Synthesis of Peracid-Type Resins and Their Characteristics as Oxygen Transfer Agents

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Synopsis

Synthesis of peracid-type resins (PAR) by oxidation of carboxylic acid-type ion exchangers with H_2O_2 in sulfonic and sulfuric acid media has been studied.   Influence of composition of the resins and acid concentration of the media on the conversion of carboxylic to percarboxylic acid groups in the resins is discussed.   PAR can oxidize various organic compounds in good conversion.   It is especially noteworthy that the increase in the polarity of the solvent increased the rate constants in the epoxidation of cyclohexene with PAR, in contrast with the low molecular weight peracids, and the epoxidation of 1-olefins, geometric isomers of cyclododecene, and cholesterol with PAR took place selectively with regard to chain length or steric configuration.   The results are discussed on the basis of distribution effect, protective effect with polymer, steric interactions between overall molecule of the substrates and polymer matrix, and other factors.

INTRODUCTION

In the investigation of oxidation–reduction polymers, the quinone-type electron transfer polymers have hitherto been studied in detail,[1] however, the study on oxygen transfer polymers has not been reported except for the pioneering work of Helfferich and Luten.[2]   They reported that the sulfonated acrylic acid–styrene–divinylbenzene (DVB) copolymers can be oxidized with H_2O_2, which converts carboxylic to percarboxylic acid groups by the intramolecular catalytic effect of sulfonic acid groups in the resin.   The oxidized resin hydroxylates olefinic compounds to glycols.

In preceding communications,[3] we have reported a new approach to the synthesis of PAR based on the oxidation of carboxylic acid-type cation exchangers with sulfonic acid–H_2O_2 reagent.[4]   In the process, the carboxylic acid group is converted to percarboxylic acid by the intermolecular catalytic effect of the sulfonic acid.   The PAR prepared from Amberlite XE-89 showed substantial oxidation capacity to epoxidize olefinic compounds.[3]

In this paper, we wish to report the detail of our studies on the effects of the important factors in the synthesis of PAR and on their peculiar behavior as a polymer reagent.   In the course of the studies, PAR has been found to be very useful for the oxidation, since the oxidant is prepared in a pure form by a simple procedure, and the oxidized products can be separated readily by filtration.   This work demonstrates that PAR may provide an additional tool for the study of the mechanism of polymer reaction.

TABLE I
Compositions and Properties of Carboxylic Acid-Type Resins Used for Preparation of PAR

| | Composition of monomer[a] | | | Water content, wt-% | Ion exchange capacity,[b] meq/g |
Resin	Ethyl acrylate, mole-%	DVB, mole-%	Vinyl acetate, mole-%		
C-1	98.2	1.8	0	49.0	11.40
C-2	95.9	4.1	0	44.5	11.24
C-3	94.0	6.0	0	30.8	10.53
C-4	92.4	7.6	0	29.1	9.87
C-5	90.1	9.9	0	27.5	8.80
C-6	87.9	12.1	0	19.4	8.51
A-1	91.2	1.8	7.0	61.2	9.94
A-2	83.5	1.7	14.8	58.4	8.44
A-3	69.6	1.7	28.7	40.7	7.59
A-4	81.5	3.6	14.9	45.9	8.36
A-5	78.8	6.1	15.1	36.4	8.03
N-1	88.2	7.1	4.7[c]	32.6	8.95
N-2	83.0	7.0	10.0[c]	31.6	8.43
S-1	93.2	2.2	4.6[d]	28.2	10.52

[a] Monomer mixtures used for the preparation of the resins.
[b] Dry resin basis.
[c] Acrylonitrile.
[d] Styrene.

EXPERIMENTAL

Preparation of Cation Exchange Resins

The crosslinked poly(acrylic acid) resins were prepared by the method described in the literature.[2] The following ingredients were added to a 1-/liter flask and maintained at a temperature of about 90°C for 4 hr with vigorous stirring: 70 ml water, 55 g monomer mixture, 0.7 g benzoyl peroxide, and 1 g each of gelatin and talc. Most of the products were separated from the aqueous solution in the spherical beads. After saponification by refluxing with 10% NaOH ethanol solution for several hours, the cation exchange resins obtained were conditioned by several ion exchange cycles with $1M$ NaOH and $1M$ HCl, and then washed with deionized water. The resins prepared are listed with the compositions of the monomer mixtures, water contents, and ion exchange capacities in Table I. Resins of limited grain size (50–100 mesh) obtained by screening a quantity of the prepared resin were used for the preparation of PAR.

Oxidation of Cation Exchangers to PAR

Methanesulfonic acid (MS) (Tokyo Kasei, extra pure grade), p-toluenesulfonic acid (TS) (Kishida Chemicals, extra pure grade, water content: found 9.6%, calcd 9.7% for $C_7H_8O_3S \cdot H_2O$), 60% aqueous H_2O_2 (Mitsubishi-Gaskagaku, practical grade: found 60.1%), and H_2SO_4 (Nakarai Chemicals, guaranteed grade 100%) were used for the preparation of PAR without further purification. The oxidizing reagents were prepared by addition of the aqueous strong acid to 60% H_2O_2 at a temperature below $-10°C$ in the following ratios, unless otherwise stated: 75% MS 5:2 v/v, TS monohydrate 5:4 w/v, and 50% H_2SO_4 2:1 v/v. The cation exchanger, 0.15 g, was oxidized with 2.0 ml of the oxidizing

reagent at 40°C and then washed with cold methanol below −10°C until the filtrate became free of H_2O_2 and the strong acid.

Determination of Per Cent Conversion

Per cent conversion of carboxylic to percarboxylic acid groups (% conversion) was obtained by iodometry. The resin, 0.2–0.3 g, was oxidized as described above, and PAR obtained was transferred from an filter to a beaker using 50 ml of $0.1M$ H_2SO_4, saturated with KI, and kept at 40°C for 20 min. The iodine liberated was titrated with $0.1M$ sodium thiosulfate. The % conversion was calculated from the equivalent of thiosulfate required (a), carboxylic acid-type resin taken for oxidation (b, in g), and the ion exchange capacity of the carboxylic acid type resin (c, in equiv/g) by the following equation (both b and c are on a dry resin basis):

$$\% \text{ conversion} = (a/2bc) \times 100.$$

Determination of Oxidation Capacity

The oxidation capacity on a dry resin basis (P) and the solvent content (S) of PAR were calculated by the following equations:

$$S \ (\%) = [1 - (B/A) - (8D/C)] \times 100$$

$$P \ (\text{equiv/g}) = (100D/C)(100 - S).$$

Two lots of the swelled PAR each 0.2–0.3 g, were taken into 100-ml beakers. One (A in g) was reduced by keeping it with 0.5 g sodium bisulfite and 20 ml $0.1M$ H_2SO_4 at room temperature for 30 min; and after drying at 110°C, the reduced resin was weighed (B, in g). Another (C, in g) was used to get the value D, equivalent of thiosulfate required to titrate the iodine liberated by addition of KI.

Weight Loss of Resin in the Oxidation Process

It was obtained from the weight loss after the oxidation–reduction cycles. The method for the oxidation and reduction was similar to that described above.

Distribution of Strong Acids and Substrates

The content and concentration of strong acid in the resins were calculated from the weight of the acid solutions in the resins and the titration of the washings from the resins. After keeping 1 g of each of the resins for 6 hr in 5 ml of the strong acid of known concentration, the swelled resins were separated by centrifuging filtration, weighed, and then washed with water. The washings were titrated with $0.1M$ NaOH, and the washed resins were weighed after drying. The weights of the solutions in the resins were calculated from the differences between the weights of the swelled and the dried resins.

The distribution coefficients of the organic substrates were calculated from the per cent remaining in the solution phase and the volumes of the solution in each phase. The analyses were carried out by gas chromatography.

Oxidation of Organic Compounds with PAR

The substrates, cyclohexene, dimethylsulfide, cyclopentanone, cyclohexanone, and diethyl ketone (Tokyo Kasei, guaranteed grade), styrene, 2-pentene, cyclo-

dodecene, dimethyl sulfoxide, and 1-olefins (Tokyo Kasei, extra-pure grade) were used after refining by distillation. Azobenzene (Tokyo Kasei, extra-pure grade) and cholesterol (Tokyo Kasei, guaranteed grade) were used after refining by recrystallization. The cholesterol derivatives were synthesized according to the literature.[5] PAR was employed for the oxidation after sufficient washing with the solvent used for the reaction. The weighed resins were taken into the action vessels kept in a thermostated bath.

The oxidation was started by the addition of the substrate solution. The conditions of the oxidation are described in each table. The chromatographic analyses of the products were carried out using a Shimadzu GC 4APF gas chromatograph with flame ionization detectors and 1-m stainless steel columns of 3-mm internal diameter containing 60–80 mesh Chromosorb W coated with 15% squalane or 10% SE-30. The epoxides in the oxidized products of cholesterol and its derivatives were determined by titration with $0.1M$ HBr–acetic acid solution using crystal violet as an indicator. IR spectra were obtained on a Shimadzu IR 27A, and NMR analyses were carried out using a JEOL 60 HL.

RESULTS AND DISCUSSION

Influence of Resin Composition on Conversion to PAR

The conversions of the various resins to PAR are shown in Table II. Generally, increase in crosslinking, e.g., resins C-1 to C-6, decreases both the rate constants and the peracid per cent in the equilibrium. In sulfonic acid medium, the decrease is not so remarkable, and all the resins listed in Table II show good conversion. In 33% H_2SO_4 medium, poly(acrylic acid) resins crosslinked with less

TABLE II
Rate Data for Conversion of Carboxylic to Percarboxylic Acid Groups in the Resins[a]

Resin	p-Toluenesulfonic acid		Sulfuric acid	
	k_1[b]	Peracid in equilibrium,[c] %	k_1[b]	Peracid in equilibrium,[c] %
C-1	8.29	63.5	12.80	61.5
C-2	7.91	62.9	7.05	58.0
C-3	7.72	55.2	0.93	19.2
C-4	7.04	49.2	0.68	17.5
C-5	6.53	49.0	0.42	13.0
C-6	5.56	47.8	0.30	11.7
A-1	10.83	63.8	12.48	64.3
A-2	11.63	64.7	8.64	64.8
A-3	14.18	62.2	9.60	57.1
A-4	11.67	62.1	7.63	59.2
A-5	10.43	63.4	2.83	39.5
N-1	7.10	65.5	1.43	24.8
N-2	6.59	63.2	1.37	37.2
S-1	7.80	63.8	0.98	10.9
IRC-84	7.35	53.0	0.82	19.5

[a] The resin, 0.15 g, was oxidized with the reagent at 40°C.

[b] First-order rate constants calculated, assuming concentration of H_2O_2 was constant at the initial period of the reaction.

[c] Reaction periods 16 to 30 hr.

TABLE III
Influence of Resin Composition on Penetration of Sulfuric and Sulfonic Acids into the Resins[a]

Resin	Sulfuric acid		Sulfonic acid[b]	
	Content,[c] %	Concn, %	Content,[c] %	Concn, %
C-1	24.9	44.5	67.2	50.8
C-2	24.7	44.0	60.4	50.1
C-3	24.5	36.7	51.9	49.2
C-4	23.9	34.7	46.8	46.4
C-5	22.5	33.9	40.2	42.5
C-6	20.1	32.2	37.0	39.1
A-1	27.8	46.8	64.0	52.3
A-2	25.2	46.5	63.1	50.3

[a] Acid concentration of the solution added to resins, 50%. Temperature for acid treatment, 40°C.

[b] p-Toluenesulfonic acid.

[c] Weight per cent of the acids in the solution contained in the resins.

than 4% DVB (resin C-1 and C-2) were converted to PAR effectively, although the higher crosslinked polymers (resins C-3 to C-6), IRC-84, and XE-89 have shown poor conversion. Preparation of PAR with H_2SO_4–H_2O_2 reagent[6] has apparently not yet been reported, except for our preliminary communication,[3] though its failure was described in the literature.[2] When several per cent of sytrene copolymerized into the resins, even low crosslinked resins showed poor conversion with H_2SO_4–H_2O_2 (resin S-1). On the contrary, the introduction of the appropriate content of hydroxyl groups by the copolymerization of vinyl acetate into the resins enables effective oxidation of the higher crosslinked resins in H_2SO_4 medium and accelerates the oxidation in the sulfonic acid medium (resins A-1 to A-5).

Koyama and co-workers[7] recently reported polymerization of methyl methacrylate initiated with PAR of oxidation capacities of 4–5 meq/g on a dry resin basis, which were prepared by the oxidation of IRC-50 with TS–H_2O_2 according to our method. We were never able to obtain PAR of oxidation capacities higher than 0.6 meq/g on a dry resin basis from IRC-50, and the oxidized resins have never acted as initiator if H_2O_2 had been carefully removed. We found that PAR reported in our paper is an effective initiator for the polymerization of methyl methacrylate. Details will be presented in a subsequent paper.

In the oxidation of carboxylic to percarboxylic acid groups with strong acid–H_2O_2, the rate and the peracid per cent in the equilibrium state increase with increase in acid concentration. Influence of the resin compositions on the penetration of the acid into the resins is demonstrated in Table III. It shows that the penetration is dependent on the resin polarity. The low conversions of the less polar resins with H_2SO_4–H_2O_2 are attributable to their low affinity to inorganic strong acid, which prevents the sufficient penetration of H_2SO_4 into the resins. In contrast, the promotion of the oxidation by the introduction of hydroxyl groups is responsible for the increase in the affinity to H_2SO_4. Copolymerization of acrylonitrile into the resins resulted in increase in the peracid per cent in equilibrium (resins N-1 and N-2). It can be attributed to the conversion of the nitrile group to peroximidic and percarboxylic acids.[8]

The ion exclusion from carboxylic acid-type resins would take place by the effect of the protonated carboxylic acid group in the strong acid medium. Since

TABLE IV
Influence of Strong Acid Concentrations on the Oxidation Capacities of PAR Obtained[a]

Acid	%	Conversion,[b] %			
		3 hr	7 hr	11 hr	16 hr
Sulfuric	16	21.0	26.5	33.4	35.5
	33	48.3	51.4	52.0	52.7
	55	61.0	64.4	54.1	46.3
	75	54.8	28.2	14.9	6.9
Methanesulfonic	16	9.8	14.6	19.0	22.5
	33	39.4	42.7	43.9	45.2
	55	62.1	63.8	63.5	62.0
	75	77.4	76.5	61.8	51.0
Toluenesulfonic	70	53.0	54.6	55.2	55.7

[a] Resin C-2. Hydrogen peroxide in the reagent, 15%. Temperature, 40°C.
[b] Calculated from the oxidation capacities of the oxidized resins obtained.

the electrolyte exclusion is favored by high valence of the coion and the high crosslinking of the resins,[9] the low concentrations of H_2SO_4 in the highly crosslinked resins shown in Table III are understandable.

In spite of the little difference in crosslinking, a remarkable difference was observed in the conversions with H_2SO_4–H_2O_2 between C-2 and C-3. It might be partially due to additional effect of the low acidity of the percarboxylic acid group.[10] As conversion to PAR progresses, the decrease in the acidity will cause increase in H_2SO_4 concentration in the resin, which promotes the conversion to PAR.

Influence of Concentration of Strong Acid on Conversion

The conversions of the carboxylic acid-type resins to PAR are shown in Table IV. The results showed a maximum of the conversion in several hours in the acid medium of the high concentration. Decrease of the conversion can be understood by formation of the soluble fraction by the degradation of the resins, as described later. The data shown in Table IV give the optimum concentrations of the strong acids in the oxidizing reagents containing 15% of H_2O_2: MS, 55%; TS, 70%; and H_2SO_4, 33%. An adequate water content in the reagent is desirable for safety to prevent excessive oxidation which often causes explosion.

The plots of log K versus $-H_0$ were nearly straight lines in the oxidation of resins C-1 to C-4 in H_2SO_4 medium of concentrations below 50% in a similiar way as reported in the formation of the low molecular weight peracid.[11] The results are shown in Figure 1. Hammett's acidity function H_0 was obtained from the literature,[12] assuming that H_2O_2 has no influence on H_0.

Stability of PAR

One advantage of PAR prepared with strong acid–H_2O_2 is its excellent stability as described already in a preliminary communication.[3] The decomposition of the active oxygen in PAR was found to follow pseudo-first-order kinetics with respect to the oxidation capacity until the resin lost 40% of total active oxygen. The rate constants are shown in Table V. tert-Butyl alcohol was the best medium in the examined solvents for the preservation and the reaction of PAR. Dioxane, diglyme, and dimethoxyethane are excellent solvents next to tert-

TABLE V
Apparent First-Order Rate Constants for Decomposition of PAR in Various Media[a]

Solvent	$k \times 10^5 \text{ sec}^{-1}$				
	$-18°C$	$20°C$	$30°C$	$40°C$	$50°C$
tert-BuOH	—	—	0.44	0.59	1.33
Dioxane	—	0.55	1.43	2.35	5.58
Diglyme	0.104	0.43	1.39	—	—
Monoglyme	0.124	0.85	1.67	—	—
$CH_3OCH_2CH_2OCH_3$	0.112	0.59	1.45	—	—
CH_3OH	0.137	0.89	1.73	4.31	8.42
EtOH	—	1.18	2.24	5.45	10.21
iso-PrOH	—	1.67	3.34	10.83	20.10

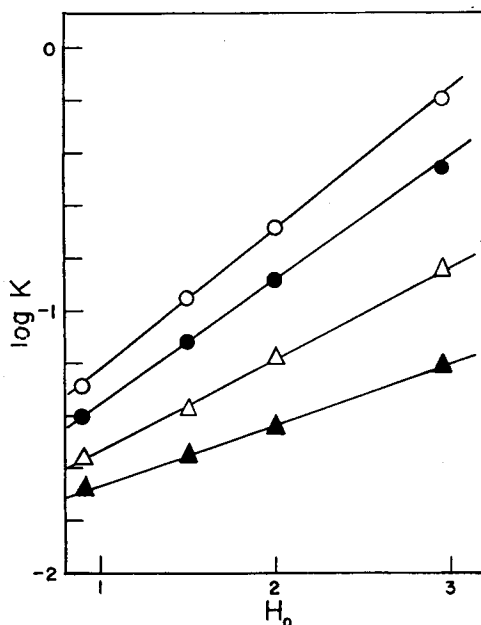[a] PAR C-2 (oxidation capacity, 5.7–6.5 meq/g) was used.

Fig. 1. Dependence of log K on H_0 in the conversion to PAR in sulfuric acid at 25°C. Resins: (O) C-1; (●) C-2; (△) C-3; (▲) C-4.

butyl alcohol. At a temperature as low as $-18°C$, methanol and monoglyme are adequate media. The removal of the solvent under reduced pressure from the PAR improved the stability significantly for preservation, but the dried resins were prone to explode by mechanical shock.

In this paper, the resistance of the resins to oxidative degradation was compared by the weight loss and change in oxidation capacity in the oxidation–reduction cycle. The results are indicated in Table VI. More degradation of the resins took place in the oxidation compared to that in the ion exchange cycle, of course. However, the resins show considerable durability as shown in Table VI. In the oxidation of the resins with H_2SO_4–H_2O_2, phenols were detected by ferric chloride test in the washings from the oxidized resins. It suggests cleavage between the tertiary carbon in the polymer chain and benzene ring by the cumene

TABLE VI
Durability of Resins in the Oxidation–Reduction Cycle[a]

Cycle	Weight loss %[b]				Oxidation capacity[c]			
	C-1	C-2	C-4	C-6	C-1	C-2	C-4	C-6
1	3.7	3.4	1.5	1.2	6.14	5.93	4.55	4.23
5	16.1	15.7	7.1	5.8	4.81	4.78	4.16	3.95

[a] Oxidation for one cycle was carried out with TS–H_2O_2 at 40°C for 7 hr.

[b] The per cent of the weight losses to the initial weight of the resin in dry resin basis.

[c] Dry resin basis, meq/g: (meq obtained by iodometry in the cycle)/(weight of the resin taken at the cycle).

oxidation mechanism. The idea was supported by little loss of the resin cross-linked with diisopropenylbenzene in the oxidation.[3]

Solvent Effects in Epoxidation of Cyclohexene with PAR

Gas chromatograms of the oxidized products from cyclohexene showed peaks of the substrate and the epoxidized product predominantly, but no peak of glycol. The epoxidation rates of cyclohexene with PAR were studied in the various solvents. Though the oxidation was carried out in a heterogeneous system, the epoxidation followed second-order kinetics apparently in all cases. The rate constants of the epoxidation with perbenzoic acid and PAR are shown in Table VII. The rate constants were larger in nonpolar solvents in the oxidation with perbenzoic acid as described by several authors.[13] On the contrary, they were definitely large in polar solvents when PAR was used for the oxidation.

At higher temperatures, the reaction rate cannot be discussed without regard to peracid decomposition in the resins. tert-Butyl alcohol was preferable to dioxane above 40°C as the reaction medium, was expected from the data shown in Table V. It is noteworthy in the data of Tables VII and VIII that the apparent rate constants shown by the resin oxidants were larger than those obtained by the low molecular weight peracids in polar solvents. There were more marked differences between the rate constants where the rate constants were

TABLE VII
Influence of Solvent on Reaction Rate in Epoxidation of Cyclohexene with PAR and Perbenzoic Acid

Reagent	Solvent	$k \times 10^3$ l./mole·min					E_a, kcal/mole	$-\Delta S\ddagger$, eu at 20°C
		10°C	15°C	20°C	25°C	30°C		
Perbenzoic acid[a]	benzene	383	545	765	—	—	13.0	24.5
	CCl_4	226	310	466	—	—	11.5	28.7
	dioxane	27.9	41.3	71.8	—	—	13.9	20.2
	t-BuOH	—	—	36.6	53.5	69.8	11.4	34.2
	EtOH	—	—	57.9	—	—	—	—
PAR[b]	dioxane	64.1	95.0	152	—	—	13.9	22.9
	t-BuOH	—	—	160	235	325	12.8	26.8
	iso-PrOH	—	—	137	178	301	13.2	25.4
	EtOH	—	—	501	—	—	—	—
	MeOH	—	—	675	—	—	—	—

[a] Initial concentration, 0.502–0.541 mole/l.

[b] Resin C-2; peracid %, 46–55%.

TABLE VIII
Kinetic Parameters for Epoxidation of Cyclohexene with PAR in Dioxane[a]

| | Original resin | | PAR | | $k \times 10^3$, l./mole·min | | | E_a, kcal/ mole | $-\Delta S\ddagger$, eu at 15°C |
No.	DVB, mole-%	Exchange capacity,[b] meq/g	Solvent content, wt-%	Oxidation capacity,[b] meq/g	10°C	15°C	20°C		
1	3.9	13.13	73.0	6.94	61.0	92.8	147.0	14.8	21.9
2	6.0	11.32	63.9	6.47	42.1	65.1	97.0	13.7	26.2
3	7.8	10.40	60.0	6.49	57.3	79.0	123.5	13.8	26.0
4	10.5	8.51	60.6	5.58	70.5	114.3	173.0	14.2	23.5
5	13.3	6.95	56.5	4.69	66.0	114.0	172.1	14.6	22.1
S-1	—	—	59.4	5.92	—	73.5	—	—	—
A-5	—	—	57.2	4.81	—	47.9	—	—	—

[a] Apparent kinetic parameters calculated for heterogeneous system consist of the solution and resin phases. Initial concentration: peracid, 0.979–1.109 meq/ml; cyclohexene, 0.247–0.293 meq/ml; equivalent ratio, 3.73–4.05.
[b] Dry resin basis.

TABLE IX
Apparent Second-Order Rate Constants for Epoxidation of Cyclohexene in the Resin Phase[a]

		Resin				
	Temp., °C	1	2	3	4	5
$k \times 10^3$, l./mole·min	10°C	124.2	99.5	129.8	147.0	162.6
	15°C	188.9	153.9	179.0	238.5	280.7
	20°C	299.3	229.3	179.9	360.7	423.9

[a] The rate constants were approximately calculated for the resin phase from data shown in Table VIII. The calculation was carried out assuming that the distribution coefficient of cyclohexene is 1.00 in every case.

calculated for the reaction in the resin phase, where the oxidation actually occurred, as shown in Table IX.

Influence of Degree of Crosslinking of the Resins on Epoxidation Rates

The rate constants increased with decrease in resin polarity introduced by the increasing of the resin crosslinking or copolymerization of styrene into the resin, when the resins were crosslinked with more than 4 mole-% DVB, as shown in Tables VIII and IX. The effect of the resin polarity will be discussed later in the relation to distribution effect. On the other hand, the crosslinking exerts a reverse effect on the rate constants when the resins are crosslinked with less than 4 mole-% DVB. It is attributable to the increase of the reaction probability due to the reduction of the crosslinking, which increases the mobility of the polymer chain and decreases the resistance to the motion of the substrate molecules in the resins. In this case, the resin polarity changes to a small degree and the distribution effect will not be so important.

Epoxidation of 1-Olefins

Epoxidation of 1-olefins was carried out in *tert*-butyl alcohol above 40°C with PAR. The pseudo-second-order rate constants of 1-olefin epoxidation are listed in Table X. It shows that the oxidation rate depends on the molecular weight. The maximum was observed at C_7–C_8 in the rate constants of 1-olefins C_5–C_{16}.

TABLE X
Kinetic Parameters for Epoxidation of 1-Olefins with PAR in *tert*-BuOH[a]

Carbon no.	PAR Solvent content, wt-%	PAR Oxidation capacity,[b] meq/g	$k \times 10^3$, l./mole·min 20°C	$k \times 10^3$, l./mole·min 25°C	$k \times 10^3$, l./mole·min 30°C	E_a, kcal/mole	$-\Delta S\ddagger$, eu at at 25°C
5	70.8	7.59	—	1.55	—	—	—
6	70.8	7.59	1.56	2.46	3.67	15.7	28.7
7	66.8	7.60	4.04	6.07	6.90	14.1	31.6
8	69.2	8.38	4.52	6.90	10.05	13.9	33.9
9	68.4	7.68	2.73	4.71	6.62	14.1	32.1
10	67.0	7.29	1.82	2.85	4.33	17.4	24.1
12	68.6	7.22	0.18	0.38	0.65	20.8	14.1
16	70.9	7.06	0.093	0.19	0.33	23.5	6.7

[a] Apparent kinetic parameters calculated for the heterogeneous system assuming it is homogeneous. Initial concentration: peracid, 0.971 meq/ml; 1-olefins, 0.469–0.586 meq/ml; equivalent ratio, 1.93–2.53.
[b] Dry resin basis.

The oxidation of methyl undecenoate shows that the introduction of an ester group depresses the oxidation.

Selective Oxidation of Cis and Trans Isomers of Cyclododecene

In the oxidation of cyclododecene with PAR, the trans isomer was converted into the epoxide selectively, as shown in Table XI. The ratio k_{trans}/k_{cis} increased almost 3 at $-18°C$.

The selectivity is quite different with those reported for the epoxidation of ordinary olefins with low molecular weight peracids. The remarkable rise in selectivity at the low temperature is ascribed to the increasing of the steric in-

TABLE XI
Relative Rates of *trans*-Cyclododecene to *cis*-Cyclododecene in Epoxidation with PAR and Perbenzoic Acid[a]

Reagent[b]	Solvent	Temp., °C	$k_t \times 10^3$, l./mole·min	k_t/k_c[c]
Resin C-2	dioxane	50	169	1.16
		30	28.5	1.48
		20	10.8	1.62
	MeOH	20	31.5	1.70
		10	19.0	2.01
		−18	2.48	2.82
Resin C-5	MeOH	10	7.51	2.03
		−18	0.54	2.79
Resin A-5	MeOH	10	17.0	1.74
		−18	1.48	2.35
Perbenzoic acid[d]	CH₂Cl₂	10	13.1	1.27
		−18	2.15	1.42

[a] Ratio of the apparent rate constants for the heterogeneous system.
[b] The peracid per cent of the resins was 47–53%.
[c] k_t, k_c: Rate constants for the trans and the cis isomers.
[d] Initial concentration, 0.572 mole/l.

teraction between the polymer matrix and cyclododecene, which is caused by the lowering of the molecular motions.

Epoxidation of Cholesterol with PAR

In the epoxidation, the neighboring group participation by hydroxyl group and the steric hindrance near the double bond have been known as important factors for stereoselectivity. In the epoxidation of cyclic allyl alcohol, e.g., cyclohex-2-en-1-ol, the cis stereoselectivity has been illustrated by the hydrogen bond formation between the hydrogen of the hydroxyl group and the carbonyl nucleophilic oxygen of the percarboxylic acid group in the transition state.[14] Stereoselectivity by the same mechanism was observed also in the oxidation of 3-β-hydroxy 5,10-unsaturated steroid, which gave β-epoxide chiefly.[15] On the contrary, the α-epoxide was reported as a major product in the epoxidation of cholesterol with percarboxylic acid, specially with m-chloroperbenzoic acid.[16]

The compositions of the epoxide determined by NMR analysis[17] are shown in Table XII. The high per cent from the free sterol and nearly equal per cent of α- and β-epoxides in the products from cholesteryl acetate and 5-cholestene-3-one are reasonably explained in terms of the steric effect, including hydrogen bond formation between β-hydroxy and percarboxylic acid groups at the β-side. The electrophilic oxygen of the percarboxylic acid will be too far from the 5:6 double bond of cholesterol for the reaction in the associated state by the hydrogen bonding. Therefore, the hydroxyl group interrupts the attack of the peracid group on the double bond from the β-side through the hydrogen bond formation, together with steric hindrance of rings B, C, and D and the side chain of cholesterol on the other angle of the double bond. The nonstereoselective epoxidation of cholesteryl acetate and cholestenone indicates that steric hindrance by the hydrogen bond formation is required for the steroselectivity. The higher α-stereoselectivity of the resin reagents in the epoxidation of the free sterol can be attributed to the fact that there is the additional effect of the steric hindrance between the bulky polymer molecule and the β-side of cholesterol molecule.

Distribution Effects in Epoxidation

A explanation of the remarkable epoxidation rates with PAR must include distribution effects. The distribution coefficients of cyclohexene between PAR and the solution phases were estimated indirectly from those of benzene and cyclohexane. The distribution coefficients increased evidently with increasing the crosslinking degree of the resins and the solvent polarity, as shown in Table XIII. The results are reasonable, since a nonpolar solute has an affinity for less

TABLE XII
Per cent of α-Epoxide in Total Epoxides Produced in Oxidation of Cholesterol and
Its Derivatives[a]

Reagent	Cholesterol	Acetate	Cholestenone
Resin C-2[b]	95.4 (50.7)[c]	67.9	65.1
Perbenzoic acid	70.2 (64.0)	54.7	51.5
m-Chloroperbenzoic acid	78.5 (75.6)	59.2	53.4

[a] Determined by NMR (α-epoxide, $\tau = 7.11$; β-epoxide, $\tau = 6.93$.

[b] Peracid per cent, 47% dry resin basis.

[c] Per cent conversion to the epoxide determined by HBr titration.

TABLE XIII

Distribution Coefficients of Benzene and Cyclohexane Between Resin and Solution Phases[a]

Resin	Oxidation capacity,[b] mole/g	Dioxane		tert-BuOH	
		Benzene	Cyclohexane	Benzene	Cyclohexane
C-1	6.18	0.93	0.97	1.75	1.86
C-2	6.22	1.05	1.13	1.91	1.99
C-3	5.72	1.08	1.15	2.08	2.03
C-4	4.05	1.16	1.20	2.14	2.07
C-5	3.47	1.21	1.26	2.19	2.15

[a] Solute, 5% v/v; temperature, 20°C.
[b] Dry resin basis.

polar phases. Thus, the acceleration of the oxidation by the employment of the polar solvents and the nonpolar resins is realized by the distribution effect.

In the course of the epoxidation, the products must be reabsorbed from the resins rapidly for the oxidation to proceed continuously. Since the epoxides are more polar than the original olefins, they are reabsorbed rapidly, and the oxidation proceeds smoothly. In the epoxidation, conversion to the epoxides was negligible when the solvent was less polar than the resin; in that case, the substrates almost remained in the solution phase. In the oxidation of the basic nitrogen compounds, hardly any oxidation products were recovered. Probably, the substrates and the oxidized products, fixed in the resin in salt forms, interrupt the oxidation process.

In the reaction with a resin reagent, the diffusional resistance in the resin and the solution phases, and at the resin–solution interface, makes the reaction rate slow. Nevertheless, the rate constants of the oxidation with PAR were considerably larger than those with low molecular weight peracids under the conditions as already described. This is attributable to the distribution effects, which exceed the retardation by the diffusion. Previously, an analogous acceleration of the reaction by distribution effects has been reported in the catalytic hydrolysis of esters with sulfonated polystyrene.[18]

Selective epoxidation of 1-olefins shown in Table X could be similarly attributed to the distribution effects. London forces may result in stronger sorption in large molecules.[19] However, sorption of large molecules is adversely affected by the swelling pressure in the resin, and molecules which exceed a critical size are excluded from the resins by the sieve action of the resin matrix.[20] The distribution coefficients of the homologs may thus have maximum values for members of medium size. The maximum rate constants in the epoxidation of 1-olefins can be attributed to the distribution effect.

Protective Effects and Intramolecular Catalytic Effects in Epoxidation

In spite of the small distribution effect, the relative rates in the oxidation with PAR were considerably higher in dioxane, as shown in Table VII. Further, it seems likely that the relative rates of the oxidation with the resins are generally higher than those expected from the rate constants of the oxidation with low molecular weight peracids under the consideration of the distribution effects. A possible explanation for the facts is the protective effect of the polymer matrix to keep the percarboxylic acid group to the intramolecularly bonded cyclic

TABLE XIV
Influence of Medium on Carbonyl and Hydroxyl Stretching Frequencies of Percarboxylic
Acid Group (cm^{-1})

Solvent[a]	Perpalmitic acid		PAR	
	$\nu_{C=O}$	ν_{OH}	$\nu_{C=O}$	ν_{OH}
Nujol	1745	3210	1767	3450
n-Octanol	1760		1762	
Dioxane	1774	$\begin{cases} 3210 \\ 3515 \\ 3590 \end{cases}$	1765	3455

[a] Measured by paste method.

TABLE XV
Oxidation of Various Organic Compounds with PAR

Substrate[a]	Temp., °C	Solvent	Time, hr	Equiv. ratio[b]	Conversion, %[c]	Product
CH$_3$SOCH$_3$	20	dioxane	0.1	1.5	98.7	sulfone
Cyclohexene	20	dioxane	0.5	2.5	83.8	epoxide
CH$_3$SCH$_3$	20	dioxane	2	1.9	92.2	sulfone
2-Pentene	30	dioxane	2	2.0	85.4	epoxide
Cyclododecene	30	t-BuOH	2	3.2	86.0	epoxide
Cyclohexanone	40	H$_2$O	1.5	2.5	96.0	lactone
Diethyl ketone	40	H$_2$O	2	4.0	86.2	lactone
1-Octene	50	t-BuOH	2	4.6	89.7	epoxide
1-Hexadecene	60	t-BuOH	3	3.2	86.5	epoxide
Styrene	60	t-BuOH	6	5.8	81.2	epoxide
Azobenzene	60	t-BuOH	6	5.3	81.6	azoxy

[a] Concentration of substrate, 5% w/v.

[b] (Oxidation equivalent of PAR)/(equivalent of the substrate).

[c] Conversions are shown by the area per cent of the product peaks in the gas chromatograms, except for azoxybenzene, which was determined by spectrometry.

structure, the intramolecular catalytic effect of the neighboring carboxylic acid group, and the ion exclusion effect, which reduces the solvation of the percarboxylic acid groups.

Comparison of the infrared spectra of PAR and perpalmitic acid is shown in Table XIV. Carbonyl and hydroxyl stretching frequencies hardly shifted by change of solvent polarity in the former, although they shifted appreciably in the latter, as already known.[13] It can therefore be presumed that the difference of the solvent polarity has less influence on the contents of the intramolecularly bonded cyclic percarboxylic acid group, which essentially acts for epoxidation. Probably, the steric hindrance of the resin matrix and the reduction of the solvent activity by the ionic solvation of the carboxylic acid group will interrupt the opening of the cyclic peracid group. In this manner, the oxidation ability of the resins would not be influenced relatively by the polar solvents. The possibility must also be considered that the catalytic effects of the neighboring carboxylic acid group in the resins are positive driving forces in the oxidation. Catalytic action of the carboxylic acid group in the polymers has been reported in several papers, e.g., in hydrolysis of p-nitrophenyl methacrylate.[21] On the other hand, intramolecular catalytic mechanism by carboxylic acid group was presented in

the Baeyer-Villiger oxidation with permaleic acid by White and Emmons,[22] while the intermolecular catalytic effects of carboxylic acid groups in the epoxidation with percarboxylic acids are rather negative.[23]   An intramolecular catalytic mechanism might be possible in this case, but further study is required to prove it.

Oxidation of Organic Compounds with PAR

Optimum conditions for the oxidation of some organic compounds are shown in Table XV, in which the substrates are listed in order of reactivity in the oxidation with PAR, which decreases from top to bottom.   The substances shown above 2-pentene in the table were selectively oxidized in the presence of the other members in dioxane.   Some basic nitrogen compounds, aniline, dimethylaniline, octylamine, and pyridine, could not be oxidized smoothly by the procedures used in this experiment.

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