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Sulfonic Resins as Catalysts for the Oxidation of Alcohols with H$_2$O$_2$/KBr

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Abstract: Sulfonic resins can replace homogeneous sulfonic acids in the oxidation of alcohols with the H$_2$O$_2$/KBr system. The performance of different resins was tested with methyl 9(10)-hydroxystearate, a secondary fatty alcohol. The structural features of the resin were more important than the acid strength for the catalytic performance of this reaction. The optimization of the reaction conditions allows the recovery of the resin, although regeneration is required due to the active role of KBr, and a significant loss of sulfonic groups can be detected after nine runs. In the case of primary fatty alcohols, the oxidation leads to carboxylic acids, which are esterified with the starting alcohol under the acidic conditions. For cyclic secondary alcohols, the steric hindrance around the hydroxyl group seems to be important for the efficiency of the oxidation to ketone.

Keywords: alcohol oxidation; sulfonic resins; swelling

1. Introduction

Fatty acids are among the most useful renewable materials as they are able to produce many types of useful compounds, such as surfactants, lubricants or polymers [1–3]. Hence, the development of new sustainable methods for their transformation, or the adaptation of existing ones to the particularities of fatty acid derivatives, is an important objective in sustainable chemistry [4,5]. Our group has been working on methods that include heterogeneous catalysts for the transformation of fatty esters, starting from unsaturated ones, through a first epoxidation step and the further conversion of the epoxide via rearrangement [6], hydrogenolysis [7], hydrolysis [8] or oxidative cleavage [9].

The oxidation of alcohols to carbonyls is one of the most useful reactions for the transformation of functional groups [10]. Some oxidation methods include the combination of organic molecules, such as in the Swern oxidation method (oxalyl chloride and triethylamine in dimethyl sulfoxide) or the Corey–Kim oxidation method (N-chlorosuccinimide/Me$_2$S/NEt$_3$), or the use of hypervalent iodine compounds, as in the Dess–Martin oxidation method. In other cases, the oxidant systems are based on metals, such as chromium trioxide (Jones oxidation), aluminum alkoxide (Oppenauer oxidation), pyridinium chlorochromate, barium permanganate, manganese dioxide, ruthenium tetroxide or silver carbonate. However, the oxidation of hydroxyfatty esters has been very seldom described in the literature. The use of CrO$_3$ as an oxidant [11,12], or the Swern oxidation [13], are examples of non-sustainable oxidation methods applied to the synthesis of ketofatty esters.

Different catalytic systems have been developed for use with benign oxidants, mostly using transition metal complexes [14]. Molecular oxygen has been used as a primary oxidant with Pd [15,16], V [17,18] and Ru [19] complexes. Hydrogen peroxide and alkyl hydroperoxides have been used with Fe and Cr complexes [20,21]. However, metal catalysts have a certain environmental impact and some disadvantages. Therefore, transition-metal-free methods are being developed; this includes, for example, using nitrosyl radicals as catalysts [22]. The Anelli–Montanari method includes the use of sodium hypochlorite as an oxidant and sodium bromide as a catalyst [23]. Moriyama et al. have described two

closely related oxidation methods [24], in which potassium bromide is the catalyst and the oxidants are the stabilized monopersulfate Oxone® or hydrogen peroxide, in this case using a sulfonic acid as an additional catalyst. The first method was successfully applied to the oxidative cleavage of fatty diols [9]. In this paper, we describe the application of the H_2O_2/KBr/sulfonic acid method for the oxidation of secondary hydroxyfatty esters, the heterogenization of the procedure via the substitution of the sulfonic acid with a solid using sulfonic groups and its application to the oxidation of other alcohols.

2. Results and Discussion

The substrate for this study was a mixture of methyl 9-hydroxy- and 10-hydroxy-stearate (**1a** + **1b**, represented as methyl 9(10)-hydroxystearate), obtained from the hydrogenolysis of methyl 9,10-epoxystearate as previously described [7]. First of all, the homogeneous method was tested using two sulfonic acids of different strengths, namely *p*-toluenesulfonic acid (*p*-TosOH, $pK_a \approx -2.8$ [25]) and triflic (trifluoromethanesulfonic) acid (TfOH, $pK_a = -5.9$ [25]), under conditions analogous to those described in the literature [24]: room temperature, 24 h, CH_2Cl_2/H_2O (9:1) as solvent, 1.5 eq 60% H_2O_2, 20 mol% KBr, and 20 mol% (*p*-TosOH) or 10 mol% (TfOH) of acid. The results of the two reactions were very similar (conversion = 97–98%, Table 1 entries 8–9), with methyl 9(10)-oxostearate (**2a** + **2b**) being the only product detected (Scheme 1).

Table 1. Oxidation of methyl 9(10)-hydroxystearate (**1a** + **1b**) with KBr/H_2O_2/sulfonic solid [1].

Entry	Sulfonic Solid	mol%	mg	t (h)	Conversion (%) [2]
1	Aquivion PW79S	20	39.4	24	66
				48	81
2	Nafion NR50	20	112.4	24	56
				48	72
3	Aquivion P98	20	102.0	6	54
				24	90
4	Amberlyst 15	20	21.7	6	52
				24	>99
5	Dowex 50W×8	20	22.2	6	75
				24	>99
6	Dowex 50W×2	20	22.2	24	96
7	Dowex 50W×2	10	11.1	24	49
				48	53
8	Triflic acid	10	7.5	24	97
9	*p*-Toluenesulfonic acid	20	17.2	24	98
10	Dowex 50W×8 [3]	20	22.2	24	26
				48	44
11	Dowex 50W×8 [4]	20	22.2	48	16

[1] Reaction conditions: 0.5 mmol of methyl 9(10)-hydroxystearate (**1a** + **1b**), 0.1 mmol of KBr, 0.75 mmol of 60% H_2O_2, 1 mL of CH_2Cl_2/H_2O (9:1 *v/v*), rt. [2] Determined by gas chromatography. [3] With TBAB instead of KBr in 1 mL of CH_2Cl_2 as solvent. [4] With TBAB instead of KBr in 1 mL of CH_2Cl_2/H_2O (9:1 *v/v*).
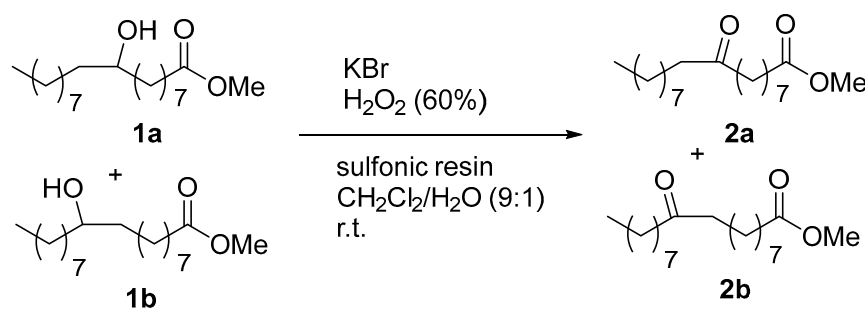

Scheme 1. Oxidation of methyl 9(10)-hydroxystearate (**1a** + **1b**).

In view of these results, this procedure could possibly be improved via the substitution of the homogeneous sulfonic acid with a sulfonic resin, acting as a recoverable heterogeneous acid. Three perfluoroalkylsulfonic resins were used: Aquivion PW79S, Aquivion P98 and Nafion NR50. Although the chemical nature of these three resins is similar, Nafion possesses longer side perfluorinated chains [26]. Aquivion PW97S is commercialized in powder form, and we observed some recovery problems due to the formation of slurries that were difficult to filter [8]. These problems were previously solved by using Aquivion P98, which is commercialized in the form of pellets with -SO$_2$F groups and must be activated by treatment with KOH/DMSO and then H$_2$SO$_4$ [8]; this was adapted from the method involving the hydrolysis of the Nafion precursor [27]. In the same way, three poly(styrene-divinylbenzene)sulfonic resins were tested: the macroreticular Amberlyst-15 (with 20% DVB crosslinker), and the gel-type Dowex 50W×8 and 50W×2, with an 8 and 2% DBV crosslinker. The functionalization with sulfonic groups was determined by titration, and in general, the results were in good agreement with the data provided by the suppliers (see Section 3). Thus, the weight of catalyst added to each oxidation reaction was calculated using this functionalization to obtain 20 mol% (0.1 mmol of sulfonic groups in the reaction scale of 0.5 mmol of substrate, unless otherwise is indicated in the tables). The oxidation results are shown in Table 1.

While the reaction was not complete after 48 h with Aquivion PW79S (81% conversion, entry 1) and Nafion NR50 (72%, entry 2), Aquivion P98 led to 90% conversion after only 24 h (entry 3), showing the importance of the structural and textural properties of the perfluoroalkylsulfonic resin. Despite their weaker acidity, the results were similar or slightly better than those obtained for arylsulfonic resins, with total or nearly total (96%) conversion after 24 h, and a faster reaction in the case of Dowex 50W×8 (entry 5). In fact, homogeneous oxidation has been also described using the much weaker acetic acid as both acid and solvent [28], showing that the acid strength is not an important parameter in this case. The kinetic effect of this resin must be related to the accessibility of the sulfonic sites, which seems to be slower in the case of the macroreticular Amberlyst 15; meanwhile, the gel-type resin is efficiently swelled in the biphasic CH$_2$Cl$_2$/H$_2$O reaction medium, leading to the improved diffusion of the reagents. A similar effect had been previously observed in the case of esterification reactions [29], where the gel-type resins were more efficient than the macroreticular ones. The amount of catalyst is very important, as shown by the poor result obtained with only 10 mol% (entry 7).

In an attempt to use a single solvent reaction medium, the source of bromide was changed from KBr to tetrabutylammonium bromide (TBAB). The oxidation reaction was tested with Dowex 50W×8 under exactly the same reaction conditions (20 mol% bromide, 20 mol% sulfonic sites, 1.5 eq 60% H$_2$O$_2$, r.t.), but only CH$_2$Cl$_2$ was used as the solvent. Much worse results were obtained (entry 10), with only 26% conversion after 24 h (total conversion with KBr) and a maximum of 44% after 48 h. The use of the biphasic CH$_2$Cl$_2$/H$_2$O reaction medium with TBAB led to even worse results (only 16% conversion after 48 h, entry 11), and hence the inorganic KBr was kept as the optimal bromide source. The importance of the nature of the bromide confirms the need for this species, as shown in the studies conducted in the homogeneous phase [24]. In fact, the proposed mechanism suggests that oxidized bromine species (hypobromite and/or molecular bromine/radical) are responsible for the alcohol oxidation; these are generated by a reaction with H$_2$O$_2$ in combination with the sulfonic catalyst. This hypothesis is confirmed by the described oxidation of alcohols with molecular bromine, which can be substituted by the H$_2$O$_2$/HBr system [30]. Moreover, recent DFT calculations using the related bromide/PhIO system point to BrO$^-$ species being responsible for the oxidation of the alcohols [31]. In Scheme 2, this proposed mechanism has been adapted to the heterogeneous reaction and one crucial detail is that the three components, H$_2$O$_2$, the sulfonic group and bromide, seem to react simultaneously; hence, the diffusion of both H$_2$O$_2$ and bromide from the solution to the sulfonic sites is crucial. This requirement would explain the poor result obtained with TBAB, given that it would be present mainly in the organic phase, whereas the hydrogen

peroxide would be in the aqueous phase. The good result with KBr indicates that the diffusion from the aqueous phase to the sulfonic sites is favored (the hydrophilic nature of the resins is demonstrated by the high water content in the commercial samples, see Section 3) and that the presence of both reagents in different phases is clearly detrimental. In contrast with the case of the hydrolysis of epoxides [8], in this case, the swollen capacity of the resin does not seem to have a so crucial role, as both macroreticular Amberlyst 15 and gel-type Dowex 50 W behave in a similar way; furthermore, the fluorinated sulfonic resins are less efficient, despite their swelling ability in the reaction medium (see Supporting Material). The more hydrophobic character of the perfluoroalkyl chains may favor the concentration of the organic phase and hamper the diffusion of the aqueous reagents to the sulfonic sites, at least in the inner part of the particles.
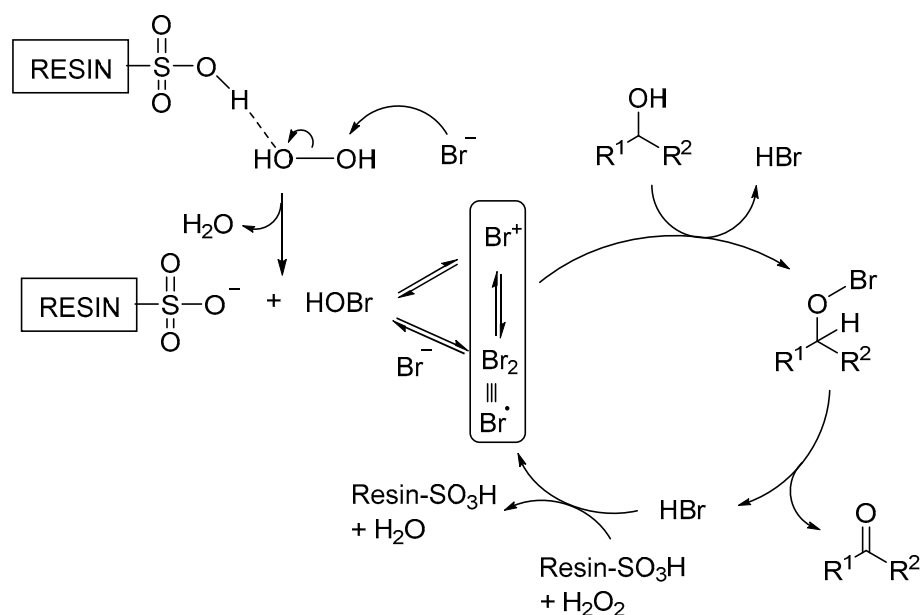

Scheme 2. Proposed mechanism for the oxidation of alcohols with the KBr/H_2O_2/sulfonic resin method (adapted from [24]).

The recoverability and reusability of the resins were studied in the case of Amberlyst 15 and Dowex 50W×8 (Table 2). In the second reaction with Amberlyst 15 (entry 2), the maximum conversion was only 63%, and the important attrition of the resin, due to its poor mechanical strength, made it impossible to recover the resin after the second run. Dowex 50W×8 showed the same loss of conversion in the second run (entry 4), but its better mechanical properties allowed the recovery of the resin after further runs. The drop in conversion was ascribed to the exchange of sulfonic acid with KBr, leading to –SO_3K and HBr (Scheme 3), an equilibrium already proposed in the mechanism of the homogeneous phase [24]. Despite being disfavored due to the pK_a difference [24], the filtration and separation of the sulfonic resin produce a cumulative effect, and as a consequence, the number of sulfonic sites in the successive runs is lower, with the already known effect on conversion (Table 1, entry 6 vs. entry 7). This was confirmed by the complete reactivation (entry 5) obtained by treatment with HCl at 80 °C for 3 h, a method able to reverse the equilibrium from –SO_3K to the acidic –SO_3H form (Scheme 3).

Table 2. Recoverability and reusability of the resins Amberlyst 15 and Dowex 50W×8 [1].

Entry	Sulfonic Solid	Run	Conversion (%) [2]
1	Amberlyst 15	1	>99
2		2	63
3	Dowex 50W×8	1	>99
4		2	62
5		3 [3]	>99

[1] Reaction conditions: 0.5 mmol of methyl 9(10)-hydroxystearate (**1a** + **1b**), 0.1 mmol of KBr, 0.75 mmol of 60% H_2O_2, 0.1 mmol of sulfonic groups, 1 mL of CH_2Cl_2/H_2O (9:1 *v/v*), r.t., 24 h. [2] Determined by gas chromatography. [3] After the treatment of the resin with HCl at 80 °C for 3 h.
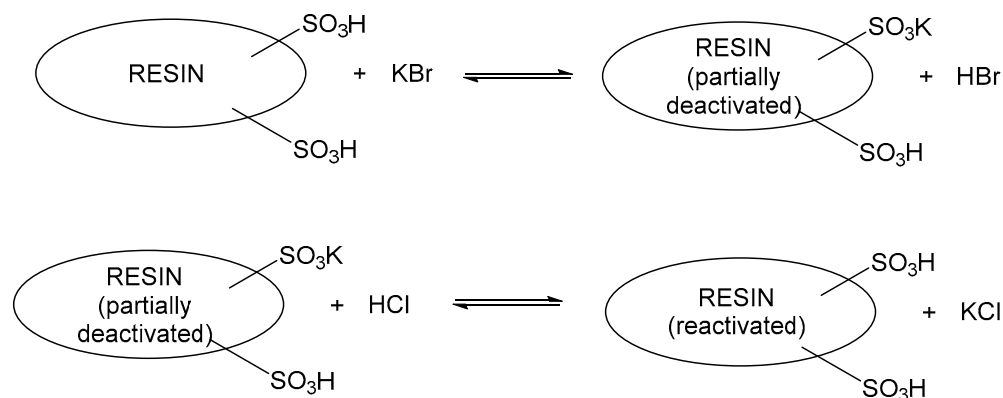
Scheme 3. Partial deactivation of sulfonic resins and reactivation with HCl.

Thus, the possibility of using a lower KBr/sulfonic molar ratio was tested with two experiments (Table 3). The reaction rate and final conversion depend on the amount of KBr, whereas the increase in the sulfonic amount has no effect, but it should be positive for the recycling of the resin.

Table 3. Variation in the KBr/sulfonic ratio in the oxidation of methyl 9(10)-hydroxystearate (**1a** + **1b**) [1].

Entry	mol% Dowex 50W×8	mol% KBr	t (h)	Conversion (%) [2]
1	20	20	6	75
			24	>99
2	20	10	24	76
			48	86
3	40	20	6	76
			24	>99

[1] Reaction conditions: 0.5 mmol of methyl 9(10)-hydroxystearate (**1a** + **1b**), Dowex 50W×8, KBr, 0.75 mmol of 60% H_2O_2, 1 mL of CH_2Cl_2/H_2O (9:1 *v/v*), rt. [2] Determined by gas chromatography.

A deeper recycling study was carried out under these conditions (Figure 1). As can be seen, the excess of resin allows full recycling in the second run and the decrease in performance is observed in the third run. As shown above, the reactivation of the resin with HCl allows the recovery of the performance in the fourth and a fifth runs, with another drop in the conversion in the sixth run. The second reactivation is less efficient than the first one, and the conversion declines faster, with a nearly inactive resin in the ninth run. This result seems to indicate a permanent deactivation mechanism, different from the cation exchange proposed to form potassium sulfonate. The analysis of the resin after nine runs shows a loss of 25% of the initial sulfur, due to a side reaction. The more important loss in activity might be due to the loss of the most accessible sulfonic groups, whereas the remaining ones are less available due to diffusion problems.
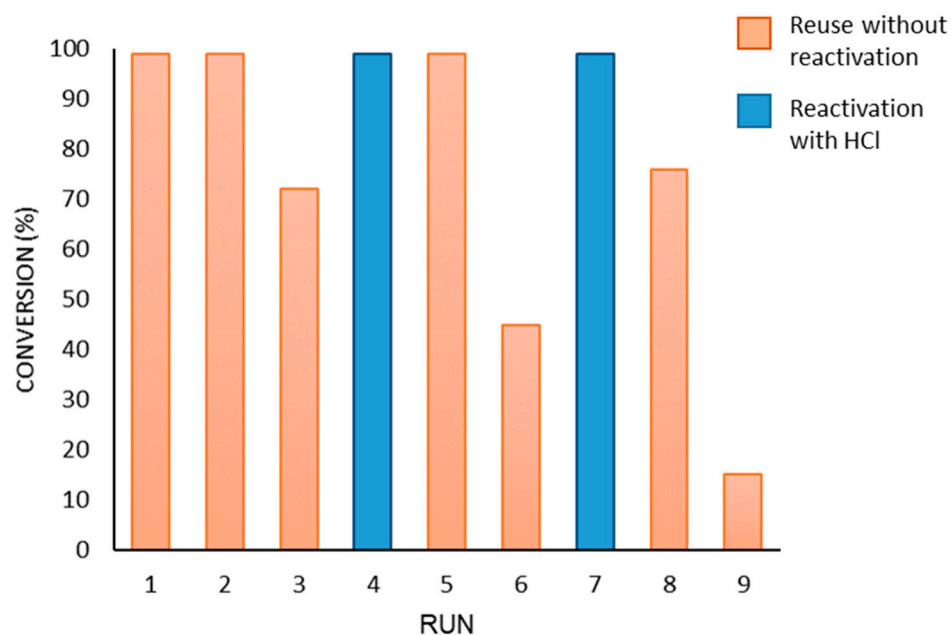
Figure 1. Recovery of Dowex 50W×8 in the oxidation of methyl 9(10)-hydroxystearate (**1a** + **1b**) with H_2O_2/KBr. Reaction conditions: 0.5 mmol of methyl 9(10)-hydroxystearate, 0.1 mmol of KBr, 0.75 mmol of 60% H_2O_2, 0.2 mmol of sulfonic groups, 1 mL of CH_2Cl_2/H_2O (9:1 *v/v*), rt, 24 h. Blue bars indicate the result after the reactivation of the resin with HCl.

Under these conditions, and after nine runs, the cumulative productivity is around 20 mol of methyl 9(10)-oxostearate (**2a** + **2b**) per mol of sulfonic group; meanwhile, in the homogeneous phase, the productivity is only five.

The method was then applied to the oxidation of other alcohols (Scheme 4), including fatty primary alcohols (**3**) and cyclic secondary alcohols (**6** and **8**). The most relevant results are shown in Table 4. The primary alcohols (**3**) were oxidized to the corresponding carboxylic acids (**4**), whereas the aldehydes were not detected, in agreement with the related oxidation methods [30]. The increase in the chain length of the fatty alcohols makes the reaction slower, as shown by the less efficient oxidation of 1-octadecanol (**3b**) in comparison with 1-dodecanol (**3a**). The presence of an acidic catalyst favors the reaction of the formed carboxylic acid with the unconverted alcohol, leading to esters (**5**) being produced as the main products and the possibility of the total conversion of the fatty alcohols being prevented, even after increasing the amount of oxidant or KBr.

In the case of secondary cyclic alcohols, they are more easily oxidized to ketones but the effectiveness of the method depends on the steric hindrance around the hydroxyl. 2-Methylcyclohexanol (**6**) was tested as a 1:1 mixture of *trans* and *cis*. The residual unconverted alcohol was always the *trans* isomer, showing that it was less reactive to oxidation. This effect explains the lower reactivity of (−)-menthol (**8**), which possesses a bulkier isopropyl group in the *trans* relative position to the hydroxyl. The corresponding cylohexanones, 2-methylcyclohexanone (**7**) and (−)-menthone (**9**), were obtained with high selectivity, namely 87%; however, some by-products were detected in low amounts. It was not possible to identify them, although the presence of Br in the molecules was confirmed by GC-MS, a result that again confirms the role of bromine species in the oxidation process.
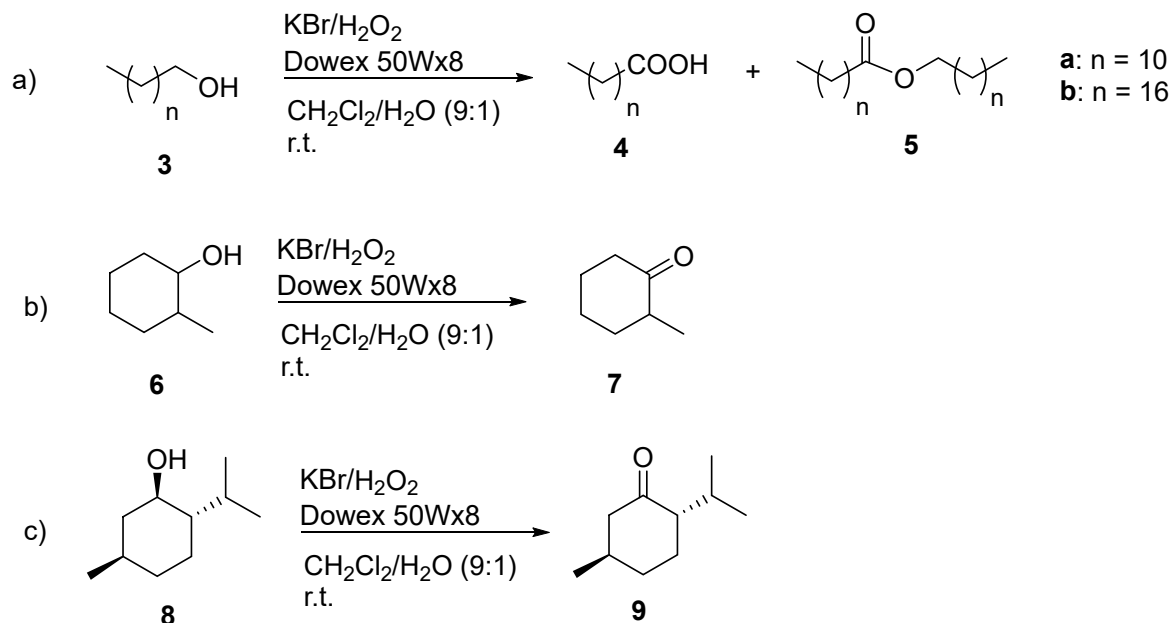
Scheme 4. Oxidation of different alcohols with KBr/H$_2$O$_2$/Dowex 50W×8.

Table 4. Oxidation of different alcohols with KBr/H$_2$O$_2$/Dowex 50W×8 [1].

Entry	Alcohol	KBr mol%	H$_2$O$_2$/Alcohol Molar Ratio	t (h)	Reaction Mixture Composition (%) [2]
1	1-Dodecanol (**3a**)	20	0.75	48	**3a** (49) + **4a** (4) + **5a** (47)
2	1-Dodecanol (**3a**)	20	2.0	96	**3a** (18) + **4a** (8) + **5a** (74)
3	1-Dodecanol (**3a**)	40	1.5	48	**3a** (12) + **4a** (8) + **5a** (80)
4	1-Octadecanol (**3b**)	40	1.5	48	**3b** (34) + **4b** (13) + **5b** (53)
5	2-Methylcyclohexanol (**6**) [3]	20	0.75	24	**6** (3) + **7** (85) + unk (12)
6	(−)-Menthol (**8**)	20	0.75	48	**8** (36) + **9** (59) + unk (5)
7	(−)-Menthol (**8**)	20	1.5	48	**8** (17) + **9** (74) + unk (9)

[1] Reaction conditions: 0.5 mmol of alcohol, 22.2 mg of Dowex 50W×8 (0.1 mmol sulfonic sites, 20 mol%), KBr, 60% H$_2$O$_2$, 1 mL of CH$_2$Cl$_2$/H$_2$O (9:1 v/v), rt. [2] Result determined by ^{1}H NMR (**3a** and **3b**) or gas chromatography (**6** and **8**). [3] Mixture 1:1 of *trans* and *cis*.

3. Materials and Methods

Triflic acid (99%) was purchased from Fluorochem, *p*-toluenesulfonic acid was purchased from Alfa Aesar, and the resins (Aquivion PW97S, Aquivion P98, Nafion NR50, Amberlyst 15, Dowex 50W×8 and Dowex 50W×2) were purchased from Merck. Methyl oleate (96%, Alfa Aesar, Tewksbury, MA, USA), (−)-menthol (99%, Sigma-Aldrich, St. Louis, MO, USA), 1-dodecanol (98%, Alfa Aesar) and 1-octadecanol (99%, Sigma-Aldrich) were used as received without further purification. 2-Methylcyclohexanol (97%, 1:1 *trans*/*cis* mixture) was a generous gift from FMC-Foret (currently Evonik Peroxide Spain, Zaragoza, Spain). The oxidized products were identified via NMR and/or GC-MS.

Activation of Aquivion P98 [8]: a mixture of 5.0 g of Aquivion P98-SO$_2$F (5.1 mmol of –SO$_2$F groups), 30 mL of aqueous KOH (2.0 M) and 5 mL of DMSO was stirred at 120 °C for 72 h. The solid was filtered off and washed with distilled water until a neutral pH was obtained. The wet potassium form was treated with 30 mL of aqueous H$_2$SO$_4$ (2.0 M) under stirring at 120 °C for 24 h. The solid was again filtered off and washed with distilled water until a neutral pH was obtained. The content of sulfonic acid sites was determined by indirect volumetric determination [32]. Then, 1.0 g of previously dried acidic Aquivion P98 was packed in a chromatographic column and a 2.0 M aqueous solution of NaCl was passed through the resin bed until a neutral pH was obtained. The resulting HCl solution was titrated with 1.0 mM of aqueous solution NaOH and phenolphthalein as an

indicator. The functionality of Aquivion P98-H$^+$ was 0.98 mmol H$^+$/g (at least 96% of active sites exchanged). All the resins were titrated in the same way and the experimental functionalization results are shown in Table 5.

Table 5. Properties of the sulfonic resins used in this work [1].

| Sulfonic Solid | Physical Form | Particle Size (mm) | | | Acid Functionalization [1] | |
		Supplier	Dry [2]	Swollen [2]	Supplier	Experim. [3]
Aquivion PW79S [33]	Powder	n.r.	n.d.	n.d.	1.23 to 1.30	1.26
Nafion NR50 [34]	Pellets	3 × 4	≈3	≈4	>0.92	0.89
Aquivion P98 [35]	Pellets	n.r.	≈2	≈3.5 to 4	0.98 to 1.06	0.98
Amberlyst 15 [36]	Beads	<0.3	≈0.5	≈0.8	4.7	4.40
Dowex 50W×8 [37]	Beads	0.075 to 0.15	n.d.	n.d.	(1.7) [4]	4.46
Dowex 50W×2 [38]	Beads				(0.6) [5]	4.45

[1] Functionalization in mmol of sulfonic groups per gram. [2] From pictures in Supporting Material. Resins were swollen in CH$_2$Cl$_2$/H$_2$O (9:1 v/v). [3] Titration of the resulting acidic solution obtained after passing 2.0 M NaCl through a resin bed. [4] Wet resin at 1.7 mmol per mL (50–58 wt% water). [5] Wet resin at 0.6 mmol per mL (74–82 wt% water).

All the resins were dried at 120 °C under vacuum overnight prior to use.

Gas chromatography was performed using Agilent 7890A and 6890N chromatographs, both equipped with FID detectors, and ZB-5HT Inferno capillary columns (30 m × 0.25 mm × 0.25 μm). Helium was used as a carrier gas at 17 psi in the column head. Injector temperature: 280 °C. Detector temperature: 250 °C. Oven program: 70 °C (4 min, initial plateau), 25 °C min^{-1} to 150 °C (ramp 1), 5 °C min^{-1} to 250 °C (ramp 2), and 250 °C (15 min, final plateau). Retention times: *trans*-2-methylcyclohexanol (**6** *trans*), 5.3 min; *cis*-2-methylcyclohexanol (**6** *cis*), 5.4 min; 2-methylcyclohexanone (**7**), 5.5 min, (−)-menthol (**8**), 7.1 min; (−)-menthone (**9**), 7.4 min; methyl 9(10)-oxostearate (**2a** + **2b**), 24.9 min; and methyl 9(10)-hydroxystearate (**1a** + **1b**), 25.2 min.

Nuclear magnetic resonance (NMR) spectroscopy was carried out with a Bruker Avance 400 (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz) and the chemical shifts were expressed in ppm. Deuterated chloroform (CDCl$_3$) was used as both the solvent and reference (7.26 ppm for ^{1}H, 77.0 ppm for ^{13}C).

Methyl 9(10)-hydroxystearate (**1a** + **1b**) was prepared via sequential epoxidation-hydrogenolysis [7]: methyl oleate was epoxidized with *tert*-butyl hydroperoxide (TBHP) in trifluorotoluene (TFT) at 120 °C using a Ti-SiO$_2$ catalyst (prepared from Merck silica and Cp$_2$TiCl$_2$ as previously described [6]). The catalyst was filtered and washed with CH$_2$Cl$_2$, and the filtrate was evaporated under reduced pressure. The methyl *cis*-9,10-epoxystearate was used without further purification. A 10 mL Büchi reactor was charged with 500 mg of methyl *cis*-9,10-epoxystearate (1.6 mmol), 5 mL of 2,2,2-trifluoroethanol and 120 mg of Pd/C (wet with 50 wt% water, 10 wt% Pd of dry solid, 0.056 mmol Pd, 3.5 mol%). The reactor was filled with H$_2$ (5 bar) and the mixture was stirred at 65 °C for 6 h. The catalyst was filtered off and washed with CH$_2$Cl$_2$. Methyl 9(10)-hydroxystearate was purified via column chromatography on silica with AcOEt/hexanes (1:9) as the eluent. Methyl 9(10)-hydroxystearate (**1a** + **1b**): ^{1}H NMR (δ ppm, CDCl$_3$, 400 MHz): 3.65 (s, 3H), 3.62–3.54 (m, 1H), 2.29 (t, 2H, *J* = 7.6 Hz), 1.64–1.57 (m, 2H), 1.45–1.27 (m, 26H), 0.87 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (δ ppm, CDCl$_3$, 100 MHz): 174.4, 71.11, 71.09, 51.5, 37.64, 37.59, 37.56, 34.23, 34.21, 32.02, 29.85, 29.77, 29.75, 29.73, 29.71, 29.61, 29.53, 29.45, 29.41, 29.34, 29.31, 29.24, 29.20, 25.79, 25.74, 25.69, 25.06, 25.04, 24.0, 22.8, 14.2.

General procedure of oxidation: KBr (12 mg, 0.1 mmol), Dowex 50W×8 (22.2 mg, 0.1 mmol of sulfonic groups) and H$_2$O$_2$ (60%, 34 μL, 0.75 mmol) were added to a solution of methyl 9(10)-hydroxystearate (**1a** + **1b**, 157.3 mg, 0.5 mmol) in 1 mL of CH$_2$Cl$_2$/H$_2$O (9:1 v/v). The mixture was stirred at room temperature and monitored via GC. After 24 or 48 h, the catalyst was filtered and washed with CH$_2$Cl$_2$. The filtrate was washed with distilled water (3 × 10 mL) and dried with anhydrous MgSO$_4$; then, the solvent was evaporated under vacuum and the methyl 9(10)-oxostearate was identified via NMR. In the recycling

experiments, the resin was left to decant, the uppernadant was separated using a pipette, and the catalyst was washed with distilled water and then dried under vacuum at 120 °C overnight prior to reuse. Methyl 9(10)-oxostearate (**2a** + **2b**): ^{1}H NMR (δ ppm, CDCl$_3$, 400 MHz): 3.64 (s, 3H), 2.36 (t, 4H, J = 8 Hz), 2.28 (t, 2H, J = 7.6 Hz), 1.61–1.52 (m, 6H), 1.28–1.25 (m, 18H), 0.86 (t, 3H, J = 7.5 Hz); ^{13}C NMR (δ ppm, CDCl$_3$, 100 MHz): 211.78; 211.72; 174.36; 174.34; 51.5 (OCH$_3$); 42.95; 42.94; 42.86; 42.81; 34.17; 34.15; 31.97; 31.93; 29.8; 29.7; 29.54; 29.53; 29.48; 29.38; 29.31; 29.28; 29.25; 29.17; 29.15; 29.05; 29.98; 25.01; 24.97; 24.0; 23.92; 23.86; 22.76; 22.74; 14.19.

4. Conclusions

Homogeneous sulfonic acids can be substituted by sulfonic resins in the oxidation of alcohols using the H$_2$O$_2$/KBr/sulfonic acid method. The acid strength of the resin is not crucial, as the less acidic arylsulfonic resins showed a similar or even better performance than the more acidic perfluoroalkylsulfonic resins. However, the structural properties, determined by the crosslinking degree, length of the side chains and other parameters, are much more important. The best results were obtained with the gel-type poly(styrene-divinyl benzene) resins. The recovery and reuse of the resins are limited by a reversible deactivation due to cation exchange and an irreversible deactivation caused by the loss of sulfonic groups due to a side reaction. This methodology can be applied to the oxidation of secondary alcohols to ketones. In the case of cyclic alcohols, the stereochemistry of the substituents close to the hydroxyl is important for the reactivity under these conditions. The primary alcohols are oxidized to carboxylic acids, which react under the acidic conditions with the remaining unconverted alcohol to produce esters.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal14010074/s1, Figure S1: Swelling behavior of the different resins used in this work.

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References

1. Zainal, N.A.; Zulkifli, N.W.M.; Gulzar, M.; Masjuki, H.H. A Review on the Chemistry, Production, and Technological Potential of Bio-Based Lubricants. *Renew. Sustain. Energy Rev.* **2018**, *82*, 80–102. [CrossRef]
2. Ronda, J.C.; Lligadas, G.; Galià, M.; Cádiz, V. A Renewable Approach to Thermosetting Resins. *React. Funct. Polym.* **2013**, *73*, 381–395. [CrossRef]
3. Lebarbé, T.; Grau, E.; Gadenne, B.; Alfos, C.; Cramail, H. Synthesis of Fatty Acid-Based Polyesters and Their Blends with Poly(l-Lactide) as a Way To Tailor PLLA Toughness. *ACS Sustain. Chem. Eng.* **2015**, *3*, 283–292. [CrossRef]
4. Metzger, J.O.; Meier, M.A.R. Fats and Oils as Renewable Feedstock for the Chemical Industry. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 1–2. [CrossRef]
5. Fraile, J.M.; García, J.I.; Herrerías, C.I.; Pires, E. Synthetic Transformations for the Valorization of Fatty Acid Derivatives. *Synthesis* **2017**, *49*, 1444–1460. [CrossRef]
6. Dorado, V.; Gil, L.; Mayoral, J.A.; Herrerías, C.I.; Fraile, J.M. Synthesis of Fatty Ketoesters by Tandem Epoxidation—Rearrangement with Heterogeneous Catalysis. *Catal. Sci. Technol.* **2020**, *10*, 1789–1795. [CrossRef]
7. Dorado, V.; Herrerías, C.I.; Fraile, J.M. Synthesis of Hydroxyfatty Esters by Sequential Epoxidation-Hydrogenolysis: Solvent Effects. *Appl. Catal. A Gen.* **2021**, *623*, 118270. [CrossRef]

8. Dorado, V.; Herrerías, C.I.; Fraile, J.M. Catalytic Hydrolysis of Epoxyfatty Esters with Solid Sulfonic Acids. *Mol. Catal.* **2023**, *547*, 113282. [CrossRef]

9. Dorado, V.; Herrerías, C.I.; Fraile, J.M. Simple Metal-Free Oxidative Cleavage of 1,2-Diols. *Tetrahedron* **2023**, *139*, 133450. [CrossRef]

10. Tojo, G.; Fernández, M. *Oxidation of Alcohols to Aldehydes and Ketones*; Springer: Berlin/Heidelberg, Germany, 2006; ISBN 9780387236070.

11. Fore, S.P.; Bickford, W.G. Catalytic Hydrogenation of Cis-6,7-Epoxyoctadecanoic Acid. *J. Org. Chem.* **1961**, *26*, 2104–2105. [CrossRef]

12. Howton, D.R.; Kaiser, R.W. Silicic Acid Chromatographic Study of the Catalytic Hydrogenation Products of 9,10-Epoxystearates. *J. Org. Chem.* **1964**, *29*, 2420–2425. [CrossRef]

13. Mancuso, A.J.; Huang, S.L.; Swern, D. Oxidation of Long-Chain and Related Alcohols to Carbonyls by Dimethyl Sulfoxide "Activated" by Oxalyl Chloride. *J. Org. Chem.* **1978**, *43*, 2480–2482. [CrossRef]

14. Kopylovich, M.N.; Ribeiro, A.P.C.; Alegria, E.C.B.A.; Martins, N.M.R.; Martins, L.M.D.R.S.; Pombeiro, A.J.L. Catalytic Oxidation of Alcohols: Recent Advances. *Adv. Organomet. Chem.* **2015**, *63*, 91–174. [CrossRef]

15. John, L.C.; Gunay, A.; Wood, A.J.; Emmert, M.H. Catalysts for Convenient Aerobic Alcohol Oxidations in Air: Systematic Ligand Studies in Pd/Pyridine Systems. *Tetrahedron* **2013**, *69*, 5758–5764. [CrossRef]

16. Giachi, G.; Frediani, M.; Oberhauser, W.; Passaglia, E. Aerobic Alcohol Oxidation Catalyzed by Polyester-Based Pd(II) Macrocomplexes. *J. Polym. Sci. Part A Polym. Chem.* **2012**, *50*, 2725–2731. [CrossRef]

17. da Silva, J.A.L.; da Silva, J.J.R.F.; Pombeiro, A.J.L. Oxovanadium Complexes in Catalytic Oxidations. *Coord. Chem. Rev.* **2011**, *255*, 2232–2248. [CrossRef]

18. Reddy, S.R.; Das, S.; Punniyamurthy, T. Polyaniline Supported Vanadium Catalyzed Aerobic Oxidation of Alcohols to Aldehydes and Ketones. *Tetrahedron Lett.* **2004**, *45*, 3561–3564. [CrossRef]

19. Taketoshi, A.; Beh, X.N.; Kuwabara, J.; Koizumi, T.A.; Kanbara, T. Aerobic Oxidative Dehydrogenation of Benzyl Alcohols to Benzaldehydes by Using a Cyclometalated Ruthenium Catalyst. *Tetrahedron Lett.* **2012**, *53*, 3573–3576. [CrossRef]

20. Fei, H.; Shin, J.; Meng, Y.S.; Adelhardt, M.; Sutter, J.; Meyer, K.; Cohen, S.M. Reusable Oxidation Catalysis Using Metal-Monocatecholato Species in a Robust Metal-Organic Framework. *J. Am. Chem. Soc.* **2014**, *136*, 4965–4973. [CrossRef]

21. Fernandes, R.R.; Lasri, J.; Guedes Da Silva, M.F.C.; Da Silva, J.A.L.; Fraústo Da Silva, J.J.R.; Pombeiro, A.J.L. Bis- and Tris-Pyridyl Amino and Imino Thioether Cu and Fe Complexes. Thermal and Microwave-Assisted Peroxidative Oxidations of 1-Phenylethanol and Cyclohexane in the Presence of Various N-Based Additives. *J. Mol. Catal. A Chem.* **2011**, *351*, 100–111. [CrossRef]

22. Ciriminna, R.; Pagliaro, M. Industrial Oxidations with Organocatalyst TEMPO and Its Derivatives. *Org. Process Res. Dev.* **2010**, *14*, 245–251. [CrossRef]

23. Anelli, P.L.; Biffi, C.; Montanari, F.; Quici, S. Fast and Selective Oxidation of Primary Alcohols to Aldehydes or to Carboxylic Acids and of Secondary Alcohols to Ketones Mediated by Oxoammonium Salts under Two-Phase Conditions. *J. Org. Chem.* **1987**, *52*, 2559–2562. [CrossRef]

24. Moriyama, K.; Takemura, M.; Togo, H. Selective Oxidation of Alcohols with Alkali Metal Bromides as Bromide Catalysts: Experimental Study of the Reaction Mechanism. *J. Org. Chem.* **2014**, *79*, 6094–6104. [CrossRef] [PubMed]

25. Guthrie, J.P. Hydrolysis of Esters of Oxy Acids: PKa Values for Strong Acids; Bronsted Relationship for Attack of Water at Methyl; Free Energies of Hydrolysis of Esters of Oxy Acids; and a Linear Relationship between Free Energy of Hydrolysis and PKa Holding over a Ran. *Can. J. Chem.* **1978**, *56*, 2342–2353. [CrossRef]

26. Li, T.; Shen, J.; Chen, G.; Guo, S.; Xie, G. Performance Comparison of Proton Exchange Membrane Fuel Cells with Nafion and Aquivion Perfluorosulfonic Acids with Different Equivalent Weights as the Electrode Binders. *ACS Omega* **2020**, *5*, 17628–17636. [CrossRef]

27. Elliott, J.A.; James, P.J.; McMaster, T.J.; Newton, J.M.; Elliott, A.M.S.; Hanna, S.; Miles, M.J. Hydrolysis of the Nafion® Precursor Studied by X-Ray Scattering and in-Situ Atomic Force Microscopy. *E-Polymers* **2001**, *1*, 1–11. [CrossRef]

28. Komagawa, H.; Maejima, Y.; Nagano, T. Sodium Bromide-Catalyzed Oxidation of Secondary Benzylic Alcohols Using Aqueous Hydrogen Peroxide as Terminal Oxidant. *Synlett* **2016**, *27*, 789–793. [CrossRef]

29. Fraile, J.M.; García-Bordejé, E.; Pires, E.; Roldán, L. Catalytic Performance and Deactivation of Sulfonated Hydrothermal Carbon in the Esterification of Fatty Acids: Comparison with Sulfonic Solids of Different Nature. *J. Catal.* **2015**, *324*, 107–118. [CrossRef]

30. Nikishin, G.I.; Sokova, L.L.; Terent'ev, A.O.; Kapustina, N.I. Primary Alkanols: Oxidative Homocondensation in Water and Cross-Condensation in Methanol. *Russ. Chem. Bull.* **2015**, *64*, 2845–2850. [CrossRef]

31. Farshadfar, K.; Bird, M.J.; Olivier, W.J.; Hyland, C.J.T.; Smith, J.A.; Ariafard, A. Computational Investigation into the Mechanistic Features of Bromide-Catalyzed Alcohol Oxidation by PhIO in Water. *J. Org. Chem.* **2021**, *86*, 2998–3007. [CrossRef]

32. Kang, S.; Li, X.; Fan, J.; Chang, J. Characterization of Hydrochars Produced by Hydrothermal Carbonization of Lignin, Cellulose, d-Xylose, and Wood Meal. *Ind. Eng. Chem. Res.* **2012**, *51*, 9023–9031. [CrossRef]

33. Aquivion PW79S. Available online: https://www.fuelcellstore.com/solvay-aquivion-pw79s-72800020 (accessed on 10 January 2024).

34. Nafion. Available online: https://www.nafion.com/en/products/resins (accessed on 10 January 2024).

35. Aquivion P98. Available online: https://www.fuelcellstore.com/solvay-aquivion-p98-so2f-72800018 (accessed on 10 January 2024).

36. Amberlyst 15. Available online: https://www.sigmaaldrich.com/ES/en/product/sial/216380 (accessed on 10 January 2024).

37.   Dowex 50Wx8. Available online: https://www.sigmaaldrich.com/ES/en/product/sial/217506 (accessed on 10 January 2024).
38.   Dowex 50Wx2. Available online: https://www.sigmaaldrich.com/ES/en/product/sial/217468 (accessed on 10 January 2024).