[f] Following the estimate made by Jenkin et al (2020), it is assumed that the indicated α substituent is on the Criegee intermediate 10% of the time, with the remainder being on the carbonyl product.

Table S19. Substituent and structure correction factors for additions of O<sub>3</sub> to double bonds.

Substituent or structure	Isolated [a]		Conjugated [a,b]		-Substituted [a,c]	
	Fac	Note	Fac	Note	Fac	Note
-aro	1.87	1	1.37	(1)		
-OH					1	(2)
-O-			0.56	(1)	0.31	2
-CO-			0.024	2	1	(2)
-CHO			0.024	(3)	1	(2)
-NO <sub>2</sub>	0.007	2	0.082	(1)		
-ONO <sub>2</sub>	0.007	(4)	0.082	(1)		
-F	0.076	3	0.27	(1)		
-Cl	0.014	3	0.118	(1)		
-O-CO-					1	(2)
-O-CO-O-					1	(2)
-CHx-OH	1.25	2	1.12	(1)		
-CHx-O-	0.34	2	0.58	(1)		
-CHx-CHO	0.34	2	0.59	(1)		
-CHx-CO-	0.26	2	0.51	(1)		
-CHx-O-CO-	0.34	(5)	0.58	(1)		
-CHx-NO <sub>2</sub>	0.042	(6)	0.21	(1)		
-CHx-ONO <sub>2</sub>	0.042	2	0.21	(1)		
-CHx-F	0.099	(7)	0.31	(1)		
-CHx-Cl	0.198	3	0.44	(1)		
Furan	1.75e-3	4				
Furan (1sub)	0.0170	4				
Furan (2sub)	0.034	4				
Furan (3sub)	0.050	(8)				
Furan (4sub)	0.066	(8)				
Ring (3)	4.00	(9)			4.00	(10)
Ring (4)	4.00	(9)	4.00	(9)	4.00	(10)
Ring (5)	4.00	5	4.00	(9)	4.00	(10)
Ring (6)	0.67	(9)	5.98	6	0.67	(10)
Ring (7)	2.75	5	0.44	6	2.75	(10)
Ring (8)	3.45	5	1	(11)	3.45	(10)
Ring (9)	1	(11)	1	(11)	1	(10)
Ring (10)	1	(11)	1	(11)	1	(10)
Fβ <sup>O3</sup> [d]	0.27	7				

[a] The derivations of the correction factors are as indicated in the following notes, given to the left of the tabulated factors. The following notes are used to indicate parameters adjusted to fit rate constant data, with the group of compounds used indicated below.

- 1 Styrenes
- 2 Unsaturated oxygenates and nitro compounds
- 3 Unsaturated halogenated compounds
- 4 Furans
- 5 Cyclic monoalkenes
- 6 Cyclic conjugated alkenes
- 7 Acyclic alkenes

Table S19 (continued)

The following indicates derivations for estimated parameters, parameters dependent on adjusted parameters, or parameters derived by other mean, as indicated below.

- (1) Use the approach of the VOC+O3 SARs of Jenkin et al (2020) and assume that the corrections for this substituent on conjugated double bonds is approximately the square root of the correction for the substituent on isolated double bonds.
  - (2) There are no data to derive corrections when this substituent is on an unsaturated oxygenate structure, so we use no correction. This is highly uncertain.
  - (3) Assume it is approximately equal to the correction derived for substitution by ketone groups.
  - (4) Estimate the correction is approximately that derived for substitution by -ONO<sub>2</sub>, though that also is uncertain.
  - (5) Assume it is the same as that for substitution by -CH<sub>x</sub>-O-.
  - (6) Estimate the correction is approximately that derived for substitution by -CH<sub>x</sub>-ONO<sub>2</sub>.
  - (7) Roughly estimate the correction factor to be half of that for substitution by -CH<sub>x</sub>-Cl.
  - (8) No data available to derive furan correction for furans with more than 2 substituents. Corrections derived by extrapolating factors for 0-2 substituents, which increased approximately linearly.
  - (9) Insufficient data to derive the correction factor for this strained ring, so we roughly estimate the factor to be the same as derived for cyclic monoalkenes with 5 member rings. This is highly uncertain. See Section S1.6.
  - (10) Insufficient data to reliably derive ring correction factors for unsaturated oxygenates. Use the same factors as derived or estimated for cyclic monoalkenes, but this is highly uncertain. See Section S1.6.
  - (11) Insufficient data to derive the correction factor for this large ring, so no correction factor is used. See Section S1.6.
- [b] The factors given are used for any substituents on the conjugated double bond structure
- [c] The factors are applied for substituents on the double bonded carbons but not on the  $\alpha$  substituent that defines the base rate constant. The factors are not used for substituents that define the base rate constant.
- [d] Correction factor applied based on the number of  $\beta$  substituents around the double bond. See Equation (7) in the main text.

Table S20. Substituent correction factors for additions to aromatic rings.

Rxn	Addition Group	Aromatic Ring substituent correction factors				[a]
		Ortho	Meta	Para	Ipsso	
OH	-CH3	9.59	1	1	1	1
	-CH2-	9.59	1	1	1	(1)
	>CH-	9.59	1	1	1	(1)
	>C<	9.59	1	1	1	(1)
	=CH-	9.59	1	1	1	(2)
	=C<	9.59	1	1	1	(2)
	#C-	9.59	1	1	1	(3)
	aro	8.22	1.73	1.68	1	1
	-OH	14.5	3.38	1.27	0.94	2
	-O-	12.7	2.96	1.11	0.83	2
	-CHO	0.79	0.79	0.79	0.79	2
	-CO-	0.79	0.79	0.79	0.79	(4)
	-NO2	0.090	0.090	0.090	0.090	2
	-ONO2	0.090	0.090	0.090	0.090	(5)
	-F	0.48	0.48	0.48	0.48	3
	-Cl	0.62	0.62	0.62	0.62	3
	-BR	0.70	0.70	0.70	0.70	3
	-CO-OH	0.79	0.79	0.79	0.79	(4)
	-CO-O-	0.79	0.79	0.79	0.79	(4)
	-CO-O-ONO2	0.79	0.79	0.79	0.79	(4)
NO3	-CH3	5.40	1	5.82	1	1
	-CH2-	5.40	1	5.82	1	(1)
	>CH-	5.40	1	5.82	1	(1)
	>C<	5.40	1	5.82	1	(1)
	=CH-	5.40	1	5.82	1	(2)
	=C<	5.40	1	5.82	1	(2)
	-OH	23.3	1	10.0	1	2
	-O-	13.0	1	140	1	2
	-CHO	212	1	176	1	2
Cl	-CH3	2.80	2.80	2.80	1	1
	-CH2-	2.80	2.80	2.80	1	(1)
	>CH-	2.80	2.80	2.80	1	(1)
	>C<	2.80	1	1	1	(1)
	=CH-	2.80	2.80	2.80	1	(2)
	=C<	2.80	2.80	2.80	1	(2)
	aro	0.73	0.73	0.73	1	1
	-OH	19.3	19.3	19.3	1	2
	-O-	0.87	0.87	0.87	0.87	4
	-CHO	0.47	0.47	0.47	0.47	2
	-NO2	0.054	0.054	0.054	0.054	2
	-O-OH	1	1	1	1	(6)
	-O-CHO	1	1	1	1	(6)
	-O-CO-	1	1	1	1	(6)

Table S20 (continued)

[a] The derivations of the correction factors are as indicated in the following notes. The following indicate parameters adjusted to fit rate constant data, with the group of compounds used indicated below.

- 1 Aromatic hydrocarbons
- 2 Oxygenated or nitro aromatics
- 3 Halogenated aromatics
- 4 Anisole

The following indicates derivations for estimated parameters, parameters dependent on adjusted parameters, or parameters derived by other mean, as indicated below.

- (1) Effects of substitutions by alkyl groups are assumed to be independent of the number of substituents on the alkyl group.
- (2) Correction factors for styrenes assumed to be the same as for alkyl substitution because estimates are not sensitive to this parameter.
- (3) Because of lack of data, the factors are assumed to be the same as derived for alkyl substitution.
- (4) Because of lack of data, the factors are assumed to be the same as derived for aldehyde substitution.
- (5) Because of lack of data, the factors for nitrate substitution are assumed to be the same as derived for nitro substitution.
- (6) Insufficient data to derive correction factor for this substituent. Based on data for anisole, it is assumed that no correction may be needed, but this is highly uncertain because large corrections are needed for -OH substitution.

### S3. Tables of Rate Constants

The tables in this section give the experimental and estimated rate constants for all the compounds with experimental data in our database, with Table S21 giving the data for OH, Table S22 for Cl, Table S23 for NO<sub>3</sub>, Table S24 for O<sub>3</sub>, and Table S25 for O<sup>3</sup>P. The A experimental factors used to derive the temperature dependences are also shown, along with the A factors estimated for these reactions. The experimental rate constants used in Table S21 through Table S24 are all from McGillen et al (2020), and footnotes to Table S25 give the sources of the O<sup>3</sup>P rate constants.

In each table, the compounds used to derive the estimation parameters are listed first, following those used for evaluation only. The compounds within each group are listed by type of compound, and then (in most cases) sorted by carbon number. The factor errors of the rate constant and A factor estimates are also shown, where a positive factor indicating overprediction, a negative factor indicating underprediction, and a "-" indicating a fit to within  $\pm 10\%$ .

Table S21. Experimental and estimated rate constants for the reactions of organics with OH radicals.

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
Used for parameter derivations						
Acyclic alkanes						
ethane	2.49e-13	2.60e-13	-	1.51e-12	7.32e-13	-2.1
propane	1.11e-12	1.18e-12	-	2.00e-12	7.95e-13	-2.5
butane	2.38e-12	2.53e-12	-	2.09e-12	1.25e-12	-1.7
pentane	3.76e-12	3.95e-12	-	2.58e-12	1.78e-12	-1.5
hexane	4.97e-12	5.37e-12	-	1.52e-12	2.31e-12	1.5
heptane	6.23e-12	6.79e-12	-	3.84e-12	2.84e-12	-1.4
octane	8.48e-12	8.21e-12	-	2.49e-12	3.38e-12	1.4
nonane	1.02e-11	9.64e-12	-	2.34e-12	3.91e-12	1.7
decane	1.31e-11	1.11e-11	-1.2	2.53e-12	4.45e-12	1.8
undecane	1.19e-11	1.25e-11	-			
dodecane	1.31e-11	1.39e-11	-			
tridecane	1.51e-11	1.53e-11	-			
tetradecane	1.67e-11	1.67e-11	-			
pentadecane	1.92e-11	1.82e-11	-			
hexadecane	2.16e-11	1.96e-11	-			
2-methylpropane	2.11e-12	2.31e-12	-			
2,2-dimethylpropane	9.10e-13	7.45e-13	-1.2	1.30e-12	2.10e-12	1.6
2-methylbutane	3.74e-12	3.76e-12	-			
2,3-dimethylbutane	5.86e-12	4.34e-12	-1.4			
2,2-dimethylbutane	2.23e-12	1.94e-12	-1.1			
3-methylpentane	5.54e-12	5.38e-12	-			
2-methylpentane	5.25e-12	5.11e-12	-			
2,3-dimethylpentane	6.57e-12	5.78e-12	-1.1			
2,2,3-trimethylbutane	3.81e-12	3.58e-12	-			
2-methylhexane	6.69e-12	6.53e-12	-			
2,2-Dimethyl Pentane	3.40e-12	3.40e-12	-			
3-methylhexane	6.30e-12	6.72e-12	-			
2,4-dimethylpentane	5.76e-12	6.34e-12	1.1			
2,3,4-trimethylpentane	6.60e-12	6.36e-12	-			
2,2-Dimethyl Hexane	4.80e-12	4.82e-12	-			
2,2,3,3-tetramethylbutane	9.70e-13	1.12e-12	1.2	1.20e-11	3.15e-12	-3.8
2,2,4-trimethylpentane	3.34e-12	4.52e-12	1.4			
2-Methyl Octane	1.01e-11	9.37e-12	-			
4-Methyl Octane	9.70e-12	9.49e-12	-			
2,3,5-Trimethyl Hexane	7.90e-12	8.36e-12	-			
3,3-diethylpentane	4.80e-12	5.53e-12	1.2			
2,6-Dimethyl Octane	1.29e-11	1.07e-11	-1.2			
2-Methyl Nonane	1.28e-11	1.08e-11	-1.2			
3,4-Diethyl Hexane	6.92e-12	1.04e-11	1.5			
Cyclic alkanes						
cyclopropane	7.60e-14	7.65e-14	-			
cyclobutane	2.00e-12	2.00e-12	-			
cyclopentane	4.77e-12	5.51e-12	1.2			
methylcyclopentane	7.56e-12	6.53e-12	-1.2			
isopropylcyclopropane	2.61e-12	2.27e-12	-1.2			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
cyclohexane	6.69e-12	8.53e-12	1.3			
cycloheptane	9.95e-12	9.95e-12	-			
methylcyclohexane	9.26e-12	9.80e-12	-			
(Z)-1,4-dimethylcyclohexane	1.49e-11	1.11e-11	-1.3			
methylcycloheptane	1.51e-11	1.12e-11	-1.3			
cyclooctane	1.39e-11	1.14e-11	-1.2			
(E)-1,4-dimethylcyclohexane	1.31e-11	1.11e-11	-1.2			
ethylcyclohexane	1.34e-11	1.16e-11	-1.2			
1,3,5-trimethylcyclohexane	1.77e-11	1.26e-11	-1.4			
isopropylcyclohexane	1.44e-11	1.18e-11	-1.2			
propylcyclohexane	1.33e-11	1.30e-11	-			
1,1,3-Trimethyl Cyclohexane	8.70e-12	9.02e-12	-			
cyclodecane	1.66e-11	1.42e-11	-1.2			
butyl-cyclohexane	1.47e-11	1.44e-11	-			
Hexyl Cyclohexane	1.78e-11	1.72e-11	-			
Acyclic monoalkenes						
propene	2.44e-11	3.07e-11	1.3	1.20e-11	7.36e-12	-1.6
1-butene	3.10e-11	3.16e-11	-	6.60e-12	7.69e-12	1.2
2-methylpropene	5.10e-11	6.16e-11	1.2	9.40e-12	9.40e-12	-
1-pentene	3.22e-11	3.29e-11	-			
2-methyl-1-butene	6.10e-11	6.25e-11	-			
3-methyl-1-butene	3.18e-11	3.27e-11	-	5.32e-12	7.64e-12	1.4
1-hexene	3.70e-11	3.43e-11	-			
2-methyl-1-pentene	6.14e-11	6.39e-11	-			
3,3-dimethyl-1-butene	2.90e-11	3.11e-11	-			
1-heptene	3.88e-11	3.58e-11	-			
2-methyl-hex-1-ene	6.50e-11	6.53e-11	-			
2,3-dimethyl-1-pentene	5.70e-11	6.51e-11	1.1			
4,4-dimethyl-pent-1-ene	2.41e-11	3.23e-11	1.3			
2-methyl-1-heptene	6.71e-11	6.67e-11	-			
1-octene	3.44e-11	3.72e-11	-			
1-nonene	4.32e-11	3.86e-11	-1.1			
2-methyl-1-octene	7.02e-11	6.81e-11	-			
1-decene	4.61e-11	4.00e-11	-1.2			
2-methyl-1-nonene	7.28e-11	6.95e-11	-			
1-undecene	4.79e-11	4.14e-11	-1.2			
2-methyl-1-decene	7.85e-11	7.10e-11	-			
1-dodecene	5.03e-11	4.29e-11	-1.2			
2-methyl-1-undecene	7.85e-11	7.24e-11	-			
1-tridecene	5.09e-11	4.43e-11	-1.1			
2-methyl-dodec-1-ene	7.96e-11	7.38e-11	-			
2-methyl-1-tridecene	8.38e-11	7.52e-11	-1.1			
1-tetradecene	4.96e-11	4.57e-11	-			
trans-2-butene	6.31e-11	6.23e-11	-	6.06e-12	7.61e-12	1.3
cis-2-butene	5.28e-11	6.23e-11	1.2	3.80e-12	7.61e-12	2.0
trans-2-pentene	6.70e-11	6.32e-11	-			
cis-2-pentene	6.50e-11	6.32e-11	-			
2-methyl-2-butene	8.69e-11	8.75e-11	-	1.92e-11	7.63e-12	-2.5
2,3-dimethyl-2-butene	1.10e-10	1.06e-10	-			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
2-methyl-2-pentene	8.90e-11	8.84e-11	-			
(Z)-3-hexene	6.27e-11	6.40e-11	-			
trans-4-methyl-2-pentene	6.10e-11	6.43e-11	-			
trans-2-hexene	6.08e-11	6.45e-11	-			
trans-hept-2-ene	6.80e-11	6.59e-11	-			
trans-2-heptene	6.80e-11	6.59e-11	-			
2,3-dimethyl-2-pentene	1.03e-10	1.07e-10	-			
trans-4,4-dimethyl-pent-2-ene	5.50e-11	6.27e-11	1.1			
trans-oct-2-ene	7.23e-11	6.73e-11	-			
trans-4-octene	6.90e-11	6.67e-11	-			
trans-non-2-ene	7.54e-11	6.88e-11	-			
trans-dec-2-ene	7.80e-11	7.02e-11	-1.1			
(E)-7-tetradecene	7.47e-11	7.53e-11	-			
Acyclic conjugated dialkenes						
1,3-butadiene	6.63e-11	6.89e-11	-			
(3E)-penta-1,3-diene	1.16e-10	1.07e-10	-			
2-methyl-1,3-butadiene	1.00e-10	9.69e-11	-			
cis-1,3-pentadiene	1.07e-10	1.07e-10	-			
trans-1,3-hexadiene	1.12e-10	1.08e-10	-			
2-methyl-1,3-pentadiene	1.36e-10	1.35e-10	-			
2,3-dimethyl-1,3-butadiene	1.22e-10	1.25e-10	-			
4-methyl-1,3-pentadiene	1.31e-10	1.36e-10	-			
cis/trans-2,4-hexadiene	1.34e-10	1.45e-10	-			
2,5-dimethyl-2,4-hexadiene	2.10e-10	2.04e-10	-			
Allenes and other acyclic di- or polyalkenes						
propadiene	9.82e-12	9.82e-12	-			
1,2-butadiene	2.60e-11	3.01e-11	1.2			
1,2-pentadiene	3.60e-11	3.10e-11	-1.2			
3-methyl-1,2-butadiene	5.70e-11	5.70e-11	-			
Alkynes						
methyl acetylene	5.40e-12	5.98e-12	1.1			
diacetylene	1.00e-11	1.17e-11	1.2			
1-butyne	7.50e-12	6.87e-12	-			
2-butyne	2.70e-11	2.70e-11	-			
pent-1-yne	9.62e-12	8.21e-12	-1.2			
hex-1-yne	1.08e-11	9.63e-12	-1.1			
Alkylbenzenes						
benzene	1.20e-12	1.22e-12	-			
toluene	5.60e-12	5.22e-12	-			
p-xylene	1.21e-11	9.21e-12	-1.3			
o-xylene	1.36e-11	1.06e-11	-1.3			
ethylbenzene	7.00e-12	6.05e-12	-1.2			
m-xylene	2.31e-11	2.43e-11	-			
p-ethyltoluene	1.23e-11	1.00e-11	-1.2			
1,2,4-trimethylbenzene	3.25e-11	2.96e-11	-			
o-ethyltoluene	1.23e-11	1.14e-11	-			
1,3,5-trimethylbenzene	5.86e-11	5.83e-11	-			



Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
1,2,3-trimethylbenzene	3.27e-11	3.69e-11	1.1			
iso-propylbenzene	6.30e-12	7.51e-12	1.2			
n-propylbenzene	5.80e-12	7.47e-12	1.3			
m-ethyltoluene	2.04e-11	2.51e-11	1.2			
p-cymene	1.52e-11	1.15e-11	-1.3			
1,2,4,5-tetramethylbenzene	5.61e-11	5.01e-11	-1.1			
1,2,3,4-tetramethylbenzene	6.64e-11	6.33e-11	-			
1,2,3,5-tetramethylbenzene	6.24e-11	7.10e-11	1.1			
tert-butylbenzene	4.50e-12	5.37e-12	1.2			
pentamethylbenzene	1.07e-10	1.05e-10	-			
hexamethylbenzene	1.41e-10	1.59e-10	1.1			
Naphthalenes						
naphthalene	2.30e-11	1.56e-11	-1.5			
1-methylnaphthalene	4.70e-11	2.90e-11	-1.6			
2-methylnaphthalene	5.05e-11	4.62e-11	-			
1,5-dimethylnaphthalene	5.77e-11	4.25e-11	-1.4			
1,4-dimethylnaphthalene	5.57e-11	4.25e-11	-1.3			
1-ethylnaphthalene	3.50e-11	2.98e-11	-1.2			
1,7-dimethylnaphthalene	6.53e-11	5.96e-11	-			
1,6-dimethylnaphthalene	6.10e-11	5.96e-11	-			
2,7-dimethylnaphthalene	6.60e-11	7.68e-11	1.2			
2,3-dimethylnaphthalene	6.80e-11	8.08e-11	1.2			
2,6-dimethylnaphthalene	6.39e-11	7.68e-11	1.2			
2-ethylnaphthalene	3.86e-11	4.70e-11	1.2			
1,2-dimethylnaphthalene	5.73e-11	7.14e-11	1.2			
1,3-dimethylnaphthalene	7.20e-11	1.03e-10	1.4			
1,8-dimethylnaphthalene	6.03e-11	1.01e-10	1.7			
Styrenes or aromatics with double bonds or non-aromatic rings						
styrene	5.80e-11	4.03e-11	-1.4			
indene	7.80e-11	5.29e-11	-1.5			
β-methylstyrene	5.70e-11	4.72e-11	-1.2			
α-methylstyrene	5.10e-11	8.24e-11	1.6			
β,β-dimethylstyrene	3.20e-11	4.74e-11	1.5			
Monofunctional acyclic alcohols, ethers, and hydroperoxides						
methanol	8.78e-13	8.78e-13	-			
ethanol	3.33e-12	3.95e-12	1.2			
2-propanol	5.24e-12	6.28e-12	1.2			
1-propanol	5.86e-12	7.73e-12	1.3			
1-butanol	9.14e-12	9.74e-12	-			
2-methyl-1-propanol	9.68e-12	1.08e-11	1.1			
2-butanol	8.69e-12	1.06e-11	1.2			
2-methyl-2-propanol	1.07e-12	1.56e-12	1.5			
3-methyl-1-butanol	1.39e-11	1.03e-11	-1.4			
1-pentanol	1.10e-11	1.12e-11	-			
2,2-dimethyl-1-propanol	5.49e-12	5.48e-12	-			
3-methyl-2-butanol	1.19e-11	1.31e-11	-			
2-pentanol	1.10e-11	1.26e-11	1.1			
3-pentanol	1.30e-11	1.54e-11	1.2			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
2-methyl-2-butanol	3.42e-12	4.35e-12	1.3			
4-methyl-2-pentanol	1.70e-11	1.32e-11	-1.3			
2-methyl-2-pentanol	7.10e-12	6.37e-12	-1.1			
2,3-dimethyl-2-butanol	9.30e-12	8.40e-12	-			
1-hexanol	1.30e-11	1.26e-11	-			
2-hexanol	1.20e-11	1.40e-11	1.2			
2,4-dimethyl-2-pentanol	1.10e-11	6.91e-12	-1.6			
1-heptanol	1.30e-11	1.40e-11	-			
4-heptanol	1.70e-11	1.94e-11	1.1			
3-Octanol	3.14e-11	2.02e-11	-1.6			
2-Octanol	2.52e-11	1.69e-11	-1.5			
4-Octanol	2.87e-11	2.08e-11	-1.4			
3,5-dimethyl-3-hexanol	1.30e-11	9.71e-12	-1.3			
1-octanol	1.30e-11	1.54e-11	1.2			
2-ethyl-1-hexanol	1.13e-11	2.01e-11	1.8			
dimethyl ether	2.83e-12	3.93e-12	1.4			
methyl ethyl ether	6.56e-12	1.02e-11	1.5			
diethyl ether	1.27e-11	1.64e-11	1.3			
1-methoxypropane	9.91e-12	1.36e-11	1.4			
methyl tert-butyl ether	3.10e-12	2.52e-12	-1.2			
methyl s-butyl ether	9.67e-12	9.78e-12	-			
methyl n-butyl ether	1.45e-11	1.51e-11	-			
methyl tert-amyl ether	5.60e-12	3.72e-12	-1.5			
ethyl n-butyl ether	2.20e-11	2.13e-11	-			
ethyl tert-butyl ether	8.70e-12	8.76e-12	-			
di-iso-propyl ether	1.00e-11	1.08e-11	-			
di-n-propyl ether	2.00e-11	2.33e-11	1.2			
isopropyl isobutyl ether	2.10e-11	1.61e-11	-1.3			
di-tert-butyl ether	3.70e-12	1.12e-12	-3.3			
di-isobutyl ether	2.60e-11	2.14e-11	-1.2			
di-n-butyl ether	2.80e-11	2.62e-11	-			
di-n-pentyl ether	3.30e-11	2.90e-11	-1.1			
methyl hydroperoxide	1.00e-11	5.61e-12	-1.8			
ethyl hydroperoxide	6.00e-12	6.66e-12	1.1			
t-butyl hydroperoxide	3.56e-12	6.01e-12	1.7			
Other monofunctional carbonyl compounds						
ethanal	1.49e-11	1.49e-11	-	2.40e-12	2.74e-12	1.1
propanal	1.99e-11	2.27e-11	1.1			
butanal	2.37e-11	2.40e-11	-			
2-methylpropanal	2.57e-11	3.20e-11	1.2	6.70e-12	5.74e-12	-1.2
pentanal	2.66e-11	2.54e-11	-	8.60e-12	5.16e-12	-1.7
3-methylbutanal	2.59e-11	2.52e-11	-			
2,2-dimethylpropanal	2.78e-11	2.78e-11	-	5.30e-12	5.26e-12	-
2-methylbutanal	3.33e-11	3.35e-11	-			
2-ethylbutanal	4.02e-11	3.51e-11	-1.1			
3-methylpentanal	2.91e-11	2.69e-11	-			
hexanal	2.85e-11	2.69e-11	-	4.28e-12	5.63e-12	1.3
4-methylpentanal	2.63e-11	2.66e-11	-			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
2-methylpentanal	3.30e-11	3.48e-11	-			
3,3-dimethylbutanal	2.14e-11	2.34e-11	-			
2,3-dimethylpentanal	4.20e-11	3.55e-11	-1.2			
heptanal	2.96e-11	2.83e-11	-			
nonanal	3.20e-11	3.11e-11	-			
acetone	1.87e-13	2.47e-13	1.3			
2-butanone	1.05e-12	1.39e-12	1.3			
3-methyl-2-butanone	3.00e-12	2.88e-12	-			
2-pentanone	4.10e-12	4.34e-12	-			
3-pentanone	2.00e-12	2.53e-12	1.3			
4-methyl-2-pentanone	1.35e-11	8.02e-12	-1.7			
2-hexanone	7.50e-12	6.33e-12	-1.2			
3-hexanone	6.40e-12	5.48e-12	-1.2			
3-methyl-2-pentanone	6.20e-12	6.13e-12	-			
3,3-dimethyl-2-butanone	1.21e-12	1.51e-12	1.2			
5-methyl-2-hexanone	1.20e-11	6.90e-12	-1.7			
2-heptanone	9.40e-12	7.75e-12	-1.2			
2,4-dimethyl-3-pentanone	4.90e-12	5.51e-12	1.1			
2-octanone	1.10e-11	9.17e-12	-1.2			
2,6-dimethyl-heptan-4-one	2.50e-11	1.58e-11	-1.6			
2-nonanone	1.22e-11	1.06e-11	-1.2			
2-decanone	1.32e-11	1.20e-11	-			
methyl formate	1.76e-13	1.84e-13	-			
methyl acetate	3.35e-13	2.89e-13	-1.2			
ethyl formate	8.75e-13	9.02e-13	-			
iso-propyl formate	2.13e-12	1.82e-12	-1.2			
methyl propionate	9.43e-13	9.09e-13	-			
ethyl acetate	1.60e-12	1.89e-12	1.2			
n-propyl formate	1.85e-12	2.19e-12	1.2			
tert-butyl formate	7.82e-13	6.43e-13	-1.2			
methyl isobutyrate	1.70e-12	1.61e-12	-			
n-butyl formate	3.68e-12	3.61e-12	-			
n-propyl acetate	3.45e-12	3.49e-12	-			
iso-propyl acetate	3.79e-12	4.14e-12	-			
2-methylpropyl formate	3.17e-12	3.48e-12	-			
methyl n-butyrate	3.36e-12	3.68e-12	-			
ethyl propionate	2.10e-12	2.51e-12	1.2			
iso-butyl acetate	6.47e-12	4.46e-12	-1.4			
n-butyl acetate	5.66e-12	4.91e-12	-1.2			
sec-butyl acetate	6.10e-12	6.16e-12	-			
tert-butyl acetate	5.75e-13	5.87e-13	-			
n-propyl propionate	4.00e-12	4.11e-12	-			
methyl n-pentanoate	5.26e-12	5.66e-12	-			
ethyl n-butyrate	4.50e-12	5.28e-12	1.2			
methyl 2-methylbutanoate	3.78e-12	4.45e-12	1.2			
methyl pivalate	1.19e-12	1.64e-12	1.4			
iso-propyl isobutyrate	6.44e-12	5.46e-12	-1.2			
n-pentyl acetate	7.39e-12	6.33e-12	-1.2			
n-butyl propionate	6.00e-12	5.53e-12	-			
methyl n-hexanoate	7.36e-12	7.08e-12	-			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
n-propyl isobutyrate	4.59e-12	4.81e-12	-			
n-propyl n-butyrate	6.00e-12	6.88e-12	1.1			
n-butyl n-butyrate	8.74e-12	8.30e-12	-			
acetic acid	7.48e-13	6.50e-13	-1.1			
propionic acid	1.20e-12	1.27e-12	-			
2-methylpropanoic acid	2.10e-12	1.97e-12	-			
butanoic acid	1.80e-12	4.04e-12	2.2			
dimethyl carbonate	3.26e-13	3.09e-13	-			
Methyl Isopropyl Carbonate	2.55e-12	2.70e-12	-			
Glycol, alcohol ether, or polyether						
butan-1,4-diol	3.67e-11	1.70e-11	-2.2			
1,2-dimethoxyethane	2.80e-11	2.47e-11	-1.1			
1,3-dimethoxypropane	4.93e-11	2.62e-11	-1.9			
1-ethoxy-2-methoxyethane	1.75e-11	3.10e-11	1.8			
1,2-diethoxyethane	5.70e-11	3.72e-11	-1.5			
1,4-dimethoxybutane	3.00e-11	2.76e-11	-			
Other acyclic saturated oxygenates						
glyoxal	9.21e-12	9.21e-12	-			
methyl glyoxal	1.19e-11	1.19e-11	-			
2,3-butanedione	2.36e-13	2.47e-13	-			
2,3-pentanedione	2.66e-12	1.39e-12	-1.9			
hexan-2,3-dione	3.60e-12	4.34e-12	1.2			
Cyclic saturated oxygenates						
ethylene oxide	9.10e-14	9.10e-14	-			
cyclobutanone	8.70e-13	8.62e-13	-			
cyclopentanone	2.90e-12	3.06e-12	-			
gamma-valerolactone	2.91e-12	2.67e-12	-			
cyclohexanone	6.40e-12	6.30e-12	-			
Monofunctional acyclic saturated oxidized nitrogen compounds						
methyl nitrate	2.30e-14	1.83e-14	-1.3			
ethyl nitrate	1.80e-13	1.66e-13	-			
n-propyl nitrate	5.80e-13	6.27e-13	-			
iso-propyl nitrate	2.90e-13	3.65e-13	1.3			
iso-butyl nitrate	1.38e-12	1.07e-12	-1.3			
sec-butyl nitrate	8.60e-13	8.71e-13	-			
n-butyl nitrate	1.60e-12	1.81e-12	1.1			
3-methyl-2-butyl nitrate	1.70e-12	1.27e-12	-1.3			
n-pentyl nitrate	3.50e-12	3.24e-12	-			
2,2-dimethyl-1-propyl nitrate	7.80e-13	7.30e-13	-			
2-methyl-1-butyl nitrate	2.23e-12	2.15e-12	-			
3-methyl-1-butyl nitrate	2.73e-12	3.21e-12	1.2			
2-pentyl nitrate	1.70e-12	2.06e-12	1.2			
3-pentyl nitrate	1.04e-12	1.40e-12	1.3			
3-methyl-2-pentyl nitrate	2.80e-12	2.35e-12	-1.2			
3-hexyl nitrate	2.50e-12	2.59e-12	-			
2-methyl-2-pentyl nitrate	1.59e-12	1.75e-12	1.1			
2-hexyl nitrate	2.94e-12	3.48e-12	1.2			
3-heptyl nitrate	3.42e-12	4.01e-12	1.2			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
3-octyl nitrate	3.60e-12	5.43e-12	1.5			
peroxyacetyl nitrate	3.00e-14	2.88e-14	-			
nitroethane	7.10e-14	7.30e-14	-			
2-nitropropane	2.50e-13	2.50e-13	-			
1-nitropropane	3.60e-13	2.63e-13	-1.4			
1-nitrobutane	6.60e-13	1.36e-12	2.1			
1-nitropentane	1.00e-12	2.78e-12	2.8			
methyl nitrite	2.70e-13	2.70e-13	-			
ethyl nitrite	6.70e-13	7.71e-13	1.2			
n-propyl nitrite	1.10e-12	2.05e-12	1.9			
tert-butyl nitrite	1.30e-12	5.59e-13	-2.3			
sec-butyl nitrite	5.60e-12	2.91e-12	-1.9			
iso-butyl nitrite	5.00e-12	3.35e-12	-1.5			
n-butyl nitrite	2.40e-12	3.47e-12	1.4			
n-pentyl nitrite	3.80e-12	4.89e-12	1.3			
Monofunctional acyclic unsaturated oxygenates						
methyl vinyl ether	3.40e-11	7.72e-11	2.3			
ethyl vinyl ether	7.30e-11	8.34e-11	1.1			
2-methoxy-1-propene	1.14e-10	1.14e-10	-			
n-propyl vinyl ether	1.00e-10	8.69e-11	-1.2			
tert-butyl vinyl ether	1.15e-10	7.58e-11	-1.5			
isobutyl vinyl ether	1.09e-10	8.59e-11	-1.3			
n-butyl vinyl ether	1.09e-10	8.83e-11	-1.2			
2-propenal	2.17e-11	2.17e-11	-			
crotonaldehyde	3.60e-11	3.63e-11	-			
2-methyl-2-propenal	2.90e-11	3.60e-11	1.2			
3-methyl-2-butenal	6.21e-11	4.79e-11	-1.3			
e-2-pentenal	4.40e-11	3.72e-11	-1.2			
(E)-2-methyl-2-butenal	4.08e-11	4.79e-11	1.2			
(E,E)-2,4-hexadienal	6.36e-11	1.14e-10	1.8			
2-hexenal (trans)	4.30e-11	3.85e-11	-1.1			
trans-2-heptenal	4.40e-11	3.99e-11	-			
(E)-2-octenal	3.96e-11	4.13e-11	-			
(E)-2-nonenal	4.35e-11	4.28e-11	-			
3-buten-2-one	2.00e-11	2.43e-11	1.2			
3-penten-2-one	6.60e-11	6.57e-11	-			
3-methyl-3-buten-2-one	5.00e-11	4.54e-11	-			
1-penten-3-one	2.62e-11	2.54e-11	-			
4-hexen-3-one	9.00e-11	6.69e-11	-1.3			
e-3-methyl-3-penten-2-one	8.00e-11	8.29e-11	-			
4-methyl-3-penten-2-one	8.41e-11	1.02e-10	1.2			
vinyl acetate	2.49e-11	2.56e-11	-			
methyl acrylate	1.29e-11	2.02e-11	1.6			
methyl crotonate	3.92e-11	3.95e-11	-			
vinyl propionate	2.46e-11	2.62e-11	-			
isopropenyl acetate	6.72e-11	5.60e-11	-1.2			
methyl methacrylate	4.07e-11	4.07e-11	-			
ethyl acrylate	1.59e-11	2.18e-11	1.4			
ethyl crotonate	5.00e-11	4.12e-11	-1.2			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
methyl-3-methyl-2-butenolate	4.63e-11	5.48e-11	1.2			
vinyl butanoate	2.61e-11	2.90e-11	1.1			
ethyl methacrylate	4.30e-11	4.23e-11	-			
(E)-ethyl tiglate	8.44e-11	5.79e-11	-1.5			
isopropyl methacrylate	5.36e-11	4.46e-11	-1.2			
propyl methacrylate	4.86e-11	4.39e-11	-			
n-butyl acrylate	1.94e-11	2.48e-11	1.3			
2-methylpropenoic acid butyl ester	6.58e-11	4.53e-11	-1.5			
i-butyl methacrylate	5.27e-11	4.49e-11	-1.2			
ethyl hexyl acrylate	2.74e-11	2.98e-11	-			
hexyl acrylate	2.28e-11	2.77e-11	1.2			
acrylic acid	1.70e-11	1.70e-11	-			
peroxymethacryloyl nitrate	2.90e-11	2.90e-11	-			
Furans						
furan	3.83e-11	6.51e-11	1.7			
3-methylfuran	9.53e-11	7.82e-11	-1.2			
2-methylfuran	7.00e-11	7.82e-11	1.1			
2-vinylfuran	8.80e-11	1.13e-10	1.3			
2-ethylfuran	1.16e-10	7.91e-11	-1.5			
2,5-dimethylfuran	1.16e-10	9.14e-11	-1.3			
Unsaturated acyclic oxidized nitrogen compounds						
nitroethene	1.20e-12	1.20e-12	-			
3-nitropropene	1.22e-11	1.22e-11	-			
4-nitrooxy-1-butanol-2-ene	2.20e-11	3.74e-11	1.7			
2-methyl-4-nitrooxy-but-2-en-1-ol (cis)	1.10e-10	5.11e-11	-2.2			
2-methyl-4-nitrooxy-but-2-en-1-ol (trans)	1.00e-10	5.11e-11	-2.0			
3-methyl-2-nitrooxybut-3-ene-1-ol	3.90e-11	3.65e-11	-			
1,4-dinitrooxy-2-butene	1.40e-11	1.86e-11	1.3			
3,4-dinitrooxy-1-butene	9.30e-12	1.68e-11	1.8			
2-methyl-4-nitrooxy-2-buten-1-al	4.10e-11	2.97e-11	-1.4			
Monofunctional aromatic oxygenates						
benzaldehyde	1.26e-11	1.46e-11	1.2			
o-tolualdehyde	1.89e-11	1.84e-11	-			
m-tolualdehyde	1.68e-11	1.78e-11	-			
p-tolualdehyde	1.68e-11	1.78e-11	-			
2,5-dimethylbenzaldehyde	3.15e-11	2.16e-11	-1.5			
2,3-dimethylbenzaldehyde	2.55e-11	2.27e-11	-1.1			
3,4-dimethylbenzaldehyde	2.36e-11	2.22e-11	-			
2,4-dimethylbenzaldehyde	3.12e-11	3.35e-11	-			
3,5-dimethylbenzaldehyde	2.78e-11	3.30e-11	1.2			
2,6-dimethylbenzaldehyde	3.03e-11	3.88e-11	1.3			
2,4,5-trimethylbenzaldehyde	4.27e-11	3.79e-11	-1.1			
4-methylacetophenone	4.71e-12	4.41e-12	-			
methoxybenzene	2.04e-11	8.81e-12	-2.3			
1-methoxy-2-methylbenzene	4.56e-11	1.74e-11	-2.6			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
phenol	2.80e-11	1.52e-11	-1.8			
p-cresol	4.90e-11	2.76e-11	-1.8			
o-cresol	4.10e-11	2.40e-11	-1.7			
m-cresol	5.90e-11	6.99e-11	1.2			
2,5-dimethylphenol	8.50e-11	7.86e-11	-			
3,4-dimethylphenol	8.30e-11	8.55e-11	-			
2,3-dimethylphenol	8.20e-11	5.58e-11	-1.5			
2,4-dimethylphenol	7.30e-11	8.72e-11	1.2			
3,5-dimethylphenol	1.14e-10	1.44e-10	1.3			
2,6-dimethylphenol	6.70e-11	7.83e-11	1.2			
2,4,6-trimethylphenol	1.67e-10	1.92e-10	1.2			
2,3,6-trimethylphenol	1.27e-10	1.10e-10	-1.1			
3,4,5-trimethylphenol	1.55e-10	1.70e-10	-			
2,4,5-trimethylphenol	1.10e-10	1.45e-10	1.3			
2,3,5-trimethylphenol	1.37e-10	1.30e-10	-			
Other aromatic oxygenates						
catechol	1.00e-10	6.23e-11	-1.6			
3-methylpyrocatechol	2.00e-10	1.37e-10	-1.5			
4-methylpyrocatechol	1.50e-10	2.46e-10	1.6			
3-methoxyphenol	6.93e-11	9.39e-11	1.4			
4-methoxyphenol	5.66e-11	5.71e-11	-			
guaiacol	5.40e-11	4.14e-11	-1.3			
2-methoxy-4-methylphenol	7.51e-11	1.24e-10	1.6			
1,2-dimethoxybenzene	3.60e-11	2.66e-11	-1.4			
2,3-dimethoxyphenol	7.49e-11	1.02e-10	1.4			
2,6-dimethoxyphenol	8.10e-11	1.41e-10	1.7			
1,3,5-trimethoxybenzene	1.56e-10	1.22e-10	-1.3			
1,2,4-trimethoxybenzene	1.29e-10	1.47e-10	1.1			
1,2,3-trimethoxybenzene	7.70e-11	8.04e-11	-			
Aromatic oxidized nitrogen compounds						
nitrobenzene	1.40e-13	1.18e-13	-1.2			
m-nitrotoluene	1.20e-12	8.48e-13	-1.4			
1-nitronaphthalene	7.45e-12	7.86e-12	-			
2-nitronaphthalene	5.48e-12	7.78e-12	1.4			
5-methyl-2-nitrophenol	6.70e-12	7.25e-12	-			
4-methyl-2-nitrophenol	3.60e-12	3.43e-12	-			
3-methyl-2-nitrophenol	3.70e-12	4.98e-12	1.3			
2-methyl-6-nitrophenol	2.80e-12	3.10e-12	1.1			
Alkyl amines						
Methylamine	2.20e-11	1.76e-11	-1.3	1.02e-11	1.20e-11	1.2
Ethyl Amine	2.77e-11	1.85e-11	-1.5	1.47e-11	1.23e-11	-1.2
Dimethyl Amine	6.82e-11	7.66e-11	1.1	2.98e-11	3.17e-11	-
ethyl(methyl)amine	7.30e-11	7.74e-11	-			
Trimethyl Amine	5.60e-11	8.28e-11	1.5	2.40e-11	2.39e-11	-
diethylamine	8.89e-11	7.83e-11	-1.1			
methyl(propyl)amine	8.30e-11	7.88e-11	-			
N,N-dimethylethylamine	7.37e-11	8.37e-11	1.1			
t-Butyl Amine	1.01e-11	1.80e-11	1.8			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
1,2-dimethylpropylamine	5.08e-11	2.17e-11	-2.3			
N,N-dimethylpropylamine	1.10e-10	8.51e-11	-1.3			
N,N-dimethylisopropylamine	9.79e-11	8.49e-11	-1.2			
N,N-diethylmethylamine	8.92e-11	8.46e-11	-			
tert-pentylamine	8.60e-12	1.92e-11	2.2			
triethylamine	9.28e-11	8.55e-11	-			
Other reduced nitrogen compounds						
acetamide	7.70e-13	7.53e-13	-			
N-methylformamide	7.93e-12	2.07e-11	2.6			
propanamide	1.78e-12	1.90e-12	-			
N-methylacetamide	5.29e-12	6.07e-12	1.1			
N,N-dimethylformamide	1.13e-11	2.85e-11	2.5			
N,N-dimethylacetamide	1.60e-11	1.39e-11	-1.2			
N-methylpropanamide	7.67e-12	7.22e-12	-			
N,N-dimethylpropanamide	2.09e-11	1.50e-11	-1.4			
O-methyl-N-methylcarbamate	4.30e-12	6.21e-12	1.4			
O-methyl-N-ethylcarbamate	1.05e-11	7.09e-12	-1.5			
O-ethyl-N-methylcarbamate	8.30e-12	7.81e-12	-			
O-ethyl-N-ethylcarbamate	1.44e-11	8.70e-12	-1.7			
Monohalo alkanes						
fluoromethane	2.10e-14	2.12e-14	-			
fluoroethane	2.10e-13	2.36e-13	1.1			
2-fluoropropane	5.80e-13	5.11e-13	-1.1			
chloromethane	3.60e-14	3.56e-14	-			
chloroethane	3.70e-13	3.48e-13	-			
2-chloropropane	6.90e-13	7.59e-13	-			
1-chloropropane	9.80e-13	1.22e-12	1.2			
2-chlorobutane	2.45e-12	1.72e-12	-1.4			
2-chloro-2-methylpropane	4.50e-13	3.47e-13	-1.3			
1-chloro-2-methylpropane	1.95e-12	2.20e-12	1.1			
1-chlorobutane	1.89e-12	2.54e-12	1.3			
1-chloropentane	3.57e-12	3.96e-12	1.1			
1-chlorohexane	3.91e-12	5.38e-12	1.4			
bromomethane	2.90e-14	3.22e-14	1.1			
bromoethane	3.30e-13	3.09e-13	-			
2-bromopropane	7.58e-13	6.75e-13	-1.1			
1-bromopropane	1.00e-12	1.08e-12	-			
1-bromobutane	2.30e-12	2.37e-12	-			
1-bromopentane	3.70e-12	3.79e-12	-			
1-bromohexane	5.50e-12	5.21e-12	-			
iodomethane	7.20e-14	5.61e-14	-1.3			
iodoethane	3.40e-13	5.34e-13	1.6			
2-iodopropane	1.29e-12	1.09e-12	-1.2			
1-iodopropane	1.36e-12	1.74e-12	1.3			
Monohalo alkenes or alkynes						
fluoroethene	4.97e-12	5.91e-12	1.2			
chloroethene	7.55e-12	7.55e-12	-			
bromoethene	6.81e-12	6.81e-12	-			



Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
2-fluoropropene	1.55e-11	1.30e-11	-1.2			
3-fluoropropene	1.60e-11	1.60e-11	-			
3-bromo-1-propene	1.75e-11	3.08e-11	1.8			
Monohalo aromatics						
fluorobenzene	6.31e-13	6.29e-13	-			
chlorobenzene	8.11e-13	8.07e-13	-			
bromobenzene	9.15e-13	9.12e-13	-			
Used for evaluations only						
Cyclic alkanes						
quadricyclo[2.2.1.02,6o3,5]heptane	1.70e-12	8.69e-13	-2.0			
bicyclo[2.2.1]heptane	5.10e-12	1.05e-11	2.1			
bicyclo[3.3.0]octane	1.03e-11	1.06e-11	-			
bicyclo[2.2.2]octane	1.37e-11	1.49e-11	-			
bicyclo[4.3.0]-nonane (avg of cis and trans)	1.65e-11	1.28e-11	-1.3			
tricyclo[3.3.1.13,7]decane	2.15e-11	2.17e-11	-			
tricyclo[5.2.1.02,6]decane	1.06e-11	1.39e-11	1.3			
1,7,7-trimethyltricyclo[2.2.1.02,6]heptane	2.70e-12	5.57e-12	2.1			
2,6,6-trimethylbicyclo[3.1.1]heptanes	1.24e-11	8.33e-12	-1.5			
bicyclo[4.4.0]decane (avg of cis and trans)	1.90e-11	1.64e-11	-1.2			
Allenenes and other acyclic di- or polyalkenes						
fulvenallene	8.80e-12	2.02e-10	23.0			
1,4-pentadiene	5.41e-11	6.20e-11	1.1			
trans-1,3,5-hexatriene	1.11e-10	2.07e-10	1.9			
cis-1,3,5-hexatriene	1.10e-10	2.07e-10	1.9			
1,5-hexadiene	6.20e-11	6.33e-11	-			
trans-1,4-hexadiene	9.10e-11	9.35e-11	-			
2-methyl-1,4-pentadiene	7.90e-11	9.29e-11	1.2			
2-methyl-1,5-hexadiene	9.60e-11	9.42e-11	-			
2,5-dimethyl-1,5-hexadiene	1.20e-10	1.25e-10	-			
3-methylene-7-methyl-1,6-octadiene	2.15e-10	1.86e-10	-1.2			
cis/trans-ocimene	2.52e-10	2.24e-10	-1.1			
beta-farnesene	2.30e-10	2.76e-10	1.2			
alpha-farnesene	2.20e-10	3.14e-10	1.4			
Cycloalkenes						
cyclopentene	6.70e-11	6.48e-11	-			
cyclohexene	6.77e-11	6.70e-11	-			
cycloheptene	7.40e-11	6.85e-11	-			
1-methyl-1-cyclohexene	9.40e-11	9.23e-11	-			
cyclooctene	5.04e-11	6.99e-11	1.4			
cyclodecene	4.18e-11	7.27e-11	1.7			
1,3-cyclohexadiene	1.64e-10	1.47e-10	-1.1			
1,4-cyclohexadiene	9.95e-11	1.26e-10	1.3			
bicyclo[2.2.1]-2,5-heptadiene	1.20e-10	1.29e-10	-			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
1,3,5-cycloheptatriene	9.70e-11	2.84e-10	2.9			
1,3-cycloheptadiene	1.39e-10	1.49e-10	-			
bicyclo[2.2.1]-2-heptene	4.90e-11	6.94e-11	1.4			
bicyclo[2.2.2]-2-octene	4.10e-11	7.28e-11	1.8			
a-phellandrene	3.20e-10	1.80e-10	-1.8			
sabinene	1.17e-10	6.65e-11	-1.8			
a-terpinene	3.50e-10	2.08e-10	-1.7			
b-phellandrene	1.70e-10	1.42e-10	-1.2			
b-pinene	7.60e-11	6.71e-11	-1.1			
terpinolene	2.20e-10	1.96e-10	-1.1			
limonene	1.65e-10	1.55e-10	-			
g-terpinene	1.70e-10	1.78e-10	-			
3-carene	8.45e-11	8.94e-11	-			
2-carene	8.00e-11	8.99e-11	1.1			
camphene	5.19e-11	7.02e-11	1.4			
a-pinene	5.30e-11	9.16e-11	1.7			
beta-caryophyllene	2.00e-10	1.56e-10	-1.3			
$\alpha$ -humulene	2.90e-10	2.41e-10	-1.2			
a-copaene	9.00e-11	9.84e-11	-			
$\alpha$ -cedrene	6.70e-11	1.01e-10	1.5			
longifolene	4.70e-11	7.50e-11	1.6			
Alkynes						
vinyl acetylene	3.27e-11	3.64e-11	1.1			
Naphthalenes						
acenaphthene	8.00e-11	1.02e-10	1.3			
Styrenes or aromatics with double bonds or non-aromatic rings						
acenaphthylene	1.09e-10	1.00e-10	-			
indane	1.90e-11	1.30e-11	-1.5			
tetralin	3.40e-11	1.54e-11	-2.2			
biphenyl	7.48e-12	9.37e-12	1.3			
fluorene	1.31e-11	2.27e-11	1.7			
anthracene	1.17e-10	1.06e-10	-			
phenanthrene	2.40e-11	5.80e-11	2.4			
9,10-dihydroanthracene	2.12e-11	2.23e-11	-			
3-methylphenanthrene	6.64e-11	8.86e-11	1.3			
2-methylphenanthrene	6.45e-11	8.86e-11	1.4			
9-methylphenanthrene	7.57e-11	1.54e-10	2.0			
1-methylphenanthrene	2.89e-11	8.44e-11	2.9			
Other monofunctional carbonyl compounds						
2,5-hexanedione	7.13e-12	4.06e-12	-1.8			
Glycol, alcohol ether, or polyether						
1,2-ethanediol	1.45e-11	6.71e-12	-2.2			
1,2-propanediol	2.10e-11	1.01e-11	-2.1			
1,3-butanediol	2.99e-11	1.49e-11	-2.0			
1,2-butanediol	2.43e-11	1.47e-11	-1.7			
2,3-butanediol	2.12e-11	1.35e-11	-1.6			
2-methyl-2,4-pentanediol	1.36e-11	1.15e-11	-1.2			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
2-methoxyethanol	1.20e-11	1.20e-11	-			
3-methoxy-1-propanol	2.15e-11	2.08e-11	-			
1-methoxy-2-propanol	2.00e-11	1.49e-11	-1.3			
2-ethoxyethanol	1.95e-11	1.82e-11	-			
3-methoxy-1-butanol	2.36e-11	1.63e-11	-1.4			
2-isopropoxyethanol	2.10e-11	1.54e-11	-1.4			
1-methoxy-2-butanol	2.19e-11	1.96e-11	-1.1			
3-ethoxy-1-propanol	2.20e-11	2.71e-11	1.2			
2-propoxyethanol	1.73e-11	2.17e-11	1.3			
3-methoxy-3-methyl-1-butanol	1.64e-11	1.12e-11	-1.5			
2-n-butoxyethanol	3.00e-11	2.31e-11	-1.3			
diethylene glycol ethyl ether	5.72e-11	3.90e-11	-1.5			
1-butoxy-2-propanol	3.80e-11	2.60e-11	-1.5			
diethylene glycol n-butyl ether	7.44e-11	4.39e-11	-1.7			
Other acyclic saturated oxygenates						
peracetic acid	3.00e-14	3.88e-14	1.3			
3-hydroxypropanal	1.99e-11	2.81e-11	1.4			
4-hydroxybutanal	3.00e-11	3.12e-11	-			
3-hydroxybutanal	2.95e-11	3.10e-11	-			
2-methoxyethyl formate	6.50e-12	1.33e-11	2.0			
ethylene glycol diformate	4.84e-13	1.85e-12	3.8			
glutaraldehyde	2.38e-11	4.69e-11	2.0			
oxopentanal	1.20e-11	2.47e-11	2.1			
2-ethoxyethyl formate	1.13e-11	1.95e-11	1.7			
2-methoxyethyl acetate	8.20e-12	1.46e-11	1.8			
1-Methoxy-2-Propyl Acetate	1.44e-11	1.51e-11	-			
2-ethoxyethyl acetate	1.21e-11	2.08e-11	1.7			
dimethyl succinate	1.64e-12	1.85e-12	1.1			
ethylene glycol diacetate	2.16e-12	4.45e-12	2.1			
ethyl levulinate	3.43e-12	4.56e-12	1.3			
ethyl 3-ethoxypropionate	2.20e-11	1.58e-11	-1.4			
dimethyl glutarate	2.24e-12	4.01e-12	1.8			
2-ethoxyethyl isobutyrate	1.48e-11	2.21e-11	1.5			
dimethyl adipate	3.65e-12	8.79e-12	2.4			
pyruvic acid	1.20e-13	7.45e-13	6.2			
4-hydroxy-2-butanone	9.10e-12	5.38e-12	-1.7			
5-hydroxy-2-pentanone	1.55e-11	8.68e-12	-1.8			
4-hydroxy-3-methyl-2-butanone	1.46e-11	8.33e-12	-1.8			
5-hydroxy-hexan-2-one	2.20e-11	1.16e-11	-1.9			
6-hydroxy-3-hexanone	1.70e-11	9.82e-12	-1.7			
4-hydroxy-4-methyl-2-pentanone	4.50e-12	3.16e-12	-1.4			
6-hydroxy-3-heptanone	1.60e-11	1.27e-11	-1.3			
5-hydroxy-2-heptanone	1.90e-11	1.63e-11	-1.2			
1-hydroxy-4-heptanone	1.00e-11	1.28e-11	1.3			
5-hydroxy-2-octanone	2.30e-11	1.83e-11	-1.3			
7-hydroxy-4-octanone	1.90e-11	1.56e-11	-1.2			
6-hydroxy-3-octanone	1.50e-11	1.75e-11	1.2			
cis/trans-4-oxo-2-pentenal	6.20e-11	3.78e-11	-1.6			
4-hydroxy-2-oxo-3-pentene	9.00e-11	1.02e-10	1.1			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
trans-4-methoxy-3-buten-2-one	1.28e-10	2.62e-10	2.0			
3-methyl-2,4-pentanedione (enol)	6.10e-11	1.12e-10	1.8			
(E)-4-hydroperoxy-2-hexenal	5.10e-11	4.57e-11	-1.1			
3,4-dihydroxy-3-hexene-2,5-dione	2.70e-10	1.03e-10	-2.6			
isopropenyl-6-oxo-heptanal	1.10e-10	9.14e-11	-1.2			
Cyclic saturated oxygenates						
methyl oxirane	4.67e-13	1.93e-13	-2.4			
oxetane	1.03e-11	7.82e-12	-1.3			
cyclopropanecarbaldehyde	2.10e-11	2.99e-11	1.4			
ethyl oxirane	1.90e-12	1.08e-12	-1.8			
tetrahydrofuran	1.70e-11	1.83e-11	-			
gamma-butyro-lactone	2.90e-12	1.96e-12	-1.5			
beta-butyro-lactone	9.70e-13	1.07e-12	-			
1,4-dioxane	1.15e-11	4.16e-11	3.6			
propylene carbonate	2.52e-12	1.36e-12	-1.9			
cyclobutanecarbaldehyde	2.63e-11	3.22e-11	1.2			
2-methyl-tetrahydrofuran	2.46e-11	1.53e-11	-1.6			
cyclo-pentanol	1.10e-11	1.53e-11	1.4			
tetrahydropyran	1.20e-11	2.51e-11	2.1			
delta-valero-lactone	5.24e-12	4.33e-12	-1.2			
3-methyl-dihydro-furan-2-one	1.81e-12	2.52e-12	1.4			
1-(2-methyl-2-oxiranyl)ethane-1,2-diol	3.52e-11	1.25e-11	-2.8			
2-(oxiran-2-yl)-propane-1,2-diol	9.20e-12	4.03e-12	-2.3			
cyclopentanecarbaldehyde	3.13e-11	3.62e-11	1.2			
cyclo-hexanol	1.70e-11	2.11e-11	1.2			
oxepane	1.80e-11	2.65e-11	1.5			
cyclohexanecarbaldehyde	3.70e-11	3.95e-11	-			
cycloheptanone	1.00e-11	1.27e-11	1.3			
cyclooctanone	1.61e-11	1.41e-11	-1.1			
nopinone	1.52e-11	6.50e-12	-2.3			
sabinaketone	6.00e-12	4.82e-12	-1.2			
borneol	2.65e-11	1.62e-11	-1.6			
fenchol	2.49e-11	1.56e-11	-1.6			
cyclodecanone	2.14e-11	1.70e-11	-1.3			
1,8-cineole	1.04e-11	1.05e-11	-			
menthol	1.48e-11	2.67e-11	1.8			
caronaldehyde	5.00e-11	2.40e-11	-2.1			
pinonaldehyde	3.90e-11	2.69e-11	-1.5			
bornyl acetate	1.25e-11	1.24e-11	-			
Multifunctional oxygenates with 2+ non-HC groups on same carbon						
hydroxymethyl hydroperoxide	7.10e-12	7.78e-12	-			
hydroxyacetaldehyde	1.10e-11	2.39e-11	2.2			
glycidaldehyde	1.60e-11	2.99e-11	1.9			
hydroxyacetone	5.87e-12	2.33e-12	-2.5			
2-hydroxypropanal	1.70e-11	3.40e-11	2.0			
1,3-dioxolane	1.00e-11	2.24e-11	2.2			
dimethoxymethane	4.54e-12	1.20e-11	2.6			
methoxymethyl formate	1.70e-12	6.39e-12	3.8			
1,3,5-trioxane	5.40e-12	2.41e-11	4.5			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
3-hydroxy-2-butanone	9.70e-12	4.24e-12	-2.3			
1-hydroxy-2-butanone	7.60e-12	3.47e-12	-2.2			
Methoxy Acetone	6.59e-12	6.51e-12	-			
2-hydroxybutanal	2.40e-11	3.79e-11	1.6			
2-hydroxy-2-methylpropanal	1.40e-11	2.83e-11	2.0			
1,3-dioxane	1.00e-11	3.03e-11	3.0			
1,1-dimethoxyethane	8.90e-12	9.22e-12	-			
methyl lactate	2.48e-12	2.01e-12	-1.2			
2,3-dihydroxy-2-methylpropanal	3.30e-11	3.12e-11	-			
2,3-dihydroxybutanal	4.10e-11	4.14e-11	-			
3,4-dihydroxy-2-butanone	1.20e-11	8.28e-12	-1.4			
ethoxymethyl formate	4.60e-12	1.26e-11	2.7			
methoxymethyl acetate	2.80e-12	6.86e-12	2.4			
trimethoxymethane	5.00e-12	1.11e-11	2.2			
3-hydroxy-3-methyl-2-butanone	8.50e-13	1.19e-12	1.4			
1,3-dioxepane	1.40e-11	3.17e-11	2.3			
4-methyl-1,3-dioxane	1.13e-11	2.63e-11	2.3			
2,2-dimethoxypropane	4.10e-12	4.30e-12	-			
diethoxymethane	1.97e-11	2.44e-11	1.2			
ethyl lactate	3.51e-12	3.61e-12	-			
ethoxymethyl acetate	6.80e-12	1.31e-11	1.9			
3-methyl-2,4-pentanedione (keto)	1.16e-11	2.45e-12	-4.7			
3-hydroxy-2-hexanone	2.20e-11	1.00e-11	-2.2			
4-hydroxy-3-hexanone	1.54e-11	9.17e-12	-1.7			
1,1,3-trimethoxypropane	1.67e-11	2.41e-11	1.4			
di-isopropoxymethane	3.80e-11	1.89e-11	-2.0			
2,2-diethoxypropane	1.11e-11	1.68e-11	1.5			
di-n-propoxymethane	2.70e-11	3.14e-11	1.2			
di-sec-butoxymethane	4.30e-11	2.37e-11	-1.8			
di-iso-butoxymethane	3.60e-11	2.95e-11	-1.2			
di-n-butoxymethane	3.60e-11	3.42e-11	-			
Monofunctional acyclic saturated oxidized nitrogen compounds						
nitromethane	1.40e-14	1.12e-14	-1.3			
Other saturated oxygenate or nitro or nitrate compounds						
1,4-dinitrooxybutane	6.30e-12	1.10e-12	-5.7			
2,3-dinitrooxybutane	1.02e-12	2.89e-13	-3.5			
1,2-dinitrooxybutane	1.63e-12	6.42e-13	-2.5			
2-nitrooxy-1-propanol	6.70e-12	3.00e-12	-2.2			
1-nitrooxy-2-propanol	5.10e-12	2.91e-12	-1.8			
2-nitrooxy-1-butanol	7.40e-12	3.71e-12	-2.0			
3-nitrooxy-1-butanol	1.19e-11	6.56e-12	-1.8			
4-nitrooxy-1-butanol	1.26e-11	9.03e-12	-1.4			
4-nitrooxy-2-butanol	1.04e-11	9.19e-12	-1.1			
1-nitrooxy-2-butanol	7.00e-12	6.26e-12	-1.1			
4-nitrooxy-1-pentanol	2.86e-11	9.27e-12	-3.1			
5-nitrooxy-2-pentanol	3.21e-11	1.19e-11	-2.7			
1-nitrooxy-2-pentanol	9.80e-12	8.27e-12	-1.2			
2-nitrooxy-1-pentanol	4.90e-12	4.90e-12	-			
6-nitrooxy-1-hexanol	3.09e-11	1.19e-11	-2.6			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
2-nitrooxy-1-cyclopentanol	3.53e-12	7.53e-12	2.1			
cyclohexyl nitrate	3.06e-12	5.51e-12	1.8			
trans-1-methyl-1,2-dinitrooxycyclohexane	1.66e-12	3.80e-12	2.3			
3-nitrooxy-2-butanone	1.20e-12	5.28e-13	-2.3			
1-nitrooxy-2-butanone	8.40e-13	1.38e-12	1.6			
3-methyl-3-nitrooxy-2-butanone	2.60e-13	4.17e-13	1.6			
2-nitrooxy-cyclohexanone	3.47e-12	4.43e-12	1.3			
Other acyclic unsaturated oxygenates						
2-propyn-1-ol	2.05e-11	8.08e-12	-2.5			
2-propen-1-ol	5.00e-11	3.40e-11	-1.5			
3-buten-2-ol	5.90e-11	3.64e-11	-1.6			
3-buten-1-ol	5.50e-11	3.81e-11	-1.4			
2-methyl-2-propen-1-ol	9.00e-11	6.50e-11	-1.4			
2-buten-1-ol	8.70e-11	6.56e-11	-1.3			
ethylene glycol monovinyl ether	1.04e-10	8.52e-11	-1.2			
2-methyl-3-buten-2-ol	6.30e-11	3.16e-11	-2.0			
cis-2-penten-1-ol	1.17e-10	6.65e-11	-1.8			
3-methyl-2-buten-1-ol	1.60e-10	9.08e-11	-1.8			
1-penten-3-ol	6.33e-11	4.07e-11	-1.6			
3-methyl-3-buten-1-ol	9.40e-11	6.91e-11	-1.4			
(E)-2-penten-1-ol	6.76e-11	6.65e-11	-			
allyl ethyl ether	3.95e-11	4.68e-11	1.2			
2-hydroperoxy-2-methyl-but-3-en-1-ol	8.30e-11	4.11e-11	-2.0			
2-hydroperoxy-3-methyl-but-3-en-1-ol	1.30e-10	7.51e-11	-1.7			
allyl ether	6.30e-11	7.72e-11	1.2			
3-methyl-1-penten-3-ol	6.20e-11	3.44e-11	-1.8			
(Z)-3-hexen-1-ol	1.08e-10	7.06e-11	-1.5			
(Z)-2-hexen-1-ol	9.77e-11	6.78e-11	-1.4			
3-hexen-1-ol (trans)	9.73e-11	7.06e-11	-1.4			
trans-2-hexen-1-ol	7.93e-11	6.78e-11	-1.2			
cis-4-hexen-1-ol	8.08e-11	7.17e-11	-1.1			
(E)-4-hexen-1-ol	7.14e-11	7.17e-11	-			
ethylene glycol divinyl ether	1.27e-10	1.71e-10	1.3			
(Z)-3-hepten-1-ol	1.28e-10	7.19e-11	-1.8			
3,5-dimethyl-1-hexyn-3-ol	2.90e-11	1.23e-11	-2.4			
(Z)-3-octen-1-ol	1.49e-10	7.34e-11	-2.0			
6-methyl-5-hepten-2-ol	1.00e-10	9.98e-11	-			
diethylene glycol divinyl ether	1.44e-10	1.92e-10	1.3			
3,7-dimethyl-1,6-octadien-3-ol	1.79e-10	1.24e-10	-1.4			
2,6-dimethyl-2,6-octadien-8-ol	2.30e-10	1.80e-10	-1.3			
3,7-dimethyl-6-octen-1-ol	1.70e-10	1.00e-10	-1.7			
2,6-dimethyl-7-octen-2-ol	3.80e-11	4.08e-11	-			
z-butenedial	5.80e-11	2.84e-11	-2.0			
2-butene-1,4-dial	5.29e-11	2.84e-11	-1.9			
(E)-2-butenedial	3.45e-11	2.84e-11	-1.2			
(Z)-3-hexenal	6.90e-11	8.55e-11	1.2			
e,z-2,4-hexadienedial	9.10e-11	8.20e-11	-			
e,e-2,4-hexadienedial	8.20e-11	8.20e-11	-			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
3(e)-4-methylhex-3,5-dienal	2.52e-10	1.59e-10	-1.6			
4-methylenehex-5-enal	1.55e-10	1.21e-10	-1.3			
4-methylhex-3(z),5-dienal	1.61e-10	1.59e-10	-			
e,e-2-methyl-2,4-hexadienedial	1.18e-10	9.55e-11	-1.2			
3(e)4-methylhex-3,5-dienal	2.52e-10	1.80e-10	-1.4			
3(z)4-methylhex-3,5-dienal	1.61e-10	1.80e-10	1.1			
3,7-dimethyl-6-octen-1-al	1.51e-10	1.15e-10	-1.3			
hex-5-en-3-one	5.18e-11	3.26e-11	-1.6			
5-hexen-2-one	5.20e-11	3.47e-11	-1.5			
4-hexen-2-one	6.00e-11	6.31e-11	-			
cis-3-hexene-2,5-dione	7.20e-11	6.06e-11	-1.2			
trans-3-hexene-2,5-dione	5.10e-11	6.06e-11	1.2			
3-methyl-3-hexene-2,5-dione	9.40e-11	8.52e-11	-			
6-methyl-5-hepten-2-one	1.57e-10	9.15e-11	-1.7			
methyl-3-butenolate	3.29e-11	3.10e-11	-			
allyl acetate	2.82e-11	3.23e-11	1.1			
2-methyl-2-propenyl acetate	7.19e-11	6.32e-11	-1.1			
4-pentenyl acetate	4.30e-11	3.53e-11	-1.2			
allyl butanoate	2.89e-11	3.57e-11	1.2			
(Z)-3-hexenylformate	4.61e-11	6.51e-11	1.4			
cis-3-hexenyl acetate	7.74e-11	6.64e-11	-1.2			
(E)-2-hexenyl acetate	6.88e-11	6.61e-11	-			
5-methyl-5-vinyl-tetrahydrofuran-2-ol	7.40e-11	4.04e-11	-1.8			
Unsaturated acyclic oxidized nitrogen compounds						
1-nitrocyclohexene	4.37e-11	8.46e-12	-5.2			
1-nitrooxy-2-butanol-3-ene	3.62e-11	3.30e-11	-			
2-methyl-1-nitrooxy-but-3-en-2-ol	3.40e-11	3.16e-11	-			
3-methyl-1-nitrooxy-but-3-en-2-ol	6.60e-11	6.39e-11	-			
Cyclic unsaturated non-aromatic oxidized nitrogen compounds						
2,5-dihydrofuran	6.45e-11	7.45e-11	1.2			
2,3-dihydrofuran	1.20e-10	3.50e-10	2.9			
3h-furan-2-one	4.90e-11	3.05e-11	-1.6			
gamma-crotonolactone	4.06e-12	3.97e-11	9.8			
maleic anhydride	3.92e-13	2.47e-11	63.0			
5-methyl-2,3-dihydrofuran	2.18e-10	3.80e-10	1.7			
3,4-dihydropyran	1.14e-10	3.54e-10	3.1			
3-furfural	4.90e-11	6.11e-11	1.2			
2-furfural	3.50e-11	6.11e-11	1.7			
5-methyl-3h-furan-2-one	6.78e-11	5.53e-11	-1.2			
4-methyl-2H-furan-5-one	1.26e-11	5.64e-11	4.5			
benzene oxide	1.00e-10	1.45e-10	1.5			
5-methyl-2-furfural	5.10e-11	7.43e-11	1.5			
toluene oxide	2.10e-10	1.45e-10	-1.4			
4-methylcyclohex-3-en-1-one	1.10e-10	8.99e-11	-1.2			
3-methyl-2-cyclohexen-1-one	3.10e-11	1.05e-10	3.4			
4-acetyl-1-methylcyclohexene	1.29e-10	9.84e-11	-1.3			
3,5,5-trimethyl-2-cyclohexene-1-one	2.40e-11	1.03e-10	4.3			
campholenic aldehyde	6.54e-11	1.14e-10	1.7			

Table S21 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
2-(4-methylcyclohex-3-en-1-yl)propan-2-ol	1.90e-10	1.03e-10	-1.8			
beta-ionone	1.21e-10	2.28e-10	1.9			
1-(1,2,3,4,5,6,7,8,-octahydro-2,3,8,8-tetramethyl-2-naphthalene)ethanone	9.90e-11	1.23e-10	1.2			
acetyl cedrene	7.70e-11	1.17e-10	1.5			
acetylcedrene	7.70e-11	1.25e-10	1.6			
Monofunctional aromatic oxygenates						
coumaran	4.00e-11	2.42e-11	-1.7			
2-naphthol	1.77e-10	1.26e-10	-1.4			
Other aromatic oxygenates						
benzyl alcohol	2.70e-11	9.19e-12	-2.9			
phthalaldehyde	2.30e-11	2.79e-11	1.2			
isochroman	3.70e-11	3.18e-11	-1.2			
2-acetylbenzaldehyde	1.70e-11	1.45e-11	-1.2			
1,2-diacetylbenzene	4.00e-12	1.12e-12	-3.6			
galaxolide	2.60e-11	7.38e-11	2.8			
3-phenylacrolein	4.80e-11	3.19e-11	-1.5			
methyl chavicol	5.20e-11	5.09e-11	-			
(E+Z)-2-formylcinnamaldehyde	2.10e-11	4.50e-11	2.1			
eugenol	8.34e-11	1.55e-10	1.9			
Alkyl amines						
piperidine	7.40e-11	8.28e-11	1.1			
Other reduced nitrogen compounds						
1-methyl-2-pyrrolidone	2.30e-11	1.55e-11	-1.5			
2-aminoethanol	7.94e-11	2.39e-11	-3.3			
N-methylethanolamine	8.26e-11	8.29e-11	-			
piperazine	2.38e-10	1.57e-10	-1.5			
morpholine	1.10e-10	9.93e-11	-			
2-amino-2-methyl-1-propanol	2.80e-11	2.28e-11	-1.2			
N,N-dimethylethanolamine	7.00e-11	8.91e-11	1.3			
N-methylsuccinimide	1.30e-11	1.48e-11	1.1			
N-formyl pyrrolidinone	6.00e-12	3.01e-11	5.0			
N-formylmorpholine	4.00e-11	5.13e-11	1.3			
N-acetylmorpholine	3.80e-11	3.66e-11	-			
Monohalo alkenes or alkynes						
3-chloro-1-propene	1.69e-11	3.08e-11	1.8			
4-chloro-1-butene	2.63e-11	3.16e-11	1.2			
3-chloro-2-methyl-1-propene	3.40e-11	6.17e-11	1.8			
1-chlorocyclopentene	5.97e-11	2.24e-11	-2.7			
Monohalo aromatics						
chloromethylbenzene	2.80e-12	5.10e-12	1.8			
3-chlorobiphenyl	4.96e-12	7.67e-12	1.5			
4-chlorobiphenyl	3.38e-12	7.67e-12	2.3			
2-chlorobiphenyl	2.67e-12	7.99e-12	3.0			

[a] Rate constants and A factors in units of  $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . "Error" shows (estimated - experimental) /



Table S21 (continued)

experimental (in parentheses) if the agreement is within  $\pm 10\%$ , otherwise it shows estimated / experimental if an overestimate or -experimental/estimated if an underestimate.

[b] From McGillen et al (2020).

Table S22. Experimental and estimated rate constants for the reactions of organics with Cl Atoms.

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
Used for parameter derivations						
Acyclic alkanes						
ethane	5.80e-11	5.77e-11	-	7.05e-11	6.25e-11	-1.1
propane	1.40e-10	1.23e-10	-1.1	1.40e-10	1.36e-10	-
butane	2.05e-10	1.88e-10	-	2.05e-10	2.10e-10	-
pentane	2.70e-10	2.54e-10	-			
hexane	3.30e-10	3.19e-10	-			
heptane	3.80e-10	3.85e-10	-			
octane	4.40e-10	4.50e-10	-			
nonane	4.60e-10	5.15e-10	1.1			
decane	5.27e-10	5.81e-10	1.1			
2-methylpropane	1.40e-10	1.38e-10	-	1.40e-10	1.40e-10	-
2,2-dimethylpropane	1.10e-10	1.15e-10	-	1.10e-10	1.25e-10	1.1
2-methylbutane	2.10e-10	2.04e-10	-			
2,3-dimethylbutane	2.20e-10	2.19e-10	-			
3-methylpentane	2.69e-10	2.69e-10	-			
2-methylpentane	2.80e-10	2.69e-10	-			
2,2,3-trimethylbutane	1.93e-10	1.96e-10	-			
2-methylhexane	3.38e-10	3.35e-10	-			
2,4-dimethylpentane	2.77e-10	2.84e-10	-			
2,2,3,3-tetramethylbutane	1.69e-10	1.73e-10	-			
2,2,4-trimethylpentane	2.50e-10	2.62e-10	-			
Cyclic alkanes						
cyclopropane	1.40e-13	1.40e-13	-			
cyclobutane	2.20e-10	2.20e-10	-			
cyclopentane	2.90e-10	2.90e-10	-			
cyclohexane	3.30e-10	3.92e-10	1.2			
cycloheptane	4.22e-10	4.58e-10	-			
methylcyclohexane	3.54e-10	4.08e-10	1.2			
(Z)-1,4-dimethylcyclohexane	2.89e-10	4.23e-10	1.5			
cyclooctane	4.53e-10	5.23e-10	1.2			
(E)-1,4-dimethylcyclohexane	3.26e-10	4.23e-10	1.3			
ethylcyclohexane	3.88e-10	4.73e-10	1.2			
1,3,5-trimethylcyclohexane	2.61e-10	4.38e-10	1.7			
cyclodecane	5.13e-10	6.54e-10	1.3			
Acyclic monoalkenes						
propene	2.70e-10	2.43e-10	-			
1-butene	3.00e-10	3.09e-10	-			
2-methylpropene	3.30e-10	3.01e-10	-			
1-pentene	4.20e-10	3.74e-10	-1.1			
2-methyl-1-butene	3.58e-10	3.66e-10	-			
3-methyl-1-butene	3.29e-10	3.24e-10	-			
1-hexene	4.00e-10	4.39e-10	-			
2-ethyl-1-butene	3.89e-10	4.32e-10	1.1			
3-methyl-1-pentene	3.85e-10	3.89e-10	-			
1-heptene	4.40e-10	5.05e-10	1.1			
1-octene	5.50e-10	5.70e-10	-			

Table S22 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
1-nonene	5.90e-10	6.36e-10	-			
trans-2-butene	3.50e-10	3.31e-10	-			
cis-2-butene	3.40e-10	3.31e-10	-			
2-methyl-2-butene	3.80e-10	3.80e-10	-			
(Z)-3-hexene	4.13e-10	4.62e-10	1.1			
(Z/E)-4-methyl-2-pentene	4.11e-10	4.12e-10	-			
(Z)-4-methyl-2-pentene	4.11e-10	4.12e-10	-			
Acyclic conjugated dialkenes						
1,3-butadiene	4.40e-10	4.33e-10	-			
2-methyl-1,3-butadiene	4.10e-10	4.23e-10	-			
2,3-dimethyl-1,3-butadiene	4.20e-10	4.14e-10	-			
Allenes and other acyclic di- or polyalkenes						
propadiene	4.38e-10	4.38e-10	-			
Alkynes						
acetylene	5.20e-11	5.20e-11	-			
Alkylbenzenes						
toluene	6.00e-11	6.30e-11	-			
p-xylene	1.44e-10	1.34e-10	-			
o-xylene	1.45e-10	1.34e-10	-			
ethylbenzene	1.29e-10	1.26e-10	-			
m-xylene	1.32e-10	1.34e-10	-			
1,3,5-trimethylbenzene	2.42e-10	2.50e-10	-			
p-cymene	1.96e-10	2.14e-10	-			
Naphthalenes						
1-methylnaphthalene	1.21e-10	1.11e-10	-			
2-methylnaphthalene	1.05e-10	1.11e-10	-			
acenaphthene	3.01e-10	3.18e-10	-			
1,5-dimethylnaphthalene	2.31e-10	2.63e-10	1.1			
1,4-dimethylnaphthalene	2.93e-10	2.67e-10	-			
1,7-dimethylnaphthalene	3.05e-10	2.63e-10	-1.2			
1,6-dimethylnaphthalene	2.15e-10	2.63e-10	1.2			
2,7-dimethylnaphthalene	2.00e-10	2.63e-10	1.3			
2,3-dimethylnaphthalene	2.93e-10	2.67e-10	-			
2,6-dimethylnaphthalene	2.34e-10	2.63e-10	1.1			
2-ethylnaphthalene	1.38e-10	1.74e-10	1.3			
1,2-dimethylnaphthalene	3.61e-10	2.67e-10	-1.3			
1,3-dimethylnaphthalene	2.90e-10	2.67e-10	-			
1,8-dimethylnaphthalene	3.07e-10	2.63e-10	-1.2			
Monofunctional acyclic alcohols, ethers, and hydroperoxides						
methanol	5.10e-11	5.10e-11	-			
ethanol	1.00e-10	9.82e-11	-			
2-propanol	8.70e-11	7.89e-11	-			
1-propanol	1.60e-10	1.43e-10	-1.1			
1-butanol	2.20e-10	2.09e-10	-			
2-methyl-1-propanol	2.10e-10	1.66e-10	-1.3			
2-butanol	1.10e-10	1.28e-10	1.2			

Table S22 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
2-methyl-2-propanol	3.50e-11	3.38e-11	-			
3-methyl-1-butanol	2.50e-10	2.24e-10	-1.1			
1-pentanol	2.40e-10	2.74e-10	1.1			
3-methyl-2-butanol	1.20e-10	1.49e-10	1.2			
2-pentanol	2.20e-10	1.93e-10	-1.1			
3-pentanol	2.00e-10	1.77e-10	-1.1			
2-methyl-2-butanol	7.30e-11	7.69e-11	-			
2,3-dimethyl-2-butanol	1.00e-10	1.00e-10	-			
1-hexanol	3.10e-10	3.39e-10	-			
1-heptanol	3.70e-10	4.05e-10	-			
1-octanol	4.20e-10	4.70e-10	1.1			
2-ethyl-1-hexanol	1.88e-10	4.28e-10	2.3			
dimethyl ether	1.80e-10	1.78e-10	-			
methyl ethyl ether	2.92e-10	1.94e-10	-1.5			
diethyl ether	2.80e-10	2.11e-10	-1.3			
1-methoxypropane	2.52e-10	2.59e-10	-			
methyl tert-butyl ether	1.50e-10	1.75e-10	1.2			
methyl s-butyl ether	2.16e-10	2.73e-10	1.3			
methyl n-butyl ether	2.86e-10	3.25e-10	1.1			
ethyl tert-butyl ether	1.50e-10	1.92e-10	1.3			
di-iso-propyl ether	1.66e-10	2.37e-10	1.4			
di-n-propyl ether	3.70e-10	3.41e-10	-			
di-tert-butyl ether	1.40e-10	1.73e-10	1.2			
di-n-butyl ether	4.70e-10	4.72e-10	-			
di-n-pentyl ether	5.30e-10	6.03e-10	1.1			
methyl hydroperoxide	5.90e-11	5.90e-11	-			
ethyl hydroperoxide	1.10e-10	1.10e-10	-			
Other monofunctional carbonyl compounds						
ethanal	8.00e-11	8.00e-11	-	8.00e-11	7.58e-11	-
propanal	1.25e-10	1.12e-10	-1.1	2.80e-11	1.11e-10	4.0
butanal	1.66e-10	1.77e-10	-	3.80e-11	1.84e-10	4.9
2-methylpropanal	1.56e-10	1.35e-10	-1.2			
pentanal	2.40e-10	2.43e-10	-	5.30e-11	2.58e-10	4.9
2,2-dimethylpropanal	1.42e-10	1.44e-10	-			
hexanal	2.79e-10	3.08e-10	1.1	8.60e-11	3.31e-10	3.9
heptanal	3.00e-10	3.73e-10	1.2	1.10e-10	4.05e-10	3.7
2-ethylhexanal	3.10e-10	3.97e-10	1.3			
acetone	2.10e-12	2.11e-12	-			
2-butanone	4.00e-11	4.63e-11	1.2			
3-methyl-2-butanone	6.80e-11	6.35e-11	-			
2-pentanone	1.16e-10	8.73e-11	-1.3			
3-pentanone	8.00e-11	9.05e-11	1.1			
4-methyl-2-pentanone	1.23e-10	1.12e-10	-			
2-hexanone	2.00e-10	1.53e-10	-1.3			
3-hexanone	1.47e-10	1.31e-10	-1.1			
3-methyl-2-pentanone	9.40e-11	1.12e-10	1.2			
3,3-dimethyl-2-butanone	4.80e-11	4.08e-11	-1.2			
2-methyl-3-pentanone	1.07e-10	1.08e-10	-			

Table S22 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
5-methyl-2-hexanone	1.40e-10	1.68e-10	1.2			
methyl formate	1.40e-12	1.40e-12	-			
methyl acetate	2.60e-12	2.95e-12	1.1			
ethyl formate	1.02e-11	2.89e-11	2.8			
iso-propyl formate	1.58e-11	5.78e-11	3.7			
methyl propionate	2.42e-11	1.23e-11	-2.0			
ethyl acetate	1.78e-11	3.17e-11	1.8			
n-propyl formate	4.60e-11	9.43e-11	2.1			
methyl isobutyrate	3.96e-11	3.64e-11	-			
n-butyl formate	1.16e-10	1.60e-10	1.4			
n-propyl acetate	7.53e-11	9.71e-11	1.3			
iso-propyl acetate	2.29e-11	6.06e-11	2.6			
2-methylpropyl formate	7.60e-11	1.10e-10	1.4			
methyl n-butyrate	4.30e-11	5.33e-11	1.2			
ethyl propionate	3.54e-11	4.11e-11	1.2			
iso-butyl acetate	1.04e-10	1.12e-10	-			
n-butyl acetate	1.22e-10	1.62e-10	1.3			
sec-butyl acetate	8.80e-11	1.26e-10	1.4			
n-propyl propionate	9.02e-11	1.06e-10	1.2			
methyl n-pentanoate	6.80e-11	1.19e-10	1.7			
ethyl n-butyrate	1.02e-10	8.21e-11	-1.2			
methyl 2-methylbutanoate	9.00e-11	8.50e-11	-			
methyl pivalate	3.93e-11	3.99e-11	-			
ethyl 2-methylpropanoate	6.08e-11	6.52e-11	-			
methyl 3-methylbutanoate	8.07e-11	7.84e-11	-			
iso-propyl isobutyrate	8.10e-11	9.40e-11	1.2			
n-pentyl acetate	1.79e-10	2.28e-10	1.3			
n-butyl propionate	1.60e-10	1.72e-10	-			
methyl n-hexanoate	9.40e-11	1.84e-10	2.0			
n-propyl isobutyrate	1.12e-10	1.31e-10	1.2			
n-propyl n-butyrate	1.40e-10	1.47e-10	-			
methyl 2-methylpentanoate	1.40e-10	1.50e-10	-			
ethyl 2,2-dimethylpropanoate	5.35e-11	6.87e-11	1.3			
ethyl 2-methylbutanoate	1.41e-10	1.14e-10	-1.2			
ethyl 3-methylbutanoate	1.25e-10	1.07e-10	-1.2			
n-butyl n-butyrate	1.70e-10	2.13e-10	1.3			
ethyl 2-methylpentanoate	1.72e-10	1.79e-10	-			
methyl n-heptanoate	1.35e-10	2.49e-10	1.8			
propionic acid	4.70e-12	5.86e-12	1.2			
dimethyl carbonate	2.30e-12	2.75e-12	1.2			
Other acyclic saturated oxygenates						
glyoxal	3.60e-11	3.60e-11	-			
methyl glyoxal	5.00e-11	5.00e-11	-			
2,3-butanedione	4.50e-13	4.50e-13	-			
2,3-pentanedione	1.60e-11	1.81e-11	1.1			
hexan-2,3-dione	8.80e-11	5.91e-11	-1.5			
Cyclic saturated oxygenates						
ethylene carbonate	7.29e-12	5.53e-12	-1.3			
propylene carbonate	1.77e-11	3.38e-11	1.9			

Table S22 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
Multifunctional oxygenates with 2+ non-HC groups on same carbon						
hydroxyacetone	5.76e-11	5.26e-11	-			
3-hydroxy-2-butanone	4.90e-11	4.53e-11	-			
Monofunctional acyclic saturated oxidized nitrogen compounds						
methyl nitrate	2.40e-13	2.40e-13	-			
ethyl nitrate	4.70e-12	4.40e-12	-			
n-propyl nitrate	2.20e-11	3.33e-11	1.5			
iso-propyl nitrate	3.80e-12	3.82e-12	-			
n-butyl nitrate	8.50e-11	9.87e-11	1.2			
n-pentyl nitrate	1.45e-10	1.64e-10	1.1			
2-pentyl nitrate	1.01e-10	9.83e-11	-			
2-heptyl nitrate	2.64e-10	2.29e-10	-1.2			
nitroethane	1.90e-13	1.86e-13	-			
1-nitropropane	9.90e-12	2.92e-11	3.0			
1-nitrobutane	5.50e-11	9.46e-11	1.7			
1-nitropentane	1.27e-10	1.60e-10	1.3			
methyl nitrite	2.10e-12	2.10e-12	-			
Monofunctional acyclic unsaturated oxygenates						
ethyl vinyl ether	2.43e-10	3.81e-10	1.6			
2-methoxy-1-propene	7.03e-10	4.30e-10	-1.6			
n-propyl vinyl ether	4.23e-10	4.46e-10	-			
2-propenal	2.23e-10	1.59e-10	-1.4			
crotonaldehyde	2.65e-10	1.88e-10	-1.4			
2-methyl-2-propenal	2.20e-10	1.88e-10	-1.2			
3-methyl-2-butenal	2.45e-10	2.17e-10	-1.1			
e-2-pentenal	1.30e-10	2.53e-10	1.9			
(E,E)-2,4-hexadienal	3.98e-10	4.04e-10	-			
(E/Z)-2-hexenal	1.90e-10	3.19e-10	1.7			
trans-2-heptenal	2.40e-10	3.84e-10	1.6			
3-buten-2-one	2.10e-10	1.84e-10	-1.1			
3-penten-2-one	2.50e-10	2.64e-10	-			
3-methyl-3-buten-2-one	2.38e-10	2.38e-10	-			
1-penten-3-one	2.90e-10	2.29e-10	-1.3			
4-hexen-3-one	3.00e-10	3.08e-10	-			
4-methyl-3-penten-2-one	2.66e-10	3.10e-10	1.2			
3-methyl-3-penten-2-one	3.00e-10	3.10e-10	-			
vinyl acetate	2.68e-10	2.52e-10	-			
methyl acrylate	1.87e-10	1.84e-10	-			
methyl crotonate	2.10e-10	2.63e-10	1.3			
vinyl propionate	2.06e-10	2.61e-10	1.3			
isopropenyl acetate	4.44e-10	3.14e-10	-1.4			
methyl methacrylate	2.54e-10	2.37e-10	-			
ethyl acrylate	2.18e-10	2.12e-10	-			
ethyl crotonate	2.52e-10	2.92e-10	1.2			
methyl-3-methyl-2-butenate	3.18e-10	3.09e-10	-			
vinyl butanoate	2.48e-10	3.02e-10	1.2			
ethyl methacrylate	2.71e-10	2.66e-10	-			

Table S22 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
(E)-ethyl tiglate	2.53e-10	3.38e-10	1.3			
n-butyl acrylate	2.72e-10	3.43e-10	1.3			
2-methylpropenoic acid butyl ester	3.70e-10	3.97e-10	-			
ethyl hexyl acrylate	3.57e-10	4.37e-10	1.2			
hexyl acrylate	3.32e-10	4.74e-10	1.4			
acrylic acid	3.70e-10	1.83e-10	-2.0			
Furans						
3-methylfuran	4.00e-10	3.91e-10	-			
2-methylfuran	3.90e-10	4.26e-10	-			
2-ethylfuran	4.40e-10	4.91e-10	1.1			
2,5-dimethylfuran	5.40e-10	4.55e-10	-1.2			
Monofunctional aromatic oxygenates						
benzaldehyde	9.90e-11	6.32e-11	-1.6			
o-tolualdehyde	1.86e-10	9.77e-11	-1.9			
m-tolualdehyde	1.71e-10	9.77e-11	-1.8			
p-tolualdehyde	1.41e-10	9.77e-11	-1.4			
2,5-dimethylbenzaldehyde	9.30e-11	1.39e-10	1.5			
2,4-dimethylbenzaldehyde	8.70e-11	1.39e-10	1.6			
3,5-dimethylbenzaldehyde	9.30e-11	1.39e-10	1.5			
methoxybenzene	1.07e-10	1.00e-10	-			
1-ethyl-2-methoxybenzene	1.20e-10	2.04e-10	1.7			
phenol	2.00e-10	1.49e-10	-1.3			
Aromatic oxidized nitrogen compounds						
nitrobenzene	9.40e-13	7.00e-13	-1.3			
2-nitrophenol	6.80e-12	8.10e-12	1.2			
5-methyl-2-nitrophenol	1.94e-11	4.21e-11	2.2			
4-methyl-2-nitrophenol	4.30e-11	4.21e-11	-			
3-methyl-2-nitrophenol	1.40e-10	4.21e-11	-3.3			
2-methyl-6-nitrophenol	2.68e-11	4.97e-11	1.9			
Alkyl amines						
Methylamine	2.90e-10	2.90e-10	-			
Dimethyl Amine	3.89e-10	3.89e-10	-			
Trimethyl Amine	3.68e-10	3.68e-10	-			
Other reduced nitrogen compounds						
acetamide	2.20e-11	2.20e-11	-			
N-methylformamide	8.60e-11	1.28e-10	1.5			
N-methylacetamide	9.00e-11	7.20e-11	-1.3			
N,N-dimethylformamide	1.70e-10	2.36e-10	1.4			
N,N-dimethylacetamide	2.30e-10	1.79e-10	-1.3			
Monohalo alkanes						
fluoromethane	3.60e-13	3.60e-13	-			
fluoroethane	7.47e-12	7.47e-12	-			
chloromethane	4.89e-13	4.79e-13	-			
chloroethane	8.32e-12	1.03e-11	1.2			
2-chloropropane	1.97e-11	1.42e-11	-1.4			
1-chloropropane	5.05e-11	4.55e-11	-			
2-chloro-2-methylpropane	1.29e-11	1.50e-11	1.2			

Table S22 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
bromomethane	4.45e-13	4.39e-13	-			
bromoethane	8.79e-12	1.18e-11	1.3			
2-bromopropane	2.71e-11	2.24e-11	-1.2			
1-bromopropane	5.81e-11	5.44e-11	-			
1-bromobutane	1.40e-10	1.20e-10	-1.2			
1-bromopentane	2.14e-10	1.85e-10	-1.2			
1-bromohexane	2.72e-10	2.51e-10	-			
iodomethane	1.07e-12	1.02e-12	-			
iodoethane	1.97e-11	3.12e-11	1.6			
2-iodopropane	4.84e-11	5.96e-11	1.2			
1-iodopropane	6.65e-11	9.66e-11	1.5			
Monohalo alkenes or alkynes						
fluoroethene	1.84e-10	1.53e-10	-1.2			
chloroethene	1.27e-10	1.27e-10	-			
2-fluoropropene	1.64e-10	2.03e-10	1.2			
Used for evaluations only						
Allenes and other acyclic di- or polyalkenes						
3-methylene-7-methyl-1,6-octadiene	7.55e-10	8.76e-10	1.2			
beta-ocimene	5.50e-10	8.40e-10	1.5			
Cycloalkenes						
cyclopentene	3.70e-10	4.47e-10	1.2			
cyclohexene	3.78e-10	5.35e-10	1.4			
cycloheptene	5.68e-10	6.00e-10	-			
1,4-cyclohexadiene	4.06e-10	6.77e-10	1.7			
1,5-cyclooctadiene	6.16e-10	8.08e-10	1.3			
b-pinene	5.30e-10	5.74e-10	-			
limonene	6.40e-10	8.42e-10	1.3			
3-carene	5.40e-10	5.11e-10	-			
2-carene	5.80e-10	5.11e-10	-1.1			
camphene	3.30e-10	5.67e-10	1.7			
a-pinene	5.00e-10	5.88e-10	1.2			
Naphthalenes						
naphthalene	4.22e-12	3.48e-11	8.3			
Styrenes or aromatics with double bonds or non-aromatic rings						
styrene	2.57e-10	2.50e-10	-			
indene	1.09e-10	4.08e-10	3.7			
α-methylstyrene	1.85e-10	3.08e-10	1.7			
trans-beta-methylstyrene	1.21e-10	3.38e-10	2.8			
acenaphthylene	4.69e-10	4.83e-10	-			
Other monofunctional carbonyl compounds						
tert-butyl formate	1.45e-11	8.66e-11	6.0			
tert-butyl acetate	1.75e-11	8.94e-11	5.1			
acetic acid	2.65e-14	2.65e-14	-			
Glycol, alcohol ether, or polyether						



Table S22 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
3-methoxy-1-propanol	2.62e-10	2.80e-10	-			
1-methoxy-2-propanol	2.28e-10	1.94e-10	-1.2			
3-methoxy-1-butanol	2.90e-10	2.93e-10	-			
1-methoxy-2-butanol	2.79e-10	2.43e-10	-1.2			
Other acyclic saturated oxygenates						
formyl acetate	1.00e-13	2.82e-12	28.2			
methyl pyruvate	5.72e-13	3.63e-13	-1.6			
formyl propanoate	2.90e-12	1.22e-11	4.2			
ethylene glycol diformate	3.20e-12	1.56e-13	-20.5			
1-Methoxy-2-Propyl Acetate	1.98e-10	1.97e-10	-			
dimethyl succinate	6.79e-12	3.76e-12	-1.8			
ethylene glycol diacetate	5.70e-12	5.75e-12	-			
dimethyl glutarate	1.90e-11	1.79e-11	-			
dimethyl adipate	6.08e-11	4.88e-11	-1.2			
4-hydroxy-2-butanone	1.45e-10	4.19e-11	-3.5			
4-hydroxy-4-methyl-2-pentanone	7.40e-11	3.90e-11	-1.9			
Cyclic saturated oxygenates						
ethylene oxide	4.90e-12	1.09e-13	-44.9			
methyl oxirane	3.00e-11	2.90e-11	-			
cyclobutanone	1.01e-10	7.05e-11	-1.4			
tetrahydrofuran	2.25e-10	2.52e-10	1.1			
1,4-dioxane	1.74e-10	3.06e-10	1.8			
cyclopentanone	1.10e-10	1.02e-10	-			
2-methyl-tetrahydrofuran	2.65e-10	2.66e-10	-			
tetrahydropyran	2.26e-10	3.49e-10	1.5			
gamma-valerolactone	3.41e-11	5.04e-11	1.5			
3-methyl-dihydro-furan-2-one	3.42e-11	5.15e-11	1.5			
cyclohexanone	1.80e-10	1.80e-10	-			
2-methylcyclopentanone	1.52e-10	1.26e-10	-1.2			
cyclo-hexanol	3.21e-10	3.15e-10	-			
2,5-dimethyltetrahydrofuran	2.84e-10	2.81e-10	-			
cycloheptanone	2.43e-10	2.45e-10	-			
2-methylcyclohexanone	1.12e-10	2.05e-10	1.8			
cyclooctanone	2.97e-10	3.11e-10	-			
methyl cyclohexanecarboxylate	2.87e-10	2.72e-10	-			
camphor	1.59e-10	2.03e-10	1.3			
fenchone	1.86e-10	1.72e-10	-			
borneol	2.72e-10	3.22e-10	1.2			
fenchol	2.93e-10	3.48e-10	1.2			
cyclodecanone	3.65e-10	4.42e-10	1.2			
1,8-cineole	2.18e-10	4.00e-10	1.8			
menthol	3.40e-10	4.32e-10	1.3			
pinonaldehyde	2.30e-10	2.41e-10	-			
Multifunctional oxygenates with 2+ non-HC groups on same carbon						
hydroxyacetaldehyde	7.30e-11	9.10e-11	1.2			
1,3-dioxolane	1.65e-10	2.03e-10	1.2			
dimethoxymethane	1.40e-10	2.54e-10	1.8			
1,3,5-trioxane	1.02e-10	2.29e-10	2.2			

Table S22 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
methylene glycol diformate	5.66e-13	2.55e-14	-22.2			
Methoxy Acetone	1.07e-10	1.36e-10	1.3			
trimethoxymethane	1.60e-10	3.27e-10	2.0			
3-hydroxy-3-methyl-2-butanone	1.13e-10	2.55e-11	-4.4			
dimethyl malonate	3.80e-12	8.94e-13	-4.3			
di-tert-butyl malonate	1.50e-10	1.74e-10	1.2			
Monofunctional acyclic saturated oxidized nitrogen compounds						
peroxypropionyl nitrate	1.10e-12	1.22e-11	11.1			
Other saturated oxygenate or nitro or nitrate compounds						
1,4-dinitrooxybutane	3.90e-11	8.87e-12	-4.4			
2-nitrooxy-1-propanol	4.20e-11	2.24e-12	-18.8			
1-nitrooxy-2-propanol	4.50e-11	1.83e-11	-2.5			
2-nitrooxy-1-butanol	9.80e-12	3.13e-11	3.2			
3-nitrooxy-1-butanol	1.39e-11	8.92e-11	6.4			
4-nitrooxy-1-butanol	1.82e-11	1.19e-10	6.5			
4-nitrooxy-2-butanol	1.40e-11	6.74e-11	4.8			
1-nitrooxy-2-butanol	8.70e-12	6.71e-11	7.7			
4-nitrooxy-1-pentanol	1.56e-11	1.18e-10	7.6			
5-nitrooxy-2-pentanol	2.05e-11	1.03e-10	5.0			
1-nitrooxy-2-pentanol	1.25e-11	1.32e-10	10.6			
2-nitrooxy-1-pentanol	1.59e-11	9.67e-11	6.1			
6-nitrooxy-1-hexanol	2.44e-11	2.49e-10	10.2			
Other acyclic unsaturated oxygenates						
2-propyn-1-ol	3.49e-10	1.37e-10	-2.5			
2-propen-1-ol	2.85e-10	2.90e-10	-			
3-butyne-2-ol	3.80e-10	1.15e-10	-3.3			
3-butyne-1-ol	4.30e-10	1.66e-10	-2.6			
3-buten-2-ol	3.00e-10	2.77e-10	-			
3-buten-1-ol	2.80e-10	3.29e-10	1.2			
2-methyl-2-propen-1-ol	2.45e-10	3.48e-10	1.4			
2-buten-1-ol	3.97e-10	3.78e-10	-			
2-methyl-3-butyne-2-ol	3.50e-10	7.45e-11	-4.7			
2-methyl-3-buten-2-ol	3.01e-10	2.37e-10	-1.3			
cis-2-penten-1-ol	3.30e-10	4.43e-10	1.3			
3-methyl-2-buten-1-ol	4.49e-10	4.27e-10	-			
1-penten-3-ol	2.74e-10	3.26e-10	1.2			
3-methyl-3-buten-1-ol	4.27e-10	3.86e-10	-			
2-methyl-3-buten-1-ol	3.63e-10	3.52e-10	-			
4-penten-2-ol	3.75e-10	3.13e-10	-1.2			
(Z)-3-hexen-1-ol	3.10e-10	4.82e-10	1.6			
3-hexen-1-ol (trans)	3.30e-10	4.82e-10	1.5			
trans-2-hexen-1-ol	3.51e-10	5.08e-10	1.4			
3-hepten-1-ol	3.80e-10	5.47e-10	1.4			
3-octen-1-ol	4.13e-10	6.13e-10	1.5			
(E)-2-butenedial	1.35e-10	3.17e-10	2.3			
5-hexen-2-one	3.62e-10	2.73e-10	-1.3			
methyl-3-butenolate	2.10e-10	2.21e-10	-			
allyl acetate	1.90e-10	2.17e-10	1.1			

Table S22 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
2-methyl-2-propenyl acetate	3.44e-10	2.75e-10	-1.3			
allyl butanoate	2.25e-10	2.68e-10	1.2			
(Z)-3-hexenylformate	2.45e-10	4.33e-10	1.8			
(E)-2-hexenyl acetate	3.10e-10	4.36e-10	1.4			
Furans						
furan	2.00e-10	3.97e-10	2.0			
Cyclic unsaturated non-aromatic oxidized nitrogen compounds						
2,5-dihydrofuran	4.48e-10	3.99e-10	-1.1			
2,3-dihydrofuran	4.52e-10	4.77e-10	-			
gamma-crotonolactone	2.94e-11	2.34e-10	8.0			
3,4-dihydropyran	6.15e-10	5.58e-10	-			
3-furfural	4.90e-11	3.57e-10	7.3			
2-furfural	3.50e-11	3.57e-10	10.2			
4-methyl-2H-furan-5-one	1.61e-10	2.80e-10	1.7			
5-methyl-2-furfural	5.10e-11	3.86e-10	7.6			
Other aromatic oxygenates						
benzyl alcohol	9.30e-11	1.16e-10	1.2			
3-methoxyphenol	2.96e-10	1.76e-10	-1.7			
4-methoxyphenol	2.86e-10	1.76e-10	-1.6			
guaiacol	2.97e-10	2.19e-10	-1.4			
2-methoxy-4-methylphenol	3.35e-10	3.58e-10	-			
2,3-dimethoxyphenol	4.73e-10	2.53e-10	-1.9			
2,6-dimethoxyphenol	2.71e-10	2.91e-10	-			
Monohalo alkanes						
2-chlorobutane	6.95e-11	4.94e-11	-1.4			
1-chlorobutane	1.11e-10	1.11e-10	-			
1-chloropentane	1.59e-10	1.76e-10	1.1			
Monohalo alkenes or alkynes						
3-fluoropropene	4.92e-11	1.67e-11	-2.9			
3-chloro-1-propene	1.70e-10	1.71e-10	-			
3-bromo-1-propene	1.23e-10	2.15e-10	1.8			
4-chloro-1-butene	2.35e-10	2.31e-10	-			
3-chloro-2-methyl-1-propene	2.25e-10	2.22e-10	-			
3-chloro-1-butene	2.10e-10	1.75e-10	-1.2			
1-chloro-2-butene	2.20e-10	2.46e-10	1.1			
(E)-1-chloro-2-butene	2.50e-10	2.46e-10	-			
1-chlorocyclopentene	3.71e-10	3.48e-10	-			
Monohalo aromatics						
chloromethylbenzene	9.71e-12	4.09e-11	4.2			

[a] Rate constants and A factors in units of  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ . "Error" shows (estimated - experimental) / experimental (in parentheses) if the agreement is within  $\pm 10\%$ , otherwise it shows estimated / experimental if an overestimate or -experimental/estimated if an underestimate.

[b] From McGillen et al (2020).

Table S23. Experimental and estimated rate constants for the reactions of organics with NO<sub>3</sub> radicals.

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
Used for parameter derivations						
Acyclic alkanes						
propane	9.20e-18	9.83e-18	-			
butane	1.50e-17	3.37e-17	2.2			
pentane	8.30e-17	6.31e-17	-1.3			
hexane	1.10e-16	9.25e-17	-1.2			
heptane	1.40e-16	1.22e-16	-1.1			
octane	1.90e-16	1.51e-16	-1.3			
nonane	2.20e-16	1.81e-16	-1.2			
decane	2.60e-16	2.10e-16	-1.2			
2-methylpropane	1.04e-16	6.78e-17	-1.5	2.14e-12	2.14e-12	-
2-methylbutane	1.70e-16	1.38e-16	-1.2	1.50e-12	1.50e-12	-
2,3-dimethylbutane	4.24e-16	2.77e-16	-1.5			
3-methylpentane	2.05e-16	2.48e-16	1.2			
2-methylpentane	1.70e-16	1.70e-16	-			
2,2,3-trimethylbutane	2.20e-16	1.73e-16	-1.3			
2,4-dimethylpentane	1.45e-16	2.78e-16	1.9			
2,2,4-trimethylpentane	7.50e-17	1.69e-16	2.3			
Acyclic monoalkenes						
propene	9.50e-15	9.09e-15	-	4.60e-13	3.39e-13	-1.4
1-butene	1.30e-14	1.16e-14	-1.1	3.20e-13	4.32e-13	1.3
2-methylpropene	3.40e-13	3.31e-13	-			
1-pentene	1.50e-14	1.38e-14	-			
2-methyl-1-butene	5.00e-13	3.95e-13	-1.3			
3-methyl-1-butene	1.40e-14	1.38e-14	-			
1-hexene	1.80e-14	1.59e-14	-1.1			
2-methyl-1-pentene	4.40e-13	4.52e-13	-			
3,3-dimethyl-1-butene	1.50e-14	1.58e-14	-			
2-ethyl-1-butene	4.50e-13	4.52e-13	-			
3-methyl-1-pentene	1.30e-14	1.59e-14	1.2			
4-methyl-1-pentene	1.30e-14	1.59e-14	1.2			
1-heptene	2.00e-14	1.77e-14	-1.1			
2-methyl-hex-1-ene	5.30e-13	5.04e-13	-			
4,4-dimethyl-pent-1-ene	1.30e-14	1.76e-14	1.4			
3,4-dimethyl-1-pentene	1.40e-14	1.79e-14	1.3			
5-methyl-1-hexene	2.10e-14	1.78e-14	-1.2			
3,3-dimethyl-1-pentene	1.40e-14	1.76e-14	1.3			
4-methyl-1-hexene	1.80e-14	1.79e-14	-			
3-methyl-1-hexene	1.60e-14	1.78e-14	1.1			
1-octene	2.50e-14	1.94e-14	-1.3			
2-methyl-1-octene	5.90e-13	5.94e-13	-			
1-decene	2.60e-14	2.23e-14	-1.2			
2-methyl-1-nonene	6.20e-13	6.32e-13	-			
1-dodecene	2.80e-14	2.46e-14	-1.1			
2-methyl-1-undecene	6.20e-13	6.99e-13	1.1			
2-methyl-1-tridecene	6.10e-13	6.99e-13	1.1			
1-tetradecene	2.80e-14	2.47e-14	-1.1			

Table S23 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
trans-2-butene	3.90e-13	3.56e-13	-			
cis-2-butene	3.50e-13	3.56e-13	-			
trans-2-pentene	3.90e-13	4.25e-13	-			
cis-2-pentene	6.80e-13	4.25e-13	-1.6			
2-methyl-2-butene	9.40e-12	7.78e-12	-1.2			
2,3-dimethyl-2-butene	5.70e-11	5.70e-11	-			
2-methyl-2-pentene	8.50e-12	8.91e-12	-			
(Z)-3-hexene	4.50e-13	4.87e-13	-			
trans-2-hexene	3.90e-13	4.87e-13	1.2			
(Z)-3-methyl-2-pentene	8.50e-12	8.91e-12	-			
(E)-3-methyl-2-pentene	8.10e-12	8.91e-12	1.1			
(E)-3-hexene	3.70e-13	4.87e-13	1.3			
(Z)-2-hexene	5.50e-13	4.87e-13	-1.1			
Acyclic conjugated dialkenes						
1,3-butadiene	1.10e-13	1.06e-13	-			
(3E)-penta-1,3-diene	1.80e-12	2.76e-12	1.5			
2-methyl-1,3-butadiene	6.50e-13	7.72e-13	1.2			
cis-1,3-pentadiene	1.60e-12	2.76e-12	1.7			
2,3-dimethyl-1,3-butadiene	1.90e-12	1.62e-12	-1.2			
(2E,4E)-2,4-hexadiene	1.60e-11	6.18e-12	-2.6			
Alkynes						
methyl acetylene	2.10e-16	5.06e-16	2.4	1.25e-11	2.55e-11	2.0
1-butyne	4.70e-16	5.15e-16	-	3.21e-11	2.22e-11	-1.4
2-butyne	6.90e-14	4.39e-14	-1.6			
pent-1-yne	6.20e-16	5.39e-16	-1.1	2.98e-11	1.61e-11	-1.8
hex-1-yne	1.46e-15	5.69e-16	-2.6	8.95e-12	1.15e-11	1.3
2-hexyne	2.80e-14	4.40e-14	1.6			
Alkylbenzenes						
toluene	6.60e-17	6.57e-17	-			
p-xylene	4.60e-16	4.73e-16	-			
o-xylene	3.90e-16	4.42e-16	1.1			
m-xylene	2.30e-16	2.14e-16	-			
p-ethyltoluene	8.00e-16	5.11e-16	-1.6			
1,2,4-trimethylbenzene	1.72e-15	1.71e-15	-			
1,3,5-trimethylbenzene	8.20e-16	8.65e-16	-			
1,2,3-trimethylbenzene	1.76e-15	1.61e-15	-			
p-cymene	1.00e-15	7.47e-16	-1.3			
4-tert-butyltoluene	2.70e-16	4.73e-16	1.8			
Styrenes or aromatics with double bonds or non-aromatic rings						
styrene	1.50e-12	1.50e-12	-			
Monofunctional acyclic alcohols, ethers, and hydroperoxides						
2-propanol	1.40e-15	2.13e-15	1.5			
1-butanol	1.87e-15	1.92e-15	-			
2-butanol	2.00e-15	2.17e-15	-			
3-methyl-1-butanol	2.28e-15	2.04e-15	-1.1			
2-methyl-1-butanol	2.39e-15	2.41e-15	-			
3,3-dimethyl-1-butanol	1.80e-15	1.94e-15	-			
3,3-dimethyl-2-butanol	3.52e-15	2.13e-15	-1.7			

Table S23 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
2-ethyl-1-hexanol	2.93e-15	2.91e-15	-			
dimethyl ether	1.87e-16	2.04e-16	-			
methyl ethyl ether	7.81e-16	1.76e-15	2.2			
diethyl ether	3.20e-15	3.31e-15	-			
1-methoxypropane	1.67e-15	2.74e-15	1.6			
methyl tert-butyl ether	7.00e-16	4.05e-16	-1.7			
methyl s-butyl ether	2.73e-15	3.32e-15	1.2			
methyl n-butyl ether	1.88e-15	2.76e-15	1.5			
methyl tert-amyl ether	2.20e-15	1.39e-15	-1.6			
ethyl tert-butyl ether	8.56e-15	1.96e-15	-4.4			
di-iso-propyl ether	5.10e-15	4.47e-15	-1.1			
di-n-propyl ether	6.00e-15	5.28e-15	-1.1			
di-tert-butyl ether	2.90e-16	6.06e-16	2.1			
Other monofunctional carbonyl compounds						
ethanal	2.70e-15	2.66e-15	-	1.40e-12	4.04e-13	-3.5
propanal	6.30e-15	1.66e-14	2.6			
butanal	1.10e-14	1.66e-14	1.5	1.70e-12	2.51e-12	1.5
2-methylpropanal	1.25e-14	2.55e-14	2.0	1.67e-12	3.96e-12	2.4
pentanal	1.62e-14	1.66e-14	-			
3-methylbutanal	2.19e-14	1.67e-14	-1.3			
2,2-dimethylpropanal	2.40e-14	2.40e-14	-			
2-methylbutanal	2.67e-14	2.56e-14	-			
2-ethylbutanal	4.63e-14	2.57e-14	-1.8			
3-methylpentanal	2.50e-14	1.68e-14	-1.5			
hexanal	1.61e-14	1.67e-14	-			
4-methylpentanal	1.74e-14	1.67e-14	-			
2-methylpentanal	2.79e-14	2.56e-14	-			
3,3-dimethylbutanal	1.77e-14	1.66e-14	-			
heptanal	1.97e-14	1.67e-14	-1.2			
octanal	1.80e-14	1.67e-14	-			
nonanal	2.00e-14	1.68e-14	-1.2			
decanal	2.20e-14	1.68e-14	-1.3			
n-propyl acetate	5.00e-17	6.42e-17	1.3			
Monofunctional acyclic unsaturated oxygenates						
methyl vinyl ether	7.20e-13	1.13e-12	1.6			
ethyl vinyl ether	1.50e-12	1.43e-12	-			
2-methoxy-1-propene	2.41e-11	4.10e-11	1.7			
n-propyl vinyl ether	1.70e-12	1.71e-12	-			
tert-butyl vinyl ether	4.81e-12	1.96e-12	-2.5			
isobutyl vinyl ether	1.99e-12	1.96e-12	-			
n-butyl vinyl ether	2.00e-12	1.96e-12	-			
2-propenal	1.10e-15	1.11e-15	-			
crotonaldehyde	5.62e-15	8.18e-15	1.5			
2-methyl-2-propenal	3.40e-15	3.43e-15	-			
e-2-pentenal	1.70e-14	9.56e-15	-1.8			
(E,E)-2,4-hexadienal	1.34e-12	3.19e-12	2.4			
2-hexenal (trans)	1.20e-14	1.08e-14	-			
trans-2-heptenal	2.00e-14	1.20e-14	-1.7			

Table S23 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
(E)-2-octenal	6.00e-15	1.30e-14	2.2			
3-methyl-3-buten-2-one	8.30e-15	5.67e-15	-1.5			
1-penten-3-one	9.90e-17	2.13e-16	2.2			
(E)-3-penten-2-one	1.00e-14	7.20e-15	-1.4			
4-methyl-3-penten-2-one	1.44e-13	1.74e-13	1.2			
3-methyl-3-penten-2-one	1.55e-13	1.28e-13	-1.2			
vinyl acetate	9.00e-15	9.00e-15	-			
methyl acrylate	1.10e-16	1.07e-16	-			
methyl crotonate	1.85e-15	2.28e-15	1.2			
methyl methacrylate	3.29e-15	3.64e-15	1.1			
ethyl acrylate	1.60e-16	1.54e-16	-			
methyl-3-methyl-2-butenate	1.40e-14	1.36e-14	-			
ethyl methacrylate	4.79e-15	4.20e-15	-1.1			
(E)-2-methyl-2-butenic acid methyl ester	4.90e-14	8.22e-14	1.7			
isopropyl methacrylate	7.90e-15	4.84e-15	-1.6			
propyl methacrylate	5.23e-15	4.72e-15	-			
n-butyl acrylate	1.90e-16	2.56e-16	1.3			
2-methylpropenoic acid butyl ester	5.71e-15	5.18e-15	-			
i-butyl methacrylate	6.02e-15	5.26e-15	-1.1			
peroxymethacryloyl nitrate	1.60e-16	1.60e-16	-			
Furans						
3-methylfuran	1.26e-11	2.10e-11	1.7			
2-methylfuran	2.57e-11	2.10e-11	-1.2			
2,5-dimethylfuran	5.80e-11	3.82e-11	-1.5			
2,3-dimethylfuran	5.80e-11	5.13e-11	-1.1			
2,4-dimethylfuran	5.80e-11	3.82e-11	-1.5			
tetramethylfuran	1.18e-10	2.26e-10	1.9			
Monofunctional aromatic oxygenates						
benzaldehyde	4.00e-15	3.58e-15	-1.1			
o-tolualdehyde	9.80e-15	1.15e-14	1.2			
m-tolualdehyde	9.50e-15	7.64e-15	-1.2			
p-tolualdehyde	9.50e-15	1.02e-14	-			
methoxybenzene	1.50e-16	3.87e-16	2.6			
phenol	4.50e-12	5.81e-12	1.3			
p-cresol	1.10e-11	1.15e-11	-			
o-cresol	1.40e-11	1.44e-11	-			
m-cresol	1.00e-11	5.81e-12	-1.7			
2,5-dimethylphenol	3.07e-11	3.05e-11	-			
3,4-dimethylphenol	2.55e-11	1.15e-11	-2.2			
2,3-dimethylphenol	2.97e-11	2.91e-11	-			
2,4-dimethylphenol	3.12e-11	4.51e-11	1.4			
3,5-dimethylphenol	1.13e-11	5.81e-12	-1.9			
2,6-dimethylphenol	5.01e-11	4.58e-11	-			
Other aromatic oxygenates						
catechol	9.80e-11	6.42e-11	-1.5			
3-methylpyrocatechol	1.72e-10	1.89e-10	-			
4-methylpyrocatechol	1.47e-10	1.97e-10	1.3			

Table S23 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
3-methoxyphenol	1.15e-11	5.81e-12	-2.0			
4-methoxyphenol	1.37e-10	1.70e-10	1.2			
guaiacol	2.69e-11	2.34e-11	-1.1			
2-methoxy-4-methylphenol	8.40e-11	9.78e-11	1.2			
1,3-dimethoxybenzene	1.20e-14	5.90e-15	-2.0			
1,4-dimethoxybenzene	1.00e-14	1.08e-14	-			
2,6-dimethoxyphenol	1.58e-10	2.13e-10	1.3			
Other reduced nitrogen compounds						
N,N-dimethylformamide	4.80e-14	3.19e-14	-1.5	8.80e-12	3.35e-11	3.8
N,N-dimethylacetamide	4.20e-14	2.92e-14	-1.4	2.70e-11	3.66e-11	1.4
N,N-dimethylpropanamide	1.40e-14	2.93e-14	2.1	1.20e-10	3.66e-11	-3.3
O-methyl-N-methylcarbamate	8.50e-16	1.37e-15	1.6			
O-methyl-N-ethylcarbamate	1.80e-15	1.38e-15	-1.3			
O-ethyl-N-methylcarbamate	9.40e-16	1.40e-15	1.5			
O-ethyl-N-ethylcarbamate	2.60e-15	1.41e-15	-1.8			
Monohalo alkanes						
iodomethane	4.10e-13	3.14e-13	-1.3			
iodoethane	2.40e-13	3.14e-13	1.3			
Monohalo alkenes or alkynes						
fluoroethene	1.90e-16	1.90e-16	-			
chloroethene	3.90e-16	1.91e-16	-2.0			
3-fluoropropene	3.90e-15	3.90e-15	-			
3-chloro-1-propene	5.52e-16	9.15e-16	1.7			
3-bromo-1-propene	3.50e-15	3.31e-15	-			
3-chloro-2-methyl-1-propene	2.25e-14	3.31e-14	1.5			
1-chloro-2-methyl-1-propene	9.00e-14	1.96e-13	2.2			
2-chloro-2-butene	1.10e-13	1.96e-13	1.8			
2-chloro-1-butene	1.70e-14	9.96e-15	-1.7			
1-chloro-1-butene	1.20e-14	1.07e-14	-1.1			
3-chloro-1-butene	3.00e-15	1.19e-15	-2.5			
1-chloro-2-butene	2.00e-14	2.00e-14	-			
2-bromo-2-butene	1.30e-13	1.30e-13	-			
3-bromo-1-butene	4.00e-15	4.23e-15	-			
Used for evaluations only						
Cyclic alkanes						
cyclopentane	1.45e-16	1.14e-16	-1.3			
cyclohexane	1.35e-16	1.76e-16	1.3			
Allenes and other acyclic di- or polyalkenes						
1,4-pentadiene	2.30e-14	2.76e-14	1.2			
3-methylene-7-methyl-1,6-octadiene	1.10e-11	1.37e-11	1.2			
cis/trans-ocimene	2.20e-11	2.90e-11	1.3			
Cycloalkenes						
methylenecyclopropane	1.40e-14	3.31e-13	23.6			
cyclopentene	4.80e-13	4.25e-13	-1.1			
methylenecyclobutane	4.20e-13	3.95e-13	-			



Table S23 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
cyclohexene	5.60e-13	4.87e-13	-1.1			
methylenecyclopentane	1.50e-12	4.52e-13	-3.3			
cycloheptene	5.00e-13	5.43e-13	-			
1-methyl-1-cyclohexene	9.31e-12	9.94e-12	-			
methylenecyclohexane	6.00e-13	5.04e-13	-1.2			
cyclooctene	5.10e-13	5.94e-13	1.2			
1,2-dimethylcyclohexene	5.10e-12	6.95e-11	13.6			
ethylidene cyclohexane	4.30e-12	1.09e-11	2.5			
methylenecycloheptane	1.00e-12	5.51e-13	-1.8			
1,6-dimethylcyclohexene	1.50e-12	1.09e-11	7.2			
1,3-cyclohexadiene	1.15e-11	6.18e-12	-1.9			
1,4-cyclohexadiene	6.60e-13	9.74e-13	1.5			
bicyclo[2.2.1]-2,5-heptadiene	1.00e-12	1.09e-12	-			
1,3,5-cycloheptatriene	1.20e-12	1.38e-11	11.5			
1,3-cycloheptadiene	6.50e-12	6.89e-12	-			
bicyclo[2.2.1]-2-heptene	2.59e-13	5.44e-13	2.1			
3-methylenecyclohexene	5.70e-12	4.35e-12	-1.3			
bicyclo[2.2.2]-2-octene	1.45e-13	5.94e-13	4.1			
3a,4,7,7a-tetrahydro-1H-4,7-methanoindene	1.20e-12	1.36e-12	1.1			
a-phellandrene	7.30e-11	2.07e-11	-3.5			
sabinene	1.00e-11	6.32e-13	-15.8			
a-terpinene	1.80e-10	3.28e-11	-5.5			
b-phellandrene	8.34e-12	5.46e-12	-1.5			
b-pinene	2.50e-12	6.33e-13	-4.0			
terpinolene	9.70e-11	9.21e-11	-			
limonene	1.20e-11	1.31e-11	-			
g-terpinene	2.90e-11	2.49e-11	-1.2			
3-carene	9.00e-12	1.25e-11	1.4			
2-carene	2.00e-11	1.25e-11	-1.6			
camphene	6.60e-13	6.33e-13	-			
a-pinene	6.20e-12	1.25e-11	2.0			
beta-caryophyllene	1.90e-11	1.45e-11	-1.3			
α-cedrene	8.20e-12	1.38e-11	1.7			
longifolene	6.80e-13	7.00e-13	-			
isolongifolene	3.90e-12	1.38e-11	3.5			
alloisolongifolene	1.40e-12	6.99e-13	-2.0			
alpha-neoclovene	8.25e-12	1.38e-11	1.7			
Monofunctional acyclic alcohols, ethers, and hydroperoxides						
methanol	1.30e-16	1.30e-16	-			
Glycol, alcohol ether, or polyether						
1-methoxy-2-propanol	1.60e-15	3.79e-15	2.4			
2-n-butoxyethanol	3.10e-15	6.04e-15	1.9			
Other acyclic saturated oxygenates						
glyoxal	4.00e-16	4.00e-16	-			
methyl glyoxal	5.00e-16	4.99e-16	-			
oxopentanal	3.10e-15	1.66e-14	5.4			
4-hydroxy-3-methyl-2-butanone	1.60e-15	2.04e-15	1.3			

Table S23 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
isopropenyl-6-oxo-heptanal	2.60e-13	6.49e-13	2.5			
Cyclic saturated oxygenates						
cyclopropanecarbaldehyde	6.30e-15	2.54e-14	4.0			
tetrahydrofuran	5.10e-15	4.09e-15	-1.2			
cyclobutanecarbaldehyde	2.06e-14	2.55e-14	1.2			
cyclopentanecarbaldehyde	2.64e-14	2.57e-14	-			
cyclohexanecarbaldehyde	3.31e-14	2.58e-14	-1.3			
sabinaketone	3.70e-16	2.24e-16	-1.7			
1,8-cineole	1.70e-16	4.58e-15	26.9			
caronaldehyde	2.50e-14	1.67e-14	-1.5			
pinonaldehyde	2.00e-14	1.70e-14	-1.2			
Multifunctional oxygenates with 2+ non-HC groups on same carbon						
3-hydroxy-2-butanone	6.50e-16	2.13e-15	3.3			
4-hydroxy-3-hexanone	1.40e-15	2.19e-15	1.6			
Monofunctional acyclic unsaturated oxygenates						
isopropenyl acetate	2.23e-14	3.07e-13	13.8			
Other acyclic unsaturated oxygenates						
2-propen-1-ol	1.30e-14	1.09e-14	-1.2			
3-buten-2-ol	1.20e-14	1.37e-14	1.1			
2-buten-1-ol	3.90e-13	3.58e-13	-			
ethylene glycol monovinyl ether	2.00e-12	1.43e-12	-1.4			
2-methyl-3-buten-2-ol	1.20e-14	1.38e-14	1.1			
cis-2-penten-1-ol	1.56e-13	4.27e-13	2.7			
3-methyl-2-buten-1-ol	9.60e-13	7.78e-12	8.1			
1-penten-3-ol	1.40e-14	1.60e-14	1.1			
3-methyl-3-buten-1-ol	2.60e-13	3.96e-13	1.5			
(Z)-3-hexen-1-ol	2.70e-13	4.89e-13	1.8			
(Z)-2-hexen-1-ol	3.70e-13	4.89e-13	1.3			
3-hexen-1-ol (trans)	4.40e-13	4.89e-13	1.1			
trans-2-hexen-1-ol	1.30e-13	4.89e-13	3.8			
cis-4-hexen-1-ol	2.90e-13	4.89e-13	1.7			
ethylene glycol divinyl ether	2.08e-12	3.91e-12	1.9			
diethylene glycol divinyl ether	6.14e-12	4.77e-12	-1.3			
3,7-dimethyl-1,6-octadien-3-ol	1.10e-11	1.25e-11	1.1			
2,6-dimethyl-2,6-octadien-8-ol	1.60e-11	2.49e-11	1.6			
3,7-dimethyl-6-octen-1-ol	1.15e-11	1.25e-11	-			
2,6-dimethyl-7-octen-2-ol	2.50e-14	2.23e-14	-1.1			
farnesol	4.40e-11	4.13e-11	-			
(E)-2-butenedial	1.70e-15	2.16e-15	1.3			
3(e)-4-methylhex-3,5-dienal	1.75e-12	1.32e-11	7.5			
4-methylenehex-5-enal	4.80e-13	1.00e-12	2.1			
4-methylhex-3(z),5-dienal	2.18e-12	1.32e-11	6.1			
(Z)-4-heptenal	3.80e-13	5.60e-13	1.5			
3(e)-4-methylhex-3,5-dienal	1.80e-12	3.48e-11	19.3			
3(z)-4-methylhex-3,5-dienal	2.20e-12	3.48e-11	15.8			
5-hexen-2-one	2.15e-14	1.59e-14	-1.4			
6-methyl-5-hepten-2-one	7.50e-12	1.09e-11	1.4			
allyl acetate	1.10e-14	1.38e-14	1.3			

Table S23 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
2-methyl-2-propenyl acetate	2.04e-14	4.52e-13	22.2			
cis-3-hexenyl acetate	2.46e-13	5.94e-13	2.4			
5-methyl-5-vinyl-tetrahydrofuran-2-ol	1.70e-14	2.10e-14	1.2			
Furans						
furan	1.20e-12	7.35e-12	6.1			
Cyclic unsaturated non-aromatic oxidized nitrogen compounds						
vinylloxirane	6.15e-15	1.16e-14	1.9			
3h-furan-2-one	1.76e-13	3.17e-13	1.8			
5-methyl-2,3-dihydrofuran	1.68e-10	9.63e-10	5.7			
2-methyl-2-vinylloxirane	9.40e-15	1.39e-14	1.5			
3-furfural	3.41e-12	4.50e-12	1.3			
2-furfural	1.20e-12	4.93e-12	4.1			
3,4-epoxy-cyclohexene	2.70e-13	4.88e-13	1.8			
2-methyl-2-(1-methyl-vinyl)-oxirane	1.55e-13	4.52e-13	2.9			
5-methyl-2-furfural	5.51e-12	1.97e-11	3.6			
toluene oxide	1.27e-11	6.89e-12	-1.8			
4-methylcyclohex-3-en-1-one	1.80e-12	9.94e-12	5.5			
2,2-dimethyl-3-(2,2-dimethyl-vinyl)-oxirane	4.74e-12	1.09e-11	2.3			
4-acetyl-1-methylcyclohexene	1.05e-11	1.17e-11	1.1			
2-(4-methylcyclohex-3-en-1-yl)propan-2-ol	1.60e-11	1.25e-11	-1.3			
beta-ionone	9.40e-12	4.40e-11	4.7			
1-(1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-naphthalene)ethanone	1.70e-11	8.80e-11	5.2			
acetyl cedrene	4.20e-15	2.70e-13	64.3			
Monofunctional aromatic oxygenates						
coumaran	1.10e-13	2.99e-15	-36.8			
Other aromatic oxygenates						
benzyl alcohol	4.00e-15	1.89e-15	-2.1			
4-ethylguaiaicol	1.10e-12	9.78e-11	89			
eugenol	1.60e-13	9.78e-11	611			
Other reduced nitrogen compounds						
1-methyl-2-pyrrolidone	1.50e-13	2.93e-14	-5.1	6.10e-11	3.65e-11	-1.7
Monohalo alkenes or alkynes						
4-chloro-1-butene	4.48e-15	1.16e-14	2.6			
4-bromo-1-butene	5.00e-15	1.16e-14	2.3			

[a] Rate constants and A factors in units of  $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . "Error" shows (estimated - experimental) / experimental (in parentheses) if the agreement is within  $\pm 10\%$ , otherwise it shows estimated / experimental if an overestimate or -experimental/estimated if an underestimate.

[b] From McGillen et al (2020).

Table S24. Experimental and estimated rate constants for the reactions of organics with ozone.

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
Used for parameter derivations						
Acyclic monoalkenes						
propene	1.05e-17	9.67e-18	-	5.77e-15	3.55e-15	-1.6
1-butene	1.00e-17	9.67e-18	-	3.55e-15	3.55e-15	-
2-methylpropene	1.15e-17	1.45e-17	1.3	2.92e-15	5.08e-15	1.7
1-pentene	1.06e-17	9.67e-18	-	2.13e-15	3.55e-15	1.7
2-methyl-1-butene	1.37e-17	1.45e-17	-	6.18e-15	5.08e-15	-1.2
3-methyl-1-butene	7.30e-18	7.08e-18	-			
1-hexene	1.15e-17	9.67e-18	-1.2	2.30e-15	3.55e-15	1.5
2-methyl-1-pentene	1.60e-17	1.45e-17	-			
3,3-dimethyl-1-butene	3.80e-18	4.49e-18	1.2			
2-ethyl-1-butene	1.30e-17	1.06e-17	-1.2			
3-methyl-1-pentene	3.80e-18	7.08e-18	1.9			
4-methyl-1-pentene	8.51e-18	9.67e-18	1.1	4.72e-15	3.55e-15	-1.3
2,3-dimethyl-1-butene	1.00e-17	1.06e-17	-			
1-heptene	1.16e-17	9.67e-18	-1.2	4.20e-15	3.55e-15	-1.2
2,3-dimethyl-1-pentene	5.12e-18	1.06e-17	2.1			
2,3,3-trimethyl-1-butene	7.80e-18	6.74e-18	-1.2			
2-methyl-1-heptene	1.35e-17	1.45e-17	-			
1-octene	1.01e-17	9.67e-18	-			
2,4,4-trimethyl-1-pentene	1.49e-17	1.45e-17	-	7.25e-15	5.08e-15	-1.4
2,4-dimethyl-3-methylenepentane	3.00e-18	2.84e-18	-			
1-nonene	9.90e-18	9.67e-18	-			
2-methyl-1-octene	1.38e-17	1.45e-17	-			
1-decene	1.11e-17	9.67e-18	-1.1			
1-undecene	1.03e-17	9.67e-18	-			
2-methyl-1-decene	1.48e-17	1.45e-17	-			
1-dodecene	1.03e-17	9.67e-18	-			
2-methyl-1-undecene	1.46e-17	1.45e-17	-			
1-tridecene	9.60e-18	9.67e-18	-			
2-methyl-1-tridecene	2.85e-17	1.45e-17	-2.0			
1-tetradecene	9.70e-18	9.67e-18	-			
trans-2-butene	2.00e-16	1.84e-16	-	7.00e-15	7.23e-15	-
cis-2-butene	1.30e-16	1.37e-16	-	3.37e-15	3.42e-15	-
trans-2-pentene	1.59e-16	1.84e-16	1.2	7.10e-15	7.23e-15	-
cis-2-pentene	1.28e-16	1.37e-16	-	3.70e-15	3.42e-15	-
2-methyl-2-butene	4.03e-16	4.20e-16	-	6.51e-15	6.51e-15	-
2,3-dimethyl-2-butene	1.10e-15	7.46e-16	-1.5	3.00e-15	3.00e-15	-
2-methyl-2-pentene	4.54e-16	4.20e-16	-			
(Z)-3-hexene	1.44e-16	1.00e-16	-1.4			
trans-2-hexene	1.53e-16	1.84e-16	1.2	7.60e-15	7.23e-15	-
(Z)-3-methyl-2-pentene	4.50e-16	4.20e-16	-			
(E)-3-methyl-2-pentene	5.60e-16	4.20e-16	-1.3			
(E)-3-hexene	1.57e-16	1.35e-16	-1.2			
(Z)-2-hexene	1.05e-16	1.37e-16	1.3	3.20e-15	3.42e-15	-
trans-4-octene	1.31e-16	1.35e-16	-			
2,4,4-trimethyl-2-pentene	1.32e-16	1.95e-16	1.5			
(Z/E)-3,4-dimethyl-3-hexene	3.70e-16	5.46e-16	1.5			

Table S24 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
(Z)-4-octene	9.00e-17	1.00e-16	1.1			
(E)-2,2-dimethylhex-3-ene	4.00e-17	3.60e-17	-1.1			
(E)-2,5-dimethylhex-3-ene	3.80e-17	3.60e-17	-			
(Z)-5-decene	1.14e-16	1.00e-16	-1.1			
(E)-5-decene	1.30e-16	1.35e-16	-			
Acyclic conjugated dialkenes						
(3E)-penta-1,3-diene	4.31e-17	3.15e-17	-1.4	2.10e-15	2.10e-15	-
2-methyl-1,3-butadiene	1.28e-17	1.28e-17	-	1.05e-14	9.90e-15	-
cis-1,3-pentadiene	2.80e-17	3.15e-17	1.1			
(Z/E)-1,3-pentadiene	4.30e-17	3.15e-17	-1.4			
2-methyl-1,3-pentadiene	8.00e-17	8.00e-17	-			
2,3-dimethyl-1,3-butadiene	2.56e-17	2.56e-17	-	6.90e-15	9.90e-15	1.4
(2E,4E)-2,4-hexadiene	3.74e-16	3.43e-16	-			
(2Z,4E)-hexa-2,4-diene	3.14e-16	3.43e-16	-			
5-methylhexa-1,3-diene	2.40e-17	3.15e-17	1.3			
2,5-dimethyl-2,4-hexadiene	3.06e-15	3.06e-15	-			
(Z/E)-5,5-dimethylhexa-1,3-diene	2.50e-17	3.15e-17	1.3			
Cycloalkenes						
cyclopentene	5.60e-16	4.01e-16	-1.4			
cyclohexene	8.10e-17	6.73e-17	-1.2			
1-methylcyclopentene	6.70e-16	1.23e-15	1.8			
3-methylcyclopentene	3.34e-16	2.54e-16	-1.3			
cycloheptene	2.50e-16	2.75e-16	1.1			
1-methyl-1-cyclohexene	1.46e-16	2.07e-16	1.4			
4-methylcyclohexene	7.31e-17	6.73e-17	-			
3-methylcyclohexene	6.87e-17	4.26e-17	-1.6			
cyclooctene	4.07e-16	3.45e-16	-1.2			
1,2-dimethylcyclohexene	2.07e-16	3.67e-16	1.8			
1-methylcycloheptene	9.30e-16	8.45e-16	-			
1-methyl-1-cyclooctene	1.42e-15	1.06e-15	-1.3			
3-methyl-1-cyclooctene	1.39e-16	2.19e-16	1.6			
1,3-cyclohexadiene	1.20e-15	2.05e-15	1.7			
1,3-cycloheptadiene	1.50e-16	1.50e-16	-			
$\alpha$ -phellandrene	2.90e-15	1.76e-15	-1.6			
$\alpha$ -terpinene	1.90e-14	1.83e-14	-			
$\alpha$ -pinene	9.60e-17	8.80e-17	-			
Alkynes						
acetylene	1.00e-20	1.00e-20	-			
methyl acetylene	1.43e-20	1.68e-20	1.2			
1-butyne	1.97e-20	1.68e-20	-1.2			
Styrenes or aromatics with double bonds or non-aromatic rings						
styrene	1.60e-17	1.81e-17	1.1			
$\alpha$ -methylstyrene	1.80e-17	2.72e-17	1.5			
2-methylstyrene	3.10e-17	1.81e-17	-1.7			
Other acyclic saturated oxygenates						
cis/trans-4-oxo-2-pentenal	4.80e-18	3.27e-18	-1.5			
4-methoxy-3-buten-2-one	1.30e-17	1.30e-17	-			

Table S24 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
Monofunctional acyclic unsaturated oxygenates						
ethyl vinyl ether	1.78e-16	2.76e-16	1.6			
2-methoxy-1-propene	1.20e-17	1.52e-17	1.3			
n-propyl vinyl ether	2.30e-16	2.76e-16	1.2			
2-ethoxypropene	1.92e-17	1.52e-17	-1.3			
tert-butyl vinyl ether	5.30e-16	2.76e-16	-1.9			
isobutyl vinyl ether	2.85e-16	2.76e-16	-			
n-butyl vinyl ether	2.60e-16	2.76e-16	-			
2-propenal	2.80e-19	2.80e-19	-			
crotonaldehyde	1.58e-18	1.86e-18	1.2			
2-methyl-2-propenal	1.20e-18	1.20e-18	-			
3-methyl-2-butenal	1.82e-18	1.82e-18	-			
e-2-pentenal	1.42e-18	1.86e-18	1.3			
(E)-2-methyl-2-butenal	5.34e-18	3.91e-18	-1.4			
2-hexenal (trans)	1.55e-18	1.86e-18	1.2			
(Z)-2-methyl-2-pentenal	7.10e-18	3.91e-18	-1.8			
(E)-2-methyl-2-pentenal	1.58e-18	3.91e-18	2.5			
trans-2-heptenal	2.47e-18	1.86e-18	-1.3			
(E)-2-octenal	2.37e-18	1.86e-18	-1.3			
(E)-2-nonenal	2.05e-18	1.86e-18	-			
3-buten-2-one	5.20e-18	5.40e-18	-			
3-penten-2-one	2.95e-17	4.18e-17	1.4			
3-methyl-3-buten-2-one	1.18e-17	1.19e-17	-			
1-penten-3-one	6.00e-18	5.40e-18	-1.1			
4-hexen-3-one	6.05e-17	4.18e-17	-1.4			
4-methyl-3-penten-2-one	8.10e-18	8.29e-18	-			
3-methyl-3-penten-2-one	4.07e-17	4.31e-17	-			
vinyl acetate	2.75e-18	3.82e-18	1.4			
methyl acrylate	1.08e-18	1.13e-18	-			
vinyl propionate	5.30e-18	3.82e-18	-1.4			
isopropenyl acetate	7.00e-19	7.00e-19	-			
methyl methacrylate	6.23e-18	8.97e-18	1.4			
ethyl acrylate	1.30e-18	1.13e-18	-1.2			
ethyl crotonate	8.00e-18	7.88e-18	-			
isopropyl methacrylate	1.12e-17	8.97e-18	-1.2			
propyl methacrylate	8.46e-18	8.97e-18	-			
ethyl 3,3-dimethyl acrylate	8.20e-18	8.78e-18	-			
2-methylpropenoic acid butyl ester	1.00e-17	8.97e-18	-1.1			
i-butyl methacrylate	1.03e-17	8.97e-18	-1.1			
acrylic acid	7.05e-19	7.05e-19	-			
methacrylic acid	3.00e-18	2.99e-18	-			
2-pentenoic acid	3.10e-18	2.07e-18	-1.5			
peroxymethacryloyl nitrate	8.20e-18	8.97e-18	-			
Other acyclic unsaturated oxygenates						
2-propen-1-ol	1.60e-17	1.21e-17	-1.3			
3-buten-2-ol	1.60e-17	1.21e-17	-1.3			
2-buten-1-ol	2.50e-16	1.98e-16	-1.3			
2-methyl-3-buten-2-ol	1.00e-17	8.83e-18	-1.1			
cis-2-penten-1-ol	1.35e-16	1.71e-16	1.3			

Table S24 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
1-penten-3-ol	1.69e-17	1.21e-17	-1.4			
allyl ethyl ether	8.69e-18	3.25e-18	-2.7			
3-methyl-1-penten-3-ol	5.20e-18	8.83e-18	1.7			
(Z)-2-hexen-1-ol	7.44e-17	1.71e-16	2.3			
trans-2-hexen-1-ol	6.54e-17	2.30e-16	3.5			
1-octen-3-ol	1.91e-17	1.21e-17	-1.6			
1-nonen-3-ol	1.89e-17	1.21e-17	-1.6			
2,6-dimethyl-2,6-octadien-8-ol	9.30e-16	9.45e-16	-			
farnesol	2.10e-15	1.25e-15	-1.7			
2-butene-1,4-dial	1.60e-18	3.27e-18	2.0			
(Z)-3-hexenal	3.50e-17	4.71e-17	1.3			
3(e)-4-methylhex-3,5-dienal	5.70e-17	3.72e-17	-1.5			
4-methylhex-3(z),5-dienal	4.40e-17	3.72e-17	-1.2			
cis-3-hexene-2,5-dione	1.80e-18	3.27e-18	1.8			
trans-3-hexene-2,5-dione	8.30e-18	3.27e-18	-2.5			
allyl acetate	2.15e-18	3.25e-18	1.5			
2-methyl-2-propenyl acetate	2.76e-18	4.88e-18	1.8			
Furans						
furan	2.40e-18	2.40e-18	-			
3-methylfuran	2.00e-17	2.00e-17	-			
2,5-dimethylfuran	4.20e-16	4.20e-16	-			
Unsaturated acyclic oxidized nitrogen compounds						
1-nitrocyclohexene	1.40e-18	1.40e-18	-			
2-methyl-4-nitrooxy-but-2-en-1-ol (cis)	2.90e-17	2.21e-17	-1.3			
2-methyl-4-nitrooxy-but-2-en-1-ol (trans)	2.70e-17	2.21e-17	-1.2			
3-methyl-2-nitrooxybut-3-ene-1-ol	3.80e-19	6.12e-19	1.6			
Cyclic unsaturated non-aromatic oxidized nitrogen compounds						
4-methylcyclohex-3-en-1-one	7.40e-17	7.40e-17	-			
beta-ionone	2.20e-17	2.20e-17	-			
Alkyl amines						
Methylamine	7.40e-21	7.40e-21	-			
Dimethyl Amine	1.67e-18	1.67e-18	-			
Trimethyl Amine	7.84e-18	7.84e-18	-			
Monohalo alkenes or alkynes						
fluoroethene	7.31e-19	7.31e-19	-			
chloroethene	2.45e-19	1.34e-19	-1.8			
3-chloro-1-propene	1.79e-18	1.91e-18	-			
2-chloro-1-propene	1.11e-19	2.02e-19	1.8			
4-chloro-1-butene	3.96e-18	9.67e-18	2.4			
3-chloro-2-methyl-1-propene	3.37e-18	2.87e-18	-1.2			
3-chloro-1-butene	2.30e-18	1.91e-18	-1.2			
1-chloro-2-butene	2.30e-17	3.14e-17	1.4			
Used for evaluations only						
Acyclic monoalkenes						
3,4-diethyl-2-hexene	4.00e-18	1.95e-16	48.7			

Table S24 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
Allenes and other acyclic di- or polyalkenes						
1,4-pentadiene	1.45e-17	1.93e-17	1.3			
1,5-hexadiene	1.45e-17	1.93e-17	1.3			
2-methyl-1,4-pentadiene	1.32e-17	2.42e-17	1.8			
2-methyl-1,5-hexadiene	2.07e-17	2.42e-17	1.2			
2,5-dimethyl-1,5-hexadiene	1.42e-17	2.91e-17	2.0			
3-methylene-7-methyl-1,6-octadiene	4.70e-16	4.33e-16	-			
cis/trans-ocimene	5.10e-16	4.84e-16	-			
3,7-dimethyl-1,6-octadiene	6.80e-16	4.27e-16	-1.6			
beta-farnesene	5.60e-16	7.41e-16	1.3			
alpha-farnesene	5.90e-16	9.04e-16	1.5			
Cycloalkenes						
methylenecyclopropane	2.80e-18	1.06e-17	3.8			
methylenecyclobutane	1.90e-17	1.06e-17	-1.8			
methylenecyclopentane	9.00e-17	1.06e-17	-8.5			
methylenecyclohexane	2.80e-17	1.06e-17	-2.6			
ethylidene cyclohexane	2.23e-16	3.08e-16	1.4			
cyclodecene	2.90e-17	1.00e-16	3.5			
1,4-cyclohexadiene	4.60e-17	1.84e-16	4.0			
bicyclo[2.2.1]-2,5-heptadiene	3.60e-15	5.38e-16	-6.7			
bicyclo[2.2.1]-2-heptene	1.23e-15	7.19e-17	-17.1			
bicyclo[2.2.2]-2-octene	7.10e-17	1.21e-17	-5.9			
1,5-cyclooctadiene	1.48e-16	6.91e-16	4.7			
4-vinylcyclohexene	2.70e-16	7.44e-17	-3.6			
(Z,Z)-1,3-cyclooctadiene	2.00e-17	3.43e-16	17.1			
3a,4,7,7a-tetrahydro-1H-4,7-methanoindene	1.46e-15	9.47e-16	-1.5			
sabinene	8.30e-17	6.74e-18	-12.3			
b-phellandrene	5.20e-17	5.37e-17	-			
b-pinene	1.90e-17	6.74e-18	-2.8			
terpinolene	1.60e-15	1.03e-15	-1.6			
limonene	2.20e-16	2.17e-16	-			
g-terpinene	1.60e-16	4.89e-16	3.1			
3-carene	4.80e-17	5.68e-16	11.8			
2-carene	2.40e-16	3.60e-16	1.5			
camphene	5.00e-19	2.84e-18	5.7			
1-tert-butyl-4-(propan-2-ylidene)cyclohex-1-ene	1.50e-15	8.01e-16	-1.9			
beta-caryophyllene	1.20e-14	3.14e-16	-38.2			
α-humulene	1.20e-14	7.91e-16	-15.2			
a-copaene	1.50e-16	8.80e-17	-1.7			
α-cedrene	2.80e-17	3.60e-16	12.8			
isolongifolene	1.00e-17	5.52e-17	5.5			
valencene	3.50e-17	6.59e-17	1.9			
Styrenes or aromatics with double bonds or non-aromatic rings						
indene	1.65e-16	1.03e-15	6.2			
acenaphthylene	3.99e-16	1.92e-15	4.8			



Table S24 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
Other acyclic saturated oxygenates						
(E)-4-hydroperoxy-2-hexenal	1.20e-18	1.86e-18	1.6			
3,4-dihydroxy-3-hexene-2,5-dione	3.60e-18	3.27e-18	-			
isopropenyl-6-oxo-heptanal	7.80e-18	1.06e-17	1.4			
Monofunctional acyclic unsaturated oxygenates						
ethyl methacrylate	7.70e-17	8.97e-18	-8.6			
n-butyl acrylate	2.40e-17	1.13e-18	-21.3			
Other acyclic unsaturated oxygenates						
3-buten-1-ol	5.55e-18	9.67e-18	1.7			
ethylene glycol monovinyl ether	2.00e-16	2.76e-16	1.4			
1,1-dimethoxyethene	4.80e-16	4.74e-18	-101			
3-methyl-3-buten-1-ol	6.80e-18	1.45e-17	2.1			
2-methyl-3-buten-1-ol	3.74e-18	7.08e-18	1.9			
4-penten-2-ol	4.88e-18	9.67e-18	2.0			
4-penten-1-ol	7.68e-18	9.67e-18	1.3			
(Z)-3-hexen-1-ol	7.21e-17	1.00e-16	1.4			
3-hexen-1-ol (trans)	5.85e-17	1.35e-16	2.3			
cis-4-hexen-1-ol	1.66e-16	1.37e-16	-1.2			
(E)-4-hexen-1-ol	1.05e-16	1.84e-16	1.8			
ethylene glycol divinyl ether	3.55e-16	5.52e-16	1.6			
6-methyl-5-hepten-2-ol	3.80e-16	4.20e-16	1.1			
diethylene glycol divinyl ether	2.70e-16	5.52e-16	2.0			
1-nonen-4-ol	8.30e-18	9.67e-18	1.2			
3,7-dimethyl-1,6-octadien-3-ol	4.24e-16	4.29e-16	-			
3,7-dimethyl-6-octen-1-ol	2.40e-16	4.20e-16	1.8			
4-methylenehex-5-enal	1.50e-17	1.28e-17	-1.2			
3,7-dimethyl-6-octen-1-al	3.50e-16	4.20e-16	1.2			
5-hexen-2-one	7.20e-17	9.67e-18	-7.4			
6-methyl-5-hepten-2-one	3.93e-16	4.20e-16	-			
(Z)-3-hexenylformate	4.06e-17	1.16e-16	2.9			
cis-3-hexenyl acetate	5.84e-17	1.00e-16	1.7			
(Z)-3-hexenylpropanoate	7.62e-17	1.00e-16	1.3			
(Z)-3-hexenylbutanoate	1.23e-16	1.00e-16	-1.2			
5-methyl-5-vinyl-tetrahydrofuran-2-ol	3.61e-18	2.38e-18	-1.5			
Unsaturated acyclic oxidized nitrogen compounds						
2-methyl-1-nitrooxy-but-3-en-2-ol	1.06e-16	8.83e-18	-12.0			
2-methyl-4-nitrooxy-2-buten-1-al	4.40e-18	3.91e-18	-1.1			
(trans)						
Cyclic unsaturated non-aromatic oxidized nitrogen compounds						
2,5-dihydrofuran	1.63e-17	6.18e-17	3.8			
2,3-dihydrofuran	4.43e-15	2.97e-16	-14.9			
vinylloxirane	1.60e-18	3.25e-18	2.0			
gamma-crotonolactone	6.73e-20	3.15e-17	468			
5-methyl-2,3-dihydrofuran	3.50e-15	1.07e-15	-3.3			
3,4-dihydropyran	3.14e-16	4.99e-17	-6.3			
2-methyl-2-vinylloxirane	2.63e-18	2.38e-18	-			
4-methyl-2H-furan-5-one	5.42e-19	1.00e-16	185			
2-cyclohexen-1-one	1.20e-18	2.81e-17	23.4			

Table S24 (continued)

Type and Name	k(298) [a]			A Factor [a]		
	Expt. [b]	Est'd	Error	Expt [b]	Est'd	Error
4-acetyl-1-methylcyclohexene	1.50e-16	2.07e-16	1.4			
2-(4-methylcyclohex-3-en-1-yl)propan-2-ol	3.00e-16	2.07e-16	-1.5			
1-(1,2,3,4,5,6,7,8,-octahydro-2,3,8,8-tetramethyl-2-naphthalene)ethanone	2.31e-18	6.58e-17	28.5			
acetylcedrene	2.20e-18	8.07e-17	36.7			
Other aromatic oxygenates						
methyl chavicol	1.03e-17	9.67e-18	-			
Other reduced nitrogen compounds						
N,N-dimethylethanolamine	6.80e-18	7.84e-18	1.2			
Monohalo alkenes or alkynes						
3-bromo-1-propene	1.90e-18	9.67e-18	5.1			
1-chloro-3-methyl-2-butene	4.40e-17	8.30e-17	1.9			
1-chlorocyclopentene	1.53e-17	1.71e-17	1.1			

[a] Rate constants and A factors in units of  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ . "Error" shows (estimated - experimental) / experimental (in parentheses) if the agreement is within  $\pm 10\%$ , otherwise it shows estimated / experimental if an overestimate or -experimental/estimated if an underestimate.

[b] From McGillen et al (2020).

Table S25. Experimental and estimated rate constants for the reactions of organics with O<sup>3</sup>P.

Type and Name	Ref [b]	k(298) [a]			A Factor [a]		
		Expt.	Est'd	Error	Expt	Est'd	Error
Used for parameter derivations							
Acyclic monoalkenes							
propene	1	3.99e-12	4.44e-12	1.1	1.02e-11	1.02e-11	-
1-butene	1	4.14e-12	4.44e-12	-			
2-methylpropene	1	1.69e-11	1.74e-11	-	1.14e-11	1.14e-11	-
1-pentene	1	4.65e-12	4.44e-12	-			
2-methyl-1-butene	1	1.80e-11	1.74e-11	-			
3-methyl-1-butene	1	4.16e-12	4.44e-12	-			
1-hexene	1	4.99e-12	4.44e-12	-1.1			
3,3-dimethyl-1-butene	1	4.80e-12	4.44e-12	-			
trans-2-butene	1	1.99e-11	1.88e-11	-	1.09e-11	1.09e-11	-
cis-2-butene	1	1.76e-11	1.88e-11	-			
trans-2-pentene	1	2.10e-11	1.88e-11	-1.1			
cis-2-pentene	1	1.71e-11	1.88e-11	1.1			
2-methyl-2-butene	1	5.11e-11	5.11e-11	-	2.44e-11	2.44e-11	-
2,3-dimethyl-2-butene	1	7.69e-11	7.69e-11	-	2.81e-11	2.81e-11	-
Acyclic conjugated dialkenes							
1,3-butadiene	1	1.98e-11	1.98e-11	-	2.26e-11	2.26e-11	-
2-methyl-1,3-butadiene	1	3.50e-11	3.50e-11	-			
Allenenes and other acyclic di- or polyalkenes							
propadiene	1	1.20e-12	1.20e-12	-	2.72e-11	2.72e-11	-
1,2-butadiene	1	5.80e-12	6.55e-12	1.1			
1,2-pentadiene	1	7.40e-12	6.55e-12	-1.1			
3-methyl-1,2-butadiene	1	3.00e-11	3.00e-11	-			
2,3-pentadiene	1	1.60e-11	1.60e-11	-			
Cycloalkenes							
cyclopentene	1	2.10e-11	2.05e-11	-			
cyclohexene	1	2.00e-11	2.05e-11	-	2.21e-11	2.21e-11	-
1-methyl-1-cyclohexene	2	9.00e-11	5.11e-11	-1.8			
b-pinene	1	2.70e-11	1.74e-11	-1.5			
terpinolene	1	1.02e-10	1.28e-10	1.3			
limonene	1	7.20e-11	6.85e-11	-			
g-terpinene	1	8.60e-11	1.02e-10	1.2			
3-carene	1	3.20e-11	5.11e-11	1.6			
2-carene	1	3.40e-11	5.11e-11	1.5			
camphene	1	2.50e-11	1.74e-11	-1.4			
a-pinene	1	3.20e-11	5.11e-11	1.6			
Alkynes							
acetylene	3	1.40e-13	1.40e-13	-			
methyl acetylene	4	8.97e-13	8.97e-13	-	2.66e-11	2.66e-11	-
2-butyne	5	8.60e-12	8.60e-12	-			
Monofunctional acyclic unsaturated oxygenates							
2-propenal	6	4.00e-13	4.00e-13	-	2.32e-11	2.32e-11	-

Table S25 (continued)

Type and Name	Ref [b]	k(298) [a]			A Factor [a]		
		Expt.	Est'd	Error	Expt	Est'd	Error
Alkyl amines							
Methylamine	7	5.56e-13	8.54e-13	1.5	9.02e-12	9.02e-12	-
Ethyl Amine	7	1.31e-12	8.54e-13	-1.5			
Dimethyl Amine	7	6.00e-12	6.00e-12	-	1.52e-11	1.52e-11	-
Trimethyl Amine	7	2.18e-11	2.18e-11	-	1.08e-11	1.08e-11	-

[a] Rate constants and A factors in units of  $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . "Error" shows (estimated - experimental) / experimental (in parentheses) if the agreement is within  $\pm 10\%$ , otherwise it shows estimated / experimental if an overestimate or -experimental/estimated if an underestimate.

[b] Sources of experimental data are as follows:

- 1 Calvert et al. 2000
- 2 Atkinson 1997
- 3 JPL 1997
- 4 Herbrechtsmeier 1973
- 5 Deslauriers and Collin 1986
- 6 Calvert et al. 2011
- 7 Atkinson and Pitts 1978a

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