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Mechanism of the Oxidation of *p,p'*-Dichlorobenzyl Sulfide by Peroxybenzoic and *para* Substituted Peroxybenzoic Acids

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A study was made of the oxidation of *p,p'*-dichlorobenzyl sulfide to sulfoxide by peroxybenzoic and *p*-methoxyperoxybenzoic acids in toluene, and by peroxybenzoic, *p*-methoxy-, *p*-methyl-, *p*-chloro- and *p*-nitroperoxybenzoic acids in isopropyl alcohol. Activation energies, frequency factors and entropies of activation were obtained. The differences in oxidation rates between peroxyacids were found to be influenced approximately 60% by differences in activation energy and 40% by differences in activation entropy with $\Delta S^{\ddagger}$ increasing approximately linearly with E. Electron attracting groups in the *p*-position increased the oxidation rate, while electron repelling groups decreased it. The Hammett treatment of the substituent effect gave an excellent straight line with the exception of the point for *p*-methoxyperoxybenzoic acid. Large differences in entropy of activation for the oxidations by peroxybenzoic, *p*-methyl- and *p*-nitroperoxybenzoic acids in isopropyl alcohol were observed. Solvent likewise had a pronounced effect on k, E and $\Delta S^{\ddagger}$. A mechanism for peroxybenzoic acid oxidations is proposed. The four *p*-substituted peroxybenzoic acids employed were isolated and characterized for the first time.

It has long been known that organic peroxyacids are much stronger oxidants than hydrogen peroxide and that of all the derivatives of hydrogen peroxide, only the peroxyacids are strong oxidants in the cold.[2] Lewin[3] in 1928, commented on the ease with which sulfides may be oxidized to sulfoxides by peroxybenzoic acid at ordinary temperatures and observed that peroxybenzoic acid will effect some oxidations where hydrogen peroxide and other oxidants fail. Criegee[2] suggested that the effectiveness of peroxyacids as oxidants is the result of strong polarization due to their dissymmetry about the O–O bond so that a peroxyacid will dissociate more readily than symmetrical hydrogen peroxide under the influence of a reductant. Medvedev and Blokh[4] in 1933 reported the rates of oxidation of cyclohexene to epoxycyclohexane in benzene and xylene by several substituted peroxybenzoic acids and concluded that the oxidations were bimolecular uncatalyzed by the corresponding carboxylic acids, and that the rates were markedly influenced by solvents. More recently Szmant, Harnsberger and Krahe[5] found that the oxidation of phenyl sulfoxide to sulfone by peroxybenzoic acid followed bimolecular reaction kinetics and that the oxidation was catalyzed by benzoic acid.

A study of the kinetics of oxidation of *p,p'*-dichlorobenzyl sulfide by peroxybenzoic and four *p*-substituted peroxybenzoic acids was made in isopropyl alcohol and toluene with the objective of obtaining an insight into the mechanism of organic peroxyacid oxidation. A similar investigation with hydrogen peroxide is reported separately.[6]

Experimental

Materials.—*p,p'*-Dichlorobenzyl sulfide, m.p. 41.5–42.0° uncor., was prepared as described by Overberger, Ligthelm and Swire[7] (40.5–41.0°).[7]

Benzoic acid, sublimed (Baker Analyzed Reagent), m.p. 121.5–122.0°, was used without further purification.

Isopropyl alcohol (Baker Analyzed Reagent) was dried with magnesium isopropoxide according to the general procedure described previously,[8] except that carbon tetrabromide was substituted for iodine as a catalyst. The dried alcohol was separated from the reaction mixture by simple distillation using a magnesium perchlorate drying tube for protection against moisture, and the distillate fractionated from sodium isopropoxide using a 100- by 2-cm. column packed with $^1/_8$-inch, single-turn glass helices. A middle one-third cut was collected, b.p. 82.1–82.8° (760 mm.), $n^{20}\mathrm{D}$ 1.3775 [b.p. 82.5° (760 mm.), $n^{20}\mathrm{D}$ 1.3776].[9]

Toluene (Baker Analyzed Reagent) was extracted with concentrated sulfuric acid followed by distilled water, dried over sodium and fractionated from sodium using the above described column. A middle one-half cut was taken, b.p. 110.3° (760 mm.), $n^{20}\mathrm{D}$ 1.4970 [b.p. 110.8° (760 mm.), $n^{20}\mathrm{D}$ 1.4955].[9]

Magnesium perchlorate, C.P. anhydrous, was obtained from the G. Frederick Smith Chemical Company.

p,p'-Disubstituted benzoyl peroxides were prepared from the corresponding benzoyl chlorides by the method of Price and Krebs.[10] *p*-Methoxy-, *p*-chloro- and *p*-nitrobenzoyl chlorides were Eastman White Label grade; *p*-methylbenzoyl chloride was prepared from *p*-methylbenzoic acid and thionyl chloride. All of the peroxides were of 95% purity or better immediately before use as determined by the Kokatnur and Jelling[11] peroxide method. The peroxides had been prepared and characterized previously: *p,p'*-dimethyl-,[12] *p,p'*-dimethoxy-,[13] *p,p'*-dichloro-[14] and *p,p'*-dinitrobenzoyl peroxide.[15]

p-Substituted peroxybenzoic acids were prepared from the peroxides essentially by the Kolthoff, Lee and Mairs modification[16] of the Braun procedure.[17] The concentration (g./100 ml. of solution) of the chloroform solutions of the *p*-substituted benzoyl peroxides employed in the peroxyacid preparations, as dictated by their solubilities, were: *p*-H–, 25.0; *p*-CH$_3$O–, 10.0; *p*-CH$_3$–, 10.0; *p*-Cl–, 8.0; *p*-NO$_2$–, 4.0. The amounts of sodium and sulfuric acid used were in proportion to the peroxide concentrations. An ice–acetone-bath was found more convenient than the customary salt–ice mixture for refrigerating the reactants. The resulting benzene solutions of the peroxyacids, containing 2.5 to 3.0 g. of peroxyacid per 100 ml., were extracted with

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(1) A portion of a thesis by R. W. Cummins submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(11) V. R. Kokatnur and M. Jelling, THIS JOURNAL, **63**, 1432 (1941).

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TABLE I

ANALYTICAL DATA FOR *p*-SUBSTITUTED PEROXYBENZOIC ACIDS: RC_6H_4COOOH

			Analytical data[c]					
			Calcd.			Found		
R	M.p., °C.[a]	Yield, %	C	H	O	C	H	O
p-CH_3O–	85–86	63	57.14	4.76	9.52	57.39	5.06	9.04
p-CH_3	95–96	69	63.16	5.26	10.53	63.29	5.54	9.93
p-H	40–41.5	55	...	..	11.59	...	..	11.46
p-Cl–	111–113[b]	67	48.69	2.90	9.28	48.98	3.16	8.68
p-NO_2	134–136[b]	40	45.90	2.73	8.74	46.20	2.80	8.38

[a] All melting points are corrected. [b] The *p*-chloro- and *p*-nitroperoxybenzoic acids decomposed without melting at the indicated temperatures using a heating rate of 7 degrees per minute. The decomposition point of *p*-nitroperoxybenzoic acid was determined in a sealed capillary tube. [c] Carbon and hydrogen analyses performed by Dr. F. Schwarzkopf, New York, N. Y.; peroxide oxygen was determined by iodometric titration employing the method of Kokatnur and Jelling.

one-half their volume of 10% aqueous sodium acetate solution at room temperature which served to remove the bulk of the stronger carboxylic acid without appreciably reducing the peroxyacid concentration. The effectiveness of the acetate extraction for peroxybenzoic acid was thoroughly demonstrated.[18] The extracted benzene solutions were stored over sodium sulfate in glass-stoppered flasks in the dark in a refrigerator at 5–10°. One specimen of peroxybenzoic acid prepared in this manner decomposed to the extent of only 6.4% in 15 days, while *p*-methoxyperoxybenzoic acid prepared and stored under similar conditions was 38% decomposed in 16 days.

The peroxybenzoic acids were isolated from benzene solution by evaporation under water aspirator vacuum in a Werner–Klein microsublimation apparatus[19] at 30–35° followed by vacuum sublimation of the residue under the full vacuum of a Hyvac oil-pump at temperatures of 40 to 75°. Peroxybenzoic acid sublimed readily at 40°, while higher temperatures were required for the *p*-substituted peroxybenzoic acids. During periods of high humidity, considerable difficulty was experienced in obtaining solid peroxybenzoic acid by sublimation. *p*-Chloro- and *p*-nitroperoxybenzoic acid were more conveniently isolated from benzene solution by crystallization at 10°. The melting points, yields and analytical data for the five peroxybenzoic acids are summarized in Table I. The melting points and analytical data for all of the peroxyacids were determined on sublimed samples, except for *p*-chloro- and *p*-nitroperoxybenzoic acid for which specimens crystallized from benzene were used. Sublimed peroxyacids were employed exclusively in the kinetic work.

Baeyer and Villiger[20] crystallized peroxybenzoic acid (m.p. 41–43°) from chloroform solution in 97.5% purity (iodometric titration). *p*-Methoxy- and *p*-nitroperoxybenzoic acids were prepared in toluene and xylene solution from the corresponding peroxides by Medvedev and Blokh,[4] but were not isolated and characterized. *p*-Methyl- and *p*-chloroperoxybenzoic acids have not previously been described.

Kinetic Measurements.—The rate of peroxyacid consumption by sulfide was followed by iodometric titration using the Kokatnur and Jelling[11] peroxide method. It was necessary to conduct the oxidation at temperatures as low as –65° to obtain measurable reaction rates, and at these temperatures it was found more convenient to quench the entire reaction mixture and titrate than to withdraw aliquots for this purpose.

The apparatus consisted of a 250-ml. Pyrex Soxhlet flask, a 15-ml. weighing bottle, a 4-quart dewar jar equipped with motor-driven stirrer, and two –100 to +50° thermometers. The Soxhlet flask and weighing bottle were cleaned with cleaning solution, rinsed with water followed by acetone, and air-dried with filtered compressed air for several minutes before use.

p,p'-Dichlorobenzyl sulfide stock solution (0.0200 *M*) was prepared by weighing 1.415 g. of *p,p'*-dichlorobenzyl sulfide into a 250-ml., glass-stoppered volumetric flask followed by dissolution and dilution to the mark with fractionated solvent.

Peroxyacid stock solutions (*ca.* 0.0200 *M*) were prepared immediately before use by dissolving and diluting the freshly sublimed peroxyacids with fractionated solvent. The peroxyacid stock solutions were maintained at 20–25° during the kinetic measurements, and their stabilities determined by iodometric titration of 10-ml. aliquots at one-hour intervals.

In investigating the effect of added salt on oxidation rate, isopropyl alcohol 0.10 *M* in magnesium perchlorate was used for preparing both the sulfide and peroxyacid stock solutions.

In a typical rate run the Soxhlet flask containing the weighing bottle was immersed in acetone contained in the dewar jar and previously cooled to within a few degrees of the reaction temperature by the addition of powdered Dry Ice. A 10-ml. aliquot of the sulfide stock solution was pipetted into the Soxhlet, taking care not to allow any of it to enter the weighing bottle. A 10-ml. aliquot of the peroxyacid stock solution was next pipetted into the weighing bottle. One of the thermometers was inserted into the sulfide stock solution contained in the Soxhlet, the other into the acetone–Dry Ice mixture. The temperature of the sulfide solution was adjusted to within ±0.5° of the desired reaction temperature at which time the peroxyacid solution was mixed with the sulfide by overturning the weighing bottle with the thermometer and stirring. After the desired time interval, during which time the temperature variation was held to ±0.5° or better, the reaction was quenched by adding as rapidly as possible a solution of 0.5 g. of sodium iodide and 2 ml. of glacial acetic acid in 10 ml. of isopropyl alcohol, freshly prepared in a 25-ml. glass-stoppered graduate. The mixture was then rapidly heated to incipient boiling and titrated at once with 0.01 *N* sodium thiosulfate to the disappearance of the iodine color. It was necessary to repeat the above-described operation for each point of the rate plots. Each titration was corrected for the peroxyacid decomposition sustained at 20–25° during the time elapsed between the first titration and each subsequent titration.

The oxidations were followed over 3-minute periods at temperatures ranging from –65 to –15°, depending on the substituent and solvent, providing coverage of 50% or more of the reaction. In one peroxybenzoic acid oxidation in isopropyl alcohol at –20°, a product melting at 162.5 to 163.8° was isolated in 87% yield; after recrystallization once from ethyl alcohol the crystals melted at 164–165° cor. The reported[7] m.p. of *p,p'*-dichlorobenzyl sulfoxide is 164.8–165.1°.

Results and Discussion

General.—Rate data were obtained at three temperature intervals for peroxybenzoic and *p*-methoxyperoxybenzoic acid in toluene, and for peroxybenzoic, *p*-methoxy-, *p*-methyl-, *p*-chloro- and *p*-nitroperoxybenzoic acid in isopropyl alcohol. The second order law was found to be obeyed accurately in all cases; activation energies and frequency factors were obtained from the variation of ln *k* with $1/T$, the method of least squares being used exclusively. The entropy of activation, $\Delta S^{\ddagger}$, was calculated from the frequency factor *A* by means of the equation[21]

$$A = e(k'T/h)e^{\Delta S/R}$$

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[18] Detailed information can be obtained on request of the senior author. Total acid was determined by titrating 2-ml. aliquots in isopropyl alcohol to the phenolphthalein end-point with 0.1 *N* sodium hydroxide; peroxyacid was determined by titrating 2-ml. aliquots with 0.01 *N* thiosulfate.

[19] G. Klein and O. Werner, *Z. physiol. Chem.*, **143**, 141 (1935).

[20] A. Baeyer and V. Villiger, *Ber.*, **33**, 1576 (1900).

[21] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.

TABLE II

SPECIFIC RATE CONSTANTS, ACTIVATION ENERGIES, FREQUENCY FACTORS AND ACTIVATION ENTROPIES FOR THE OXIDATION OF *p,p'*-DICHLOROBENZYL SULFIDE IN TOLUENE AND ISOPROPYL ALCOHOL BY *p*-SUBSTITUTED PEROXYBENZOIC ACIDS: *p*-RC_6H_4COOOH[a]

R	Temp., °C.	k, l. mole^{-1} sec.$^{-1}$	E, kcal. mole^{-1}	ln A	$\Delta S^{\ddagger}$, cal. mole^{-1} deg.$^{-1}$, −35°
		Toluene			
p-CH_3O–	−65	0.61 ± 0.03			
	−55	1.32 ± .07			
	−45	2.44 ± 12	6.6 ± 0.4	15.4 ± 1.2	−29.5 ± 2.3
p-H–	−65	1.47, 1.29 ± 0.07			
	−55	2.32, 2.50 ± 0.12			
	−45	4.17 ± 0.21	5.2 ± 0.3	13.0 ± 1.0	−34.3 ± 2.7
		Isopropyl alcohol			
p-CH_3O	−35	0.19, 0.19 ± 0.01			
	−25	.49, .44 ± .02			
	−15	.95, .95 ± .05	9.9 ± 0.5	19.3 ± 1.5	−21.7 ± 1.7
p-CH_3	−40	.11 ± 0.01			
	−30	.29 ± .02			
	−20	.70 ± .04	11.3 ± 0.6	22.1 ± 1.8	−16.2 ± 1.3
p-H–	−40	0.18, 0.15 ± 0.01			
	−30	.43, .38 ± .02			
	−20	.86, .79 ± .04	9.6 ± 0.5	19.0 ± 1.5	−22.3 ± 1.7
p-Cl–	−45	.12, .17 ± .01			
	−35	.43, .45 ± .02			
	−25	.88, .89 ± .05	9.6 ± 0.5	19.5 ± 1.6	−21.4 ± 1.7
p-NO_2	−55	.43 ± 0.02			
	−45	.88 ± .05			
	−35	1.60 ± .08	6.9 ± 0.4	15.1 ± 1.2	−30.1 ± 2.4

[a] The indicated uncertainties in the experimental values are estimated indeterminate errors.

The rate constants, E and ln A, obtained in the temperature range studied as well as $\Delta S^{\ddagger}$ at −35° are collected in Table II. Some typical second order rate plots are shown in Fig. 1, while several representative Arrhenius plots are set forth in Fig. 3. Representative experimental data used to determine order (Fig. 2) are summarized in Table III and clearly demonstrate over-all second order kinetics by the integration method.

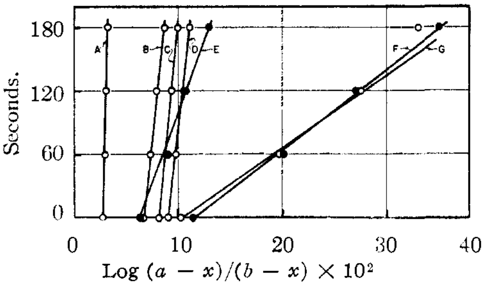

Fig. 1.—Second-order rate plots for *p*-RC_6H_4COOOH oxidation of *p,p'*-dichlorobenzyl sulfide: ●, points obtained in toluene; O, points obtained in isopropyl alcohol; A, *p*-CH_3 at −40°; B, *p*-CH_3O at −35°; C, *p*-H at −40°; D, *p*-Cl at −45°; E, *p*-CH_3O at −65°; F, *p*-H at −65°; G, *p*-NO_2 at −35°.

The indicated uncertainties in k, E, ln A and $\Delta S^{\ddagger}$ are indeterminate errors estimated from relative errors in the experimental measurements. The largest errors originated in the determination of peroxyacid concentration and time.

A plot of E *vs.* $T\Delta S^{\ddagger}$ for the oxidation in both isopropyl alcohol and toluene, presented in Fig. 4,

TABLE III

(A) DETERMINATION OF THE OVER-ALL ORDER OF THE OXIDATION OF *p,p'*-DICHLOROBENZYL SULFIDE BY PEROXYBENZOIC ACID IN TOLUENE AT −55° BY THE INTEGRATION METHOD[a]

Time, sec.	$b - x$	log $(b - x)$	$1/(b - x)$	$1/(b - x)^2$
0	0.01004	−1.99827	99.60	9,921
60	.00373	−2.42829	268.1	71,875
120	.00246	−2.60906	406.5	165,242
180	.00183	−2.73755	546.4	298,607

(B) DETERMINATION OF THE OVER-ALL ORDER OF THE OXIDATION OF *p,p'*-DICHLOROBENZYL SULFIDE BY *p*-METHOXYPEROXYBENZOIC ACID IN ISOPROPYL ALCOHOL AT −15° BY THE INTEGRATION METHOD[b]

Time, sec.	$b - x$	log $(b - x)$	$1/(b - x)$	$1/(b - x)^2$
0	0.00996	−2.00174	100.4	10,081
60	.00620	−2.20761	161.3	26,015
120	.00457	−2.34008	218.8	47,881
180	.00366	−2.43652	273.2	74,652

(C) DETERMINATION OF THE OVER-ALL ORDER OF THE OXIDATION OF *p,p'*-DICHLOROBENZYL SULFIDE BY *p*-METHYLPEROXYBENZOIC ACID IN ISOPROPYL ALCOHOL AT −20° BY THE INTEGRATION METHOD[c]

Time, sec.	$b - x$	log $(b - x)$	$1(b - x)$	$1/(b - x)^2$
0	0.00952	−2.02136	105.0	11,034
60	.00650	−2.18709	153.8	23,669
120	.00497	−2.30364	201.2	40,484
180	.00416	−2.38091	240.4	57,786

[a] a = 0.01000, b = 0.01004; 82% of reaction covered.
[b] a = 0.01000, b = 0.00996; 63% of reaction covered.
[c] a = 0.01000, b = 0.00952; 54% of reaction covered.

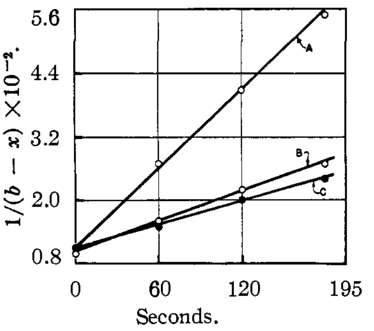

Fig. 2.—Second-order rate plots for peroxybenzoic acid oxidation of p,p'-dichlorobenzyl sulfide: A, peroxybenzoic acid oxidation in toluene at −55°; B, p-methoxyperoxybenzoic acid oxidation in isopropyl alcohol at −15°; C, p-methylperoxybenzoic acid oxidation in isopropyl alcohol at −20°.

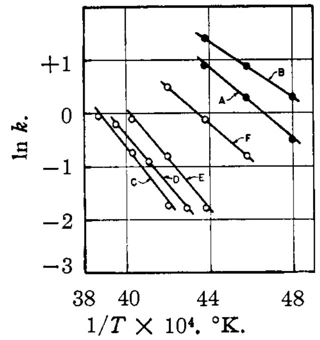

Fig. 3.—Arrhenius plots for p-RC_6H_4COOOH oxidation of p,p'-dichlorobenzyl sulfide: ●, points obtained in toluene; O, points obtained in isopropyl alcohol; A, p-CH_3O; B, p-H; C, p-CH_3O; D, p-H; E, p-Cl; F, p-NO_2.

shows that $\Delta S^{\ddagger}$ increases approximately linearly with increasing activation energy. The hydrolysis of esters and amides and many other reactions behave similarly.[22]

Effect of Acid.—The effect of added benzoic acid on oxidation rate of peroxybenzoic acid in isopropyl alcohol was measured at −20, −30 and −40°. At the three temperatures investigated the addition of benzoic acid to bring the initial concentration to 0.01 M did not change the rate constants beyond the estimated limits of error. (Detailed data will be furnished on request.) Furthermore, the excellent adherence to the second order law observed over wide limits in all cases shows that the corresponding benzoic acid formed as a reaction product does not catalyze the rate.

Effect of Solvent.—Specific rate constants for the peroxybenzoic and p-methoxyperoxybenzoic acid oxidations in toluene and isopropyl alcohol are compared in Table IV at −35° by extrapolation of the data in Table II using the relation $\ln k = \ln A - E/RT$. The specific rate constants were 24 to 26 times greater in toluene than in isopropyl alcohol. A comparison of the activation energies and entropies of activation for these oxidations, also presented in Table IV reveals differences: the activation energies were 3 to 4 kcal. per mole higher in isopropyl alcohol than in toluene while the entropies of activation were 8 to 12 entropy units lower in toluene than in isopropyl alcohol. The differences in specific rate constants were estimated[23] to be about 60% dependent on differences in energies of activation and 40% on activation entropies.

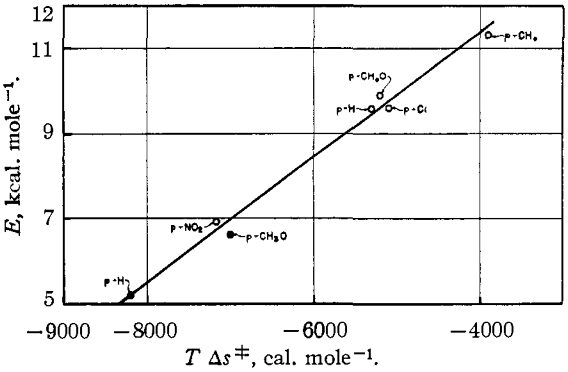

Fig. 4.—Plot of E vs. $T\Delta S^{\ddagger}$ for p-substituted peroxybenzoic acid oxidations in isopropyl alcohol and toluene: O points obtained in isopropyl alcohol; ● points obtained in toluene.

TABLE IV

EFFECT OF SOLVENT ON SPECIFIC RATE CONSTANTS AND ACTIVATION ENERGIES AND ENTROPIES AT −35[a]

	R p-CH_3O–	p-H–
Toluene	4.6 ± 0.2	6.8 ± 0.4
	6.6 ± 0.4	5.2 ± 0.3
	29.5 ± 2.3	−34.3 ± 2.7
Isopropyl alcohol	0.19 ± 0.01	0.26 ± 0.01
	9.9 ± 0.5	9.6 ± 0.5
	−21.7 ± 1.7	−22.3 ± 1.7

[a] The specific rate constants at −35° were obtained from the data in Table II by extrapolation using the relation—$\ln k = \ln A - E/RT$.

The Substituent Effect.—The influence of substituents may be considered with reference to the substituent constants σ and ρ introduced by Hammett.[24]

The oxidation rates increased with increasing electron-attracting power of the p-substituent, as may be seen when the specific rate constants for the five peroxybenzoic acids in isopropyl alcohol are compared at −35°. A plot of $\log k/k_0$ vs. the Hammett σ-values defined an excellent straight line, as shown in Fig. 5, with the exception of the point for p-methoxyperoxybenzoic acid. A ρ-value of +1.05 was calculated by the method of least squares, disregarding the point for p-methoxyperoxybenzoic acid.

The rate data of Medvedev and Blokh[4] showing the effect of p-methoxy and p-nitro substituents on the rate of oxidation of cyclohexene to epoxycyclohexane by peroxybenzoic acid in xylene at 25° are plotted in Fig. 5 for comparison with the sulfide oxidations. A ρ-value of 0.94 was calculated by the method of least squares.

Significant differences in entropies of activation appear among the p-methyl-, unsubstituted and p-nitroperoxybenzoic acids. These differences were

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[23] E. G. Foster, A. C. Cope and F. Daniels, THIS JOURNAL, **69**, 1893 (1947).

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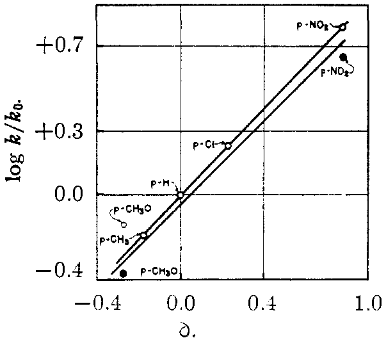
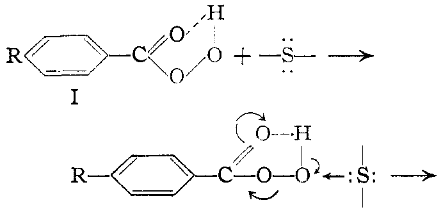


Fig. 5.—Variation of reactivity with σ-value: O points are for the oxidation of *p,p'*-dichlorobenzyl sulfide by *p*-substituted peroxybenzoic acids in isopropyl alcohol at −35°; ● points are for the oxidation of cyclohexene to epoxycyclohexane in xylene at 25° (Medvedev and Blokh).

not anticipated inasmuch as *p*-substituents generally have a relatively small influence upon entropy of activation in the reactions of benzene derivatives[25] and indicate some additional change in the steric requirements of the transition state.

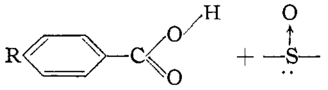
Salt Effect.—If the transition state in the peroxybenzoic acid oxidation consists of an internally hydrogen bonded non-ionic structure, a suggestion which is consistent with the preceding data, an increase in the ionic strength of the reaction medium by salt addition should not change the oxidation rate. The effect of added salt on reaction rate was investigated by determining the rate of oxidation of *p,p'*-dichlorobenzyl sulfide by peroxybenzoic acid in isopropyl alcohol 0.10 *M* in magnesium perchlorate at −20°. In duplicate runs specific rate constants of 0.84 and 0.81 ± 0.04 l. mole^{-1} sec.$^{-1}$ were obtained as compared to an average value of 0.83 ± 0.04 l. mole^{-1} sec.$^{-1}$ in the absence of added salt; thus an increase of 0.3 unit in the ionic strength of the reaction medium did not change the oxidation rate beyond the limits of experimental error. The calculated ionic strength is 0.3; the actual value may have been less than this due to incomplete ionization of the magnesium perchlorate. The absence of any salt effect helps to support the previous kinetic evidence indicating a second order reaction. The absence of any salt effect rules out any first order process dependent on the ionization of the peroxy acid as the rate-determining step.

Oxidation Mechanism.—A possible mechanism for peroxyacid oxidation is one involving nucleophilic attack of a cyclic hydrogen-bonded form of the peroxyacid (I) by sulfide



I

(transition state)



Intramolecularly bonded I is in a unique position for promoting the nucleophilic displacement reaction without the formation of ionic intermediates as required by the Criegee mechanism.[2] That the oxidations proceed faster in toluene than in isopropyl alcohol, with lowered energies and entropies of activation, suggests that ions are probably not formed in the reaction. This is further substantiated by the absence of a salt effect. In a non-hydroxylic solvent having a low dielectric constant, such as toluene, the likelihood that the peroxyacid is largely in the cyclic form both before and during reaction is considerably better than it is in isopropyl alcohol where the peroxyacid may be strongly solvated and intramolecular hydrogen bonding hindered. Although infrared evidence[26] has been presented in support of intramolecularly bonded peroxypropionic acid in carbon tetrachloride, it cannot be concluded that peroxybenzoic acid is similarly bonded in either toluene or isopropyl alcohol.[27]

Evidence consistent with the cyclic structure for peroxybenzoic acid in the transition state is furnished by the observation that the oxidations are not acid-catalyzed by benzoic acid and show no salt effect.

However, regardless of whether or not the peroxyacid is present in the cyclic bonded form either before reaction or while in the transition state, the smaller decreases in entropy for oxidations in isopropyl alcohol than in toluene may be explained as due to solvation of the peroxyacid before reaction. In the solvated form the peroxyacid presumably loses many of its degrees of freedom and thus undergoes less restriction on proceeding from the unreacted to the transition state.

Although the apparent decrease in activation entropy with increasing electronegativity of *p*-substituent, noted previously, could be due to increased polarization of the O–O bond, it may be due to a decrease in the facility with which the hydrogen bonded ring structure is formed. With an electron-withdrawing group in the *p*-position it is to be expected that the peroxyacid would be less predominantly in the cyclic form before reaction because of reduced electron density at the carbonyl oxygen. As a result a greater decrease in entropy on going from reactants to the transition state would be anticipated. Since the activation energy decreases with decreasing entropy of activation, the proposed mechanism is consistent with the effect of substituent on oxidation rate.

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[25] Reference 24, p. 121.

[26] B. S. Neporent, T. E. Pavlovskaya, N. M. Emanuel and N. G. Yaroslavskiĭ, *Doklady Akad. Nauk* (*USSR*), **70**, 1025 (1950) [*C. A.*, **44**, 5195 (1950)].

[27] An attempt to demonstrate intramolecular hydrogen bonding in peroxybenzoic acid in toluene solution by the infrared spectral method was made but was abandoned because of complications introduced by the solvent and the aromatic nucleus.