

## Oxygen-Transfer Resins, a New Type of Oxidation-Reduction Polymers

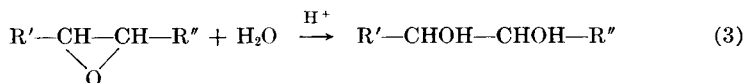
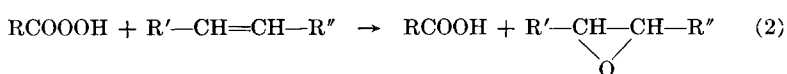
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### Synopsis

Bifunctional cation exchangers with carboxylic and sulfonic acid groups can be oxidized with aqueous hydrogen peroxide which converts the carboxylic to percarboxylic acid groups. The oxidized resins can be used to hydroxylate compounds with olefinic double bonds to form  $\alpha$ -glycols. The resins thus transfer active oxygen from a peroxide to an unsaturated substrate. Oxidation and reduction of the resins is reversible.

### INTRODUCTION

It is well known that hydrogen peroxide can be used for epoxidizing or hydroxylating organic compounds with olefinic double bonds. Hydrogen peroxide alone is not effective but is used to oxidize a mediator, as a rule formic or acetic acid, which in turn epoxidizes the organic substrate.<sup>1,2</sup> Epoxidation may be followed by hydration to give the  $\alpha$ -glycol. The reaction of hydrogen peroxide and the hydration of the epoxide are catalyzed by acids.



Several industrial epoxidation processes are based on such reaction sequences, usually with sulfuric acid<sup>3-7</sup> or strong-acid ion-exchange resins<sup>6,12</sup> as catalysts.

The present communication describes solid, polymeric carboxylic acid gels which can be used as reversible agents instead of monomeric acids, RCOOH, in reaction sequence as above. These materials can be called "oxygen-transfer resins" since their action is transfer of active oxygen from a peroxide to the substrate. The resins can also be regarded as a special type of so-called electron exchangers,<sup>13,15</sup> in that they are reversible polymeric oxidation-reduction agents in gel form.

TABLE I  
Resin Compositions and Properties

Resin	Composition of monomer mixture				Water content, wt.-% <sup>b</sup>	Ion-exchange capacity <sup>c</sup>		Oxidation capacity, meq./g. <sup>c,d</sup>	Fraction of -COOH oxidized <sup>d</sup>
	Ethyl acrylate, mole-%	Styrene + ethylstyrene, mole-% <sup>a</sup>	Divinylbenzene, mole-%	None		-SO <sub>3</sub> H, meq./g.	-COOH, meq./g.		
Dowex 50-X8	None	92	8	54	5.3	None	<0.05	—	
CS-1	49	43	8	48	4.4	ca. 1.3	0.8	ca. 0.6	
CS-2	62	32	6	52	3.3	3.1	1.5	0.5	
CS-3	76	18	6	52	3.2	5.5	1.7	0.3	
CS-4	93	3	4	58	2.9	5.5	2.0	0.35	
Amberlite IRC-50		Unknown		53	None	9.4	<0.1	<0.01	

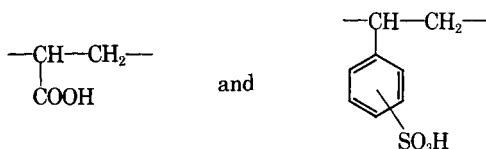
<sup>a</sup> Ethylstyrene content of divinylbenzene solution included in this column.

<sup>b</sup> H<sup>+</sup> form, swollen in deionized water.

<sup>c</sup> Reference state: gram of unoxidized resin in anhydrous H<sup>+</sup> form.

<sup>d</sup> Attained with 45 wt.-% aqueous hydrogen peroxide in 24 hr. at 45°C.

One might have expected that conventional weak-acid cation exchangers with carboxylic acid groups, such as Amberlite IRC-50 (crosslinked polyacrylic acid), could serve as oxygen-transfer resins. However, efforts to oxidize the carboxylic acid groups of such resins with aqueous hydrogen peroxide and sulfuric acid as the catalyst met with little success. To achieve the desired reactivity we had to equip carboxylic acid resins with a sufficient proportion of sulfonic acid groups, which act as built-in catalysts. The resins, thus, are bifunctional cation exchangers with the units



## EXPERIMENTAL

### Resin Preparation

The resins were prepared essentially as described by Ferris and Lyman<sup>16</sup> by using amounts of the reactants controlled so as to produce resins with the required proportions of sulfonic to carboxylic acid groups. A 2000-ml. three-necked flask equipped with stirrer, reflux condenser, and thermometer in a thermostated bath kept at 90°C. was filled with 1500 ml. deionized water to which 1.5–2 g. each of gelatin and talc were added as suspension stabilizers, and stirring was started. When thermal equilibrium had been attained, 110 ml. of polymerization mixture made up from ethyl acrylate (destabilized by distillation under nitrogen), styrene and divinylbenzene (both destabilized by percolation through a silicagel column), and 1.1 g. benzoyl peroxide as the initiator were added. The relative amounts used are listed in Table I. After 4 hr. stirring at 90°C. the flask was removed from the bath and was allowed to cool. The copolymer was separated by filtration and was thoroughly washed with deionized water. Most of the copolymer (65–90%) was obtained in the form of spherical beads. A small amount of spongy copolymer was discarded.

About 60 g. of copolymer beads was stirred overnight with 600 ml. dichloroethane. The flask with the slurry was transferred to an ice bath and 60 ml. chlorosulfonic acid was added dropwise under stirring. After heating for 3 hr. at 80°C. the slurry was cooled and was then poured into 1600 ml. ice water. Dichloroethane was driven off by passing steam through the slurry. The beads were separated from the aqueous phase and were thoroughly washed with ethanol.

Prior to use, the resins were conditioned by 10 ion-exchange cycles with 1M NaOH and 1M HCl alternating and were washed with deionized water after each conversion. The resins were stored under 0.1M HCl.

### Oxidation of Resins

The resin (ca. 3 g.) was washed with deionized water, centrifuged to remove adherent liquid, weighed in a stoppered weighing bottle, and transferred into a 250-ml. Erlenmeyer flask. There was added 150 ml. of 45 wt.-% aqueous  $\text{H}_2\text{O}_2$ . The flask was placed in a thermostat and kept at 45°C. for 24 hr. The aqueous phase was now decanted and the resin was washed on a filter with 100 ml. methanol at  $-10^\circ\text{C}$ . Then the resin was stirred for 5 min. with 25 ml. methanol at  $-10^\circ\text{C}$ . and was again washed on a filter with methanol at this temperature until the effluent was free of  $\text{H}_2\text{O}_2$ . The treatment with cold methanol removes sorbed  $\text{H}_2\text{O}_2$  and most of the sorbed water without causing significant reversion of the percarboxylic group formation. Oxidations were carried out immediately before use, except when storage stability was tested.

For oxidation rate studies the same procedure was used, except that the oxidation capacity (see farther below) was determined after contact times of only 2, 4, 7, and 13 hr.

In some experiments the effect of sulfuric acid as oxidation catalyst was studied. Here, 2 ml. of concentrated sulfuric acid was added.

### Oxidation of Substrates

Oxidized resins were used to oxidize three typical substrates; namely, butenediol, cyclohexene, and acetic acid. The resin (ca. 3 g., weighed before oxidation) was placed in a 250-ml. Erlenmeyer flask kept in a thermostated bath. Substrate with or without solvent was added, and aliquots were withdrawn from the supernatant solution at different times for analysis. Conditions are shown in Table II.

In some experiments the resins were used with their sulfonic-acid groups converted to the  $\text{NH}_4^+$  or  $\text{Na}^+$  forms. Conversion to the  $\text{NH}_4^+$  form was achieved by stirring the oxidized resin for 10 min. with a stoichiometric amount of 0.05M  $\text{NH}_3$  in methanol at  $0^\circ\text{C}$ . Conversion to the  $\text{Na}^+$  form was achieved by washing the resin with 300 ml. 1M aqueous  $\text{NaCl}$  at  $0^\circ\text{C}$ . The converted resins were washed with cold methanol to remove sorbed agents and were then used for oxidation as described above.

### Determination of Ion-Exchange Capacities

The ion-exchange capacities of the resins before oxidation, in terms of milliequiv. of sulfonic and carboxylic acid groups per gram dry resin in  $\text{H}^+$  form, were determined by pH titration as described in the literature.<sup>17,19</sup> To a series of resin samples in the  $\text{H}^+$  form, water,  $\text{NaCl}$ , and  $\text{NaOH}$  were added in such a way that each had 100 ml. 0.025M  $\text{NaCl}$  per gram swollen resin, but different amounts of  $\text{NaOH}$ . Two days proved ample for attaining constant pH in the supernatant solution. Curves as shown in Figure 1 are obtained, with two recognizable steps from which the sulfonic and carboxylic acid capacities can be derived as indicated. The water contents of the resins, required for converting capacities per gram swollen to those

TABLE II  
 Oxidations with CS Resins

Resin	Ionic form of sulfonic acid group	Substrate	Solvent	Concentration of solution, vol.-%	Temp., °C.	Contact time, hr.	Yield <sup>a</sup>		
							$\alpha$ -Glycol, %	Epoxide, %	Peraoid, %
CS-1	H <sup>+</sup>	Acetic acid	None	—	45	4			75
CS-4	H <sup>+</sup>	Acetic acid	Methanol	67-97	45	4			60-70
CS-1 to 4	H <sup>+</sup>	Acetic acid	Methanol	50	45	4			60-80
CS-4	H <sup>+</sup>	Butenediol	Dioxane	9	45	2	25	<2	
CS-4	H <sup>+</sup>	Butenediol	Dioxane	9	45	21	25	<2	
CS-4	H <sup>+</sup>	Cyclohexene	Dioxane	9	45	4	75	<2	
CS-4	H <sup>+</sup>	Cyclohexene	Dioxane	9	45	21	75	<2	
CS-4	NH <sub>4</sub> <sup>+</sup>	Butenediol	Dioxane	9	45	2.5	<3	<2	
CS-4	NH <sub>4</sub> <sup>+</sup>	Butenediol	Dioxane	9	45	5	8	<2	
CS-4	NH <sub>4</sub> <sup>+</sup>	Butenediol	Dioxane	9	45	22	10	<2	
CS-4	NH <sub>4</sub> <sup>+</sup>	Cyclohexene	Dioxane	9	45	2.5	8	<2	
CS-4	NH <sub>4</sub> <sup>+</sup>	Cyclohexene	Dioxane	9	45	5	30	<2	
CS-4	NH <sub>4</sub> <sup>+</sup>	Cyclohexene	Dioxane	9	45	22	25	<2	
CS-4	Na <sup>+</sup>	Butenediol	Dioxane	9	45	2	<1	15	
CS-4	Na <sup>+</sup>	Butenediol	Methanol	9	45	3	20	<2	
CS-4	Na <sup>+</sup>	Butenediol	Methanol	9	45	24	15	<2	
CS-4	Na <sup>+</sup>	Butenediol	Water	9	45	3	20	<2	
CS-4	Na <sup>+</sup>	Butenediol	Water	9	45	24	45	<2	
CS-4	Na <sup>+</sup>	Butenediol	Dioxane	9	80	24	10	6	
CS-4	Na <sup>+</sup>	Cyclohexene	Dioxane	9	45	2	<2	<2	
CS-4	Na <sup>+</sup>	Cyclohexene	Methanol	9	45	3	40	<2	
CS-4	Na <sup>+</sup>	Cyclohexene	Methanol	9	45	24	60	<2	
CS-4	Na <sup>+</sup>	Cyclohexene	Dioxane	9	80	24	50	10	

<sup>a</sup> Based on utilization of peracid groups.

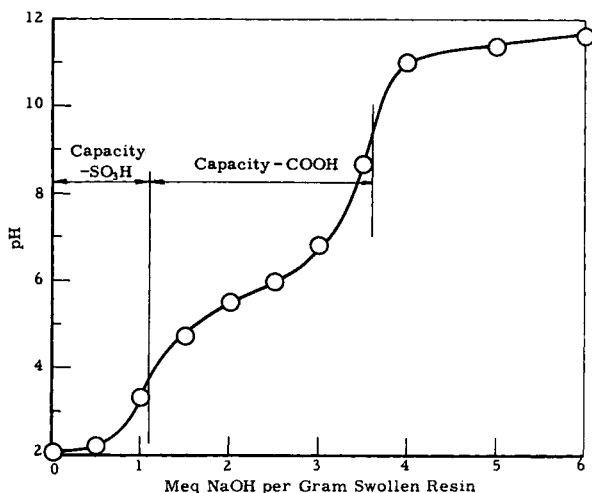


Fig. 1. Titration curve of CS-4 resin.

per gram dry resin, were determined by drying to constant weight in vacuum over  $P_2O_5$  at  $60^\circ C$ . The capacity determination was reproducible only within about  $\pm 10\%$ . This reflects some lack of uniformity of the resins.

#### Determination of Oxidation Capacities

The percarboxylic acid contents of the oxidized and methanol-washed resins were determined by reaction with aqueous KI solution (20 min. at  $60^\circ C$ .) and titration of the generated iodine with  $0.1N$  thiosulfate (Kingzett method). Corrections calculated from blank determinations with the respective unoxidized resins were applied. Hydrogen peroxide, which would interfere, was shown to be absent by failure of the resins to react with ceric sulfate at low temperature. The results were reproducible only within about  $\pm 20\%$ .

#### Analytical Procedures

Hydrogen peroxide was determined by titration with  $0.1N$  ceric sulfate and ferroin indicator. The peroxide is oxidized according to



Percarboxylic acids do not interfere.

Peracetic acid was determined by reaction with KI solution (10 min. at  $60^\circ C$ .) and titration of generated iodine with thiosulfate (Kingzett method). Corrections for blanks and for  $H_2O_2$ , if present, must be applied.

$\alpha$ -Epoxides were determined by converting the epoxide to the chlorohydrin with HCl in dioxane and backtitrating excess HCl with  $0.1M$  NaOH in methanol with cresol red as indicator.

Cyclohexane-1,2-diol was determined by oxidation with periodate followed by reduction of iodate and excess periodate with iodide and titration of iodine formed with 0.1*N* thiosulfate. The glycol concentration is calculated from the difference in used titrant between this titration and that of a blank with the same amount of periodate.

Butanetetraol was determined by oxidation with periodate followed by reduction of excess oxidant with ethylene glycol and titration of the formic acid oxidation product with 0.1*M* NaOH with phenolphthalein indicator.

### Reagents

Hydrogen peroxide was Shell Chemical 90 wt.-% stabilized aqueous solution, diluted with deionized water to 45 wt.-%. Ethyl acrylate and benzoyl peroxide were Eastman Kodak standard grades. Styrene was Shell Chemical polymerization grade, 99.8% pure. Divinylbenzene was Chemical Process Co., 55.8% solution in ethylstyrene. Chlorosulfonic acid was Eastman Kodak practical grade. Gelatin was Braun-Knecht-Heimann gelatin sheet. All others were standard analytical grade or pure laboratory reagents.

## RESULTS AND DISCUSSION

The compositions and properties of a series of our sulfonated ethyl acrylate-styrene-divinylbenzene resins, CS-1, CS-2, CS-3, and CS-4, are shown in Table I in the order of increasing content of carboxylic and decreasing content of sulfonic acid groups. The commercial monofunctional resins, Dowex 50-X8 and Amberlite IRC-50, are included for comparison. The crosslinking, adjusted through the divinylbenzene content, was chosen such that all resins swelled in water to roughly the same extent.

The pH titration curves of the CS resins, as shown for CS-4 in Figure 1, demonstrated clearly that bifunctional resins had indeed been obtained, with the sulfonic and carboxylic group contents listed in Table I. The carboxylic group value for CS-1 is somewhat uncertain because the respective step in the titration curve is not too well defined. Throughout, the carboxylic group contents of the CS resins are slightly lower than expected on the basis of the monomer ratios; apparently, not all ethylacrylate monomer is incorporated in the resins.

The column "oxidation capacity" in Table I lists the peracid group contents (calculated per gram anhydrous H<sup>+</sup> form of unoxidized resin) after treatment with 45 wt.-% aqueous hydrogen peroxide. Essentially identical values were obtained with and without addition of concentrated sulfuric acid as catalyst. By separate analysis of the oxidized resins for hydrogen peroxide it was established that the oxidation capacities result indeed from peracid groups rather than from retained hydrogen peroxide. Virtually no peracid groups were formed in Dowex 50 and Amberlite IRC-50, even when sulfuric acid was added. The failure of Dowex 50 to react was expected and is evidence that carboxylic rather than sulfonic acid

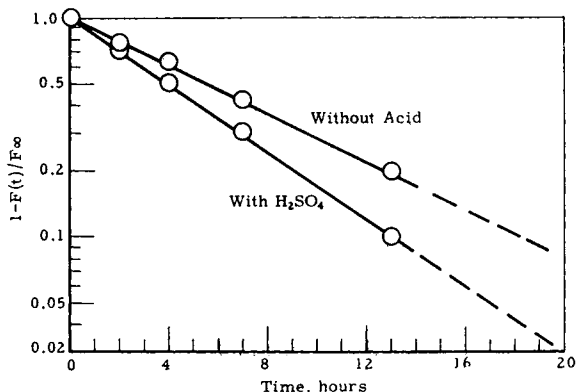


Fig. 2. Rate of oxidation of CS-2 resin with 45% hydrogen peroxide at 45°C.

groups are oxidized. The failure of Amberlite IRC-50 to be oxidized with sulfuric acid as the catalyst is surprising and demonstrates the need of having a sufficient proportion of strong-acid groups as built-in catalysts in the resin. A tentative explanation of the difficulties with Amberlite IRC-50 is insufficient penetration of sulfuric acid into the resin.

The last column in Table I shows the fractions of carboxylic-acid groups converted to preacid groups. The value for CS-1 is possibly too high. The other values are in the expected range and compare reasonably well with the fractional conversion of acetic to peracetic acid, which is 0.55 under comparable conditions.

The oxidation rate of the resin CS-2 with 45 wt.-% aqueous hydrogen peroxide was studied in both the presence and absence of 2 wt.-% concentrated sulfuric acid. The results are shown in Figure 2 and conform, as expected, with the kinetics of a pseudo-first-order reversible reaction; straight lines are obtained when the experimental points are plotted as  $\log [1 - F(t)/F_{\infty}]$  versus time, where  $F(t)$  is the conversion at time  $t$  and  $F_{\infty}$  is the conversion at equilibrium. Addition of sulfuric acid accelerates the oxidation slightly. Times required for 95% of equilibrium conversion are about 17 hr. with added acid and about 24 hr. without acid. These rates are low compared with those of diffusion in comparable resins; therefore, one may safely conclude that the actual chemical reaction of the carboxylic groups is the rate-controlling step.

The results of experiments in which the oxidized and methanol-washed CS resins were used to oxidize acetic acid, cyclohexene, and 2-butene-1,4-diol in the presence and absence of solvents are shown in Table II. In all cases the substrate was present in considerable excess over the stoichiometric amount. Acetic acid is oxidized to peracetic acid, and cyclohexene is hydroxylated to cyclohexane-1,2-diol, with reasonably high degrees of utilization of the percarboxylic-acid groups. Hydroxylation of butenediol to butanetetraol is markedly less efficient. Maximum conversion is attained in 2-4 hr. at 45°C. With the olefinic reactants, very little of the



epoxide intermediates are found; apparently, with the sulfonic acid groups of the resin in the  $H^+$  form, hydrolysis of the epoxide intermediate [reaction (3)] is fast, although most of the water had been removed from the resin by washing with methanol.

In an effort to obtain higher yields of epoxides we used oxidized CS resins with their sulfonic-acid groups converted, after oxidation, to the  $NH_4^+$  and  $Na^+$  forms (see Table II, lower part). It was first established that the percarboxylic acid groups survive the ion-exchange treatment. Even with the salt forms, however, more glycol than epoxide was obtained in most cases, and the degrees of utilization of peracid groups were unusually lower. Conversion to the salt forms, for as yet unexplained reasons, greatly reduces the reactivity of the percarboxylic acid groups; thus, with the sulfonic acid groups in the  $Na^+$  form, about one-third of the peracid groups survived even at 24-hr. treatment at  $80^\circ C.$  with excess olefinic substrates.

Several tests were made in which spent resin, after oxidation of a substrate, was reoxidized with hydrogen peroxide and was used again to oxidize a substrate. The results were essentially the same as in the first oxidation cycle, with only the exception that, because of partial oxidative decross-linking, the resins swelled to a noticeably greater extent in the second cycle.

Several tests were made to assess resin life both in contact with hydrogen peroxide and under storage conditions. Prolonged exposure to hydrogen peroxide results in oxidative decrosslinking; the resins become soft and gelatinous and eventually dissolve completely. Useful resin life is greatly shortened by the presence of even traces of heavy-metal ion contaminants, which act as degradation catalysts; if no particular precautions are taken the useful life of the CS resins in contact with 45 wt.-% hydrogen peroxide at  $45^\circ C.$  is only about three days, i.e., is sufficient for only three oxidation-reduction cycles. No such degradation occurs in the absence of hydrogen peroxide. At ambient temperature the oxidized resins, however, gradually lose active oxygen through reversion of percarboxylic to carboxylic acid groups; 50% reversion occurs in about 2 days, and 75% in about 6 days. In contrast, no loss of active oxygen was observed with resins stored at  $-10^\circ C.$  under methanol over a period of one week.

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### Résumé

Les échangeurs de cations bifonctionnels, qui contiennent des groupements acides carboxyliques et acides sulfoniques, peuvent être oxydés avec le peroxyde d'hydrogène dans l'eau, pour transformer les groupements acides carboxyliques en groupements acides percarboxyliques. Les résines oxydées peuvent être employées pour hydroxyler des produits qui contiennent des doubles liaisons oléfiniques pour former des alpha-glycols. Les résines transfèrent l'oxygène actif d'un peroxyde à un produit non-saturé. L'oxydation et la réduction des résines sont réversibles.

### Zusammenfassung

Bifunktionelle Kationenaustauscher mit Carboxyl- und Sulfonsäuregruppen können mit wässrigem Wasserstoffperoxyd oxydiert werden, welches die Carboxyl- zu Percarboxylsäuregruppen umwandelt. Die oxydierten Harze können zur Hydroxylierung von Verbindungen mit olefinischen Doppelbindungen unter Bildung von  $\alpha$ -Glykolen verwendet werden. Die Harze übertragen also aktiven Sauerstoff von Peroxyd an ein ungesättigtes Substrat. Oxydation und Reduktion der Harze erfolgt reversibel.

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