

Experiments Bearing on the Role of Solvent in the Oxidation of Some Organic Compounds by Peroxy Acids

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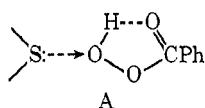
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A kinetic study of the solvent effects on the oxidation of *p*-nitrodiphenyl sulfide to sulfoxide and of *p*-nitrodiphenyl sulfoxide to sulfone by peroxybenzoic acid is reported. A series of solvents of varying characteristics was employed. The kinetic results are compared with the data obtained for the epoxidation of cyclohexane by the same peroxy acid in the same solvent series. The reaction rates are not markedly affected by the medium polarity as measured by the dielectric constant, but rather reflect specific interactions of the solvent molecules with the reactants in their initial states as well as in the transition state. The results are discussed on the basis of the possible solvation phenomena involving both the nucleophiles and the peroxy acid. Two significant interactions seem to be intramolecular and intermolecular hydrogen bonding with the solvent.

Recently, studies²⁻⁵ on the influence of solvent on the oxidation of organic sulfides by H₂O₂ and *t*-BuOOH have given evidence for participation of solvent molecules in the transition state. By means of cyclic proton transfers, such solvent participation can bypass the otherwise obligatory endothermic charge separation in the transition state.

A large amount of data on the stoichiometry and the mechanism of the oxidation of sulfides, sulfoxides, and alkenes by peroxybenzoic acids is available in the literature, and the general kinetic features of these reactions (such as rate law, substituent effects, etc.) have been elucidated and reviewed. On the contrary, a detailed study of the solvent effects has not been, to our knowledge, carried out.

A kinetic study⁶ on the oxidation of *p,p'*-dichlorodiphenyl sulfide to the sulfoxide by peroxybenzoic acid suggested a mechanism involving nucleophilic attack by the sulfide on the intramolecularly hydrogen-bonded form of the peroxy acid, as in a transition state of type A.



Similar conclusions were reached by other authors.⁷ Since the oxidation proceeds more slowly in 2-propanol than in toluene, with higher energies and less negative entropies of activation in the former solvent, it was suggested that the peroxy acid molecule may be solvated and the intramolecular hydrogen transfer hindered in the alcohol. A preliminary investigation⁸ of the solvent effect had indicated that the rates appeared to be dominated by specific effects.

We now have studied some of the factors in peroxy acid oxidation of sulfides, sulfoxides, and olefins by measuring the rate constants and the activation param-

eters in a series of diverse solvents. Our results are presented here.

After the present study was completed, we became aware of a series of papers on the oxidation of some diphenyl sulfoxides with peroxy acids in a few solvents. The results,⁹ insofar as general kinetic features and substituent effects on rates are concerned, agree with previous results.⁶⁻⁸ On the other hand, the claim⁹ that the rate constants depend simply on the dielectric constant of the solvent is not well substantiated by their results and is contradicted by the findings of the present paper.

Experimental Section

Reagents and Solvents.—*p*-Nitrodiphenyl sulfide, mp 54–55°, was prepared and purified as previously described;¹⁰ *p*-nitrodiphenyl sulfoxide was obtained by oxidation of the sulfide with a stoichiometric amount of peroxybenzoic acid in CHCl₃; after the usual isolation procedure,¹⁰ the sulfoxide was purified by several recrystallizations from absolute ethanol, mp 106–107° (lit.¹¹ mp 107–107.5°).

Cyclohexene (Fluka, high purity) was fractionally distilled over Drierite several times: bp 83° (760 mm); *n*_D²⁰ 1.4451 [lit.¹² bp 82.8° (759 mm); *n*_D^{20.06D} 1.44637].

Peroxybenzoic acid was prepared using 98% H₂O₂ (kindly supplied by FMC Corp.) according to the method given by Swern, *et al.*;¹³ after three recrystallizations from Et₂O-petroleum ether, iodometric analysis showed the peracid content to be 97–99% in different samples, mp 41–42° (lit.¹³ mp 41–42°). The peroxy acid was checked for its characteristic infrared^{14,15} spectrum and was stored at ca. –10° in a vacuum desiccator.

Benzene, methylene chloride, dioxane, *t*-BuOH, *i*-PrOH, EtOH, and MeOH solvents (C. Erba, high purity) were purified according to standard procedures¹⁶ and fractionally distilled.

***N,N*-Dimethylformamide (DMF)** (C. Erba, high purity) was shaken over KOH pellets for a few hours, distilled, passed slowly through a 4A molecular-sieve (B.D.H.) column,¹⁷ and frac-

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(2) M. A. P. Dankleff, R. Curci, J. O. Edwards, and H. Y. Pyun, *J. Amer. Chem. Soc.*, **90**, 3209 (1968).

(3) L. Bateman and K. B. Hargrave, *Proc. Roy. Soc., Ser. A*, **224**, 389, 399 (1954).

(4) C. G. Overberger and R. W. Cummins, *J. Amer. Chem. Soc.*, **75**, 4783 (1953).

(5) J. O. Edwards in "Peroxide Reactions Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, pp 67–106.

(6) C. G. Overberger and R. W. Cummins, *J. Amer. Chem. Soc.*, **75**, 4250 (1953).

(7) G. Modena and P. E. Todesco, *J. Chem. Soc.*, 1962, 4920; see also previous papers.

(8) G. Modena and P. E. Todesco, *Boll. Sci. Fac. Chim. Ind. Bologna*, **23**, 31 (1965).

(9) (a) S. A. Khan, M. Ashraf, and A. B. Chughtai, *Sci. Res. Dacca, Pakistan*, **IV**, 135 (1967); (b) S. A. Khan, M. Ashraf, A. B. Chughtai, and I. Ahmad, *Pakistan J. Sci. Ind. Res.*, **10**, 151 (1967); (c) S. A. Khan and M. Ashraf, *ibid.*, **11**, 105 (1968).

(10) (a) G. Modena and L. Maioli, *Gazz. Chim. Ital.*, **87**, 1306 (1957); (b) A. Mangini and R. Passerini, *J. Chem. Soc.*, 4954 (1956); (c) G. Leandri, A. Mangini, and R. Passerini, *ibid.*, 1386 (1957).

(11) H. H. Szmant and J. J. McIntosh, *J. Amer. Chem. Soc.*, **73**, 1356 (1951).

(12) H. I. Waterman and H. A. Van Westen, *Rec. Trav. Chim. Pays-Bas*, **48**, 637 (1929).

(13) L. S. Silbert, E. Siegel, and D. Swern, *Org. Syn.*, **43**, 93 (1963); *J. Org. Chem.*, **27**, 1336 (1962).

(14) W. H. T. Davison, *J. Chem. Soc.*, 2456 (1951).

(15) D. Swern and L. S. Silbert, *Anal. Chem.*, **35**, 880 (1963).

(16) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., London, 1956.

(17) G. R. Pettit, M. V. Kalnins, T. M. Liw, E. G. Thomas, and K. Parent, *J. Org. Chem.*, **26**, 2563 (1961).

TABLE I
RATE CONSTANTS (k_2') AND ACTIVATION PARAMETERS FOR THE OXIDATION
OF *p*-NITRODIPHENYL SULFIDE (PNDS) BY PEROXYBENZOIC ACID IN VARIOUS SOLVENTS

Solvent	ϵ^a	Temp, °C	$10^4 k_2'^b$	ΔH^\ddagger^c	ΔS^\ddagger^c
CHCl ₃	4.81	25.0	146.0 ^d	8.5	-29
CH ₂ Cl ₂	9.08	25.0	106.0	8.3	-30
		15.0	62.1		
		5.0	36.5		
CCl ₄	2.24	25.0	63.4	8.7	-31
		12.0	59.1		
Benzene	2.28	25.0	134.0	10.2	-24
		25.0	129.0 ^d		
Nitrobenzene	34.8	25.0	41.5 ^f	11.6	-21
		30.0	58.6		
		40.0	112.0		
Sulfolane	41.4 ^e	25.0	41.5 ^f	11.6	-21
		30.0	58.6		
		40.0	112.0		
DMF	36.7	25.0	4.21	11.6	-32
		15.0	2.13		
		5.0	0.96		
Dioxane	2.21	25.0	13.1	11.6	-26
		12.0	5.12		
Dioxane-H ₂ O ^g	34.0	25.0	52.7 ^d	10.2	-26
<i>t</i> -BuOH	10.9 ^h	26.0	7.26		
<i>i</i> -PrOH	18.3	25.0	8.71 ^d	12.2	-22
		25.0	9.05 ⁱ		
EtOH	24.3	25.0	9.40 ⁱ	13.2	-24
		25.0	10.9 ⁱ		
MeOH	32.6	15.0	5.03 ⁱ	13.2	-24
		5.0	2.48 ⁱ		
		25.0	154.0 ⁱ		
CF ₃ CH ₂ OH	26.5 ⁱ	25.0	154.0 ⁱ	8.8	-33

^a Dielectric-constant values at 25° (A. A. Maryott and E. R. Smith, National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951), unless otherwise noted. ^b In $M^{-1} \text{sec}^{-1}$, from second-order-kinetics integrated plots; reactant concentrations were kept within the range $0.6\text{--}1.1 \times 10^{-2} M$. ^c ΔH^\ddagger values in kcal/mol, ΔS^\ddagger values in cal/deg mol. ^d Data from ref 8. ^e At 30.0° [U. LaManna, O. Sciacovelli, and L. Jannelli, *Gazz. Chim. Ital.*, **96**, 11 (1966)]. ^f Estimated at 25° from the rate constants at 30 and 40° and the calculated E_a value. ^g 50:50, by volume; ϵ estimated at 25° from other known values [G. Åkerlöf and O. A. Short, *J. Amer. Chem. Soc.*, **58**, 1241 (1936)]. ^h At 30°. ⁱ In the presence of $0.6\text{--}0.8 \times 10^{-3} M$ *p*-benzoquinone (see Experimental Section). ^j J. Mukherjee and E. Grunwald, *J. Phys. Chem.*, **62**, 1311 (1958).

tionally distilled at reduced pressure: bp 76° (39 mm); n_D^{25} 1.4273 (lit.¹⁸ n_D^{25} 1.4269).

Tetrahydrothiophene 1,1-dioxide (Sulfolane) (Schuchardt GmbH).—The commercial solvent (containing oxidizable contaminants) was purified following the procedure of Alder and Whiting¹⁹ and fractionally distilled *in vacuo* once over P₂O₅ and twice over NaOH pellets: bp 99–101° (0.5×10^{-3} mm); mp 28–28.3°; n_D^{20} 1.4814 [lit.^{19,20} bp 100–105° (0.02 mm); mp 28.45°; $n_D^{29,27}$ 1.48177].

2,2,2-Trifluoroethanol (Schuchardt GmbH, high purity) was dried (Drierite) and distilled: bp 74° (760 mm); n_D^{20} 1.2916 (lit.²¹ bp 74.05°; n_D^{20} 1.2907).

Kinetics.—The rates were followed by iodometric determination of the peroxy acid (PBA) as previously described.^{8,22,23} For the oxidations of *p*-nitrodiphenyl sulfide (PNDS) and *p*-nitrodiphenyl sulfoxide (PNDSO), clean second-order kinetics were observed up to 70–90% reaction. The epoxidation of cyclohexene (CH) by PBA also follows a second-order rate law;²⁴ the rate constants (k_2 values) were obtained from pseudo-first-order experiments wherein $[CH]_0$ (brackets denote concentrations and the subscript zero denotes initial state) is 8–30 times greater than $[PBA]_0$. The possible errors in the rate-constant values were estimated to be $\pm 1\text{--}2\%$ in the majority of runs, and $\pm 2\text{--}4\%$ for some of the fastest runs. The kinetic experiments were carried out in constant-temperature baths with control being better than $\pm 0.05^\circ$. The rate constants obeyed the Arrhenius equation and the activation parameters were evaluated

by the standard methods;^{25,26} the precision in the estimation of the activation parameters was generally better than ± 0.8 kcal/mol for ΔH^\ddagger and better than ± 3 cal/deg mol for ΔS^\ddagger .

The PBA stock solutions in the various solvents were kept in the thermostatic bath during the kinetic runs and their stability was checked before and immediately after every kinetic run; the titer loss generally observed was less than 1%. In the case of some of the alcoholic solvents (see tables), however, we found it necessary to add *p*-benzoquinone, mp 114–115° (C. Erba, high purity), in small amounts (generally 5–10% of $[PBA]_0$) to the stock solutions; this addition was found to prevent a side reaction of rapid (radical)^{27–29} decomposition of the oxidizing agent which was occasionally observed.

Results and Discussion

We have investigated the influence of solvents on the rates of oxidation by peroxybenzoic acid of three quite different substrates, namely, *p*-nitrodiphenyl sulfide, cyclohexene, and *p*-nitrodiphenyl sulfoxide. The kinetic results are presented in Tables I, II, and III, respectively.

The first two substrates, even if chemically very different, have rates that respond similarly to solvent change. This is clearly shown in the linear free-energy correlation of Figure 1. Similar mecha-

(18) J. R. Ruhoff and E. Reid, *J. Amer. Chem. Soc.*, **59**, 401 (1937).

(19) R. W. Alder and M. C. Whiting, *J. Chem. Soc.*, 1964, 4707.

(20) L. Jannelli, M. Della Monica, and A. Della Monica, *Gazz. Chim. Ital.*, **94**, 552 (1964); U. LaManna, O. Sciacovelli, and L. Jannelli, *ibid.*, **94**, 567 (1964).

(21) F. Swarts, *Compt. Rend.*, **197**, 1261 (1933); *Chem. Abstr.*, **28**, 1987 (1934).

(22) R. Curci and G. Modena, *Gazz. Chim. Ital.*, **94**, 1257 (1964).

(23) G. Modena and P. E. Todesco, *J. Chem. Soc.*, 4920 (1962), and references cited therein.

(24) B. M. Lynch and K. H. Pausacker, *ibid.*, 1525 (1955).

(25) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, Chapter 5.

(26) Institute Francais du Petrole, "Cinetique chimique appliquee," J. C. Jungers, Ed., Societe des Editions Technip, Paris, 1958, Chapter 6.

(27) K. Tokumaru, O. Simamura, and M. Fukuyama, *Bull. Chem. Soc. Jap.*, **35**, 1673 (1962).

(28) W. E. Parker, L. P. Witnauer, and D. Swern, *J. Amer. Chem. Soc.*, **80**, 323 (1958).

(29) S. R. Cohen and J. O. Edwards, *J. Phys. Chem.*, **64**, 1086 (1960).

TABLE II
RATE CONSTANTS (k_2) AND ACTIVATION PARAMETERS FOR THE EPOXIDATION
OF CYCLOHEXENE BY PEROXYBENZOIC ACID IN VARIOUS SOLVENTS

Solvent	ϵ^a	Temp, °C	$10^4 k_2^b$	ΔH^\ddagger^c	ΔS^\ddagger^c
CHCl ₃	4.81	20.0	472.0 ^d	9.6	-32
CH ₂ Cl ₂	9.08	20.0	225.0 ^d	9.8	-33
CCl ₄	2.24	20.0	77.2 ^d	9.9	-35
Benzene	2.28	20.0	156.0 ^d	11.0	-29
Sulfolane	41.4 ^e	20.0	32.7 ^f	11.2	-31
		30.0	64.1		
		40.0	120.0		
Dioxane	2.21	20.0	9.75 ^d	13.3	-27
		20.0	9.64		
DMF	37.6	20.0	2.22	12.3	-33
		10.0	1.03		
		30.0	4.73		
<i>t</i> -BuOH	10.9 ^g	20.0	2.5 ^f	13.8	-28
		30.0	5.55		
		40.0	11.9		
<i>i</i> -PrOH	18.2	20.0	6.91	13.0	-29
		10.0	2.60		
		30.0	13.4		
EtOH	25.7	20.0	5.56 ^h		
MeOH	32.6	20.0	5.44 ^h	12.7	-30
		10.0	2.29 ^h		
		30.0	11.1 ^h		
CF ₃ CH ₂ OH	26.5 ⁱ	20.0	268.0 ^h	8.7	-36
		10.0	152.0 ^h		

^a See footnote a, Table I. ^b Second-order rate constants, in $M^{-1} \text{sec}^{-1}$, were estimated as $k_2 = k_1/[\text{CH}]_0$; k_1 values were obtained from pseudo-first-order integrated plots. Peroxy acid initial concentration was kept in the range $0.6\text{--}1.3 \times 10^{-2} M$ and $[\text{CH}]_0$ ranged from 0.080 to 0.400 M in the majority of the runs. ^c See footnote c, Table I. ^d Data from P. Renolen and J. Ugelstad, *J. Chim. Phys.*, **57**, 634 (1960). ^e See footnote e, Table I. ^f See footnote f, Table I. ^g See footnote h, Table II. ^h See footnote i, Table I. ⁱ See footnote j, Table I.

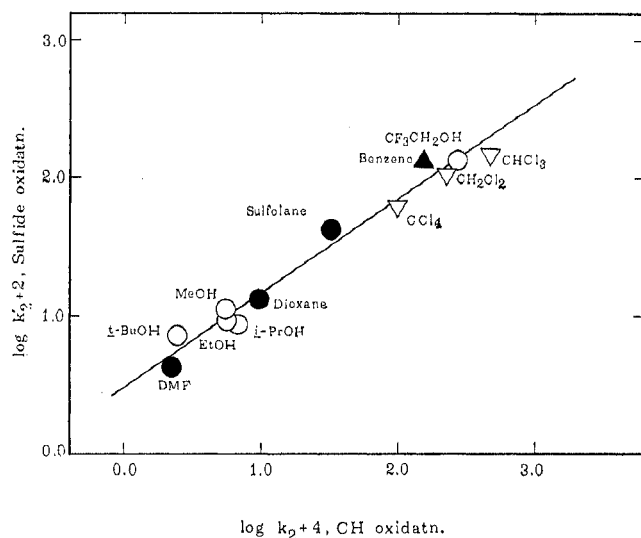


Figure 1.—Linear trend in the plot of the logarithms of PNDS oxidation rate constants vs. the logarithms of rate constants for CH epoxidation by peroxybenzoic acid in various solvents.

nisms have been suggested^{6-9,24,30-33} for the oxidations of sulfides and alkenes, and the above correlation stresses the point that the relevant details of the two mechanisms are similar even if not identical. The slope of the correlation line is 0.68. The behavior of sulfoxides (see below for detailed discussion) is quite

(30) D. Swern, *Chem. Rev.*, **45**, 1 (1949).

(31) D. Barnard, L. Bateman, and J. I. Cunneen in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p 229.

(32) E. J. Behrman and J. O. Edwards, *Progr. Phys. Org. Chem.*, **4**, 93 (1967).

(33) J. B. Lee and B. C. Uff, *Quart. Rev. (London)*, **21**, 429 (1967).

TABLE III

RATE CONSTANTS (k_2'') FOR THE OXIDATION OF *p*-NITRODIPHENYL SULFOXIDE (PNDSO) BY PEROXYBENZOIC ACID AND RATIOS OF PNDS OXIDATION RATE TO PNDSO OXIDATION RATE IN VARIOUS SOLVENTS AT 25.0^a

Solvent	ϵ_{25}	$10^4 k_2''$	k_1'/k''
CHCl ₃	4.81	2.40 ^b	60.8
CCl ₄	2.24	7.60 ^b	8.34
Benzene	2.28	5.60 ^b	24.3
Nitrobenzene	34.8	3.80 ^b	33.9
Sulfolane	44.0 ^c	2.03 ^d	20.4
DMF	36.7	0.966	4.36
Dioxane	2.21	3.83 ^b	3.42
Dioxane-H ₂ O ^e	34.0	1.25 ^b	42.2
<i>t</i> -BuOH	10.9 ^g	1.60 ^f	4.54
<i>i</i> -PrOH	18.3	1.44	6.04
MeOH	32.6	1.09	10.0
CF ₃ CH ₂ OH	26.5	0.170	906.0

^a k_2'' are in $M^{-1} \text{sec}^{-1}$. ^b Data from ref 8. ^c At 30°. ^d Calculated at 25.0° through the activation energy obtained from $10^4 k_2'' = 2.85$ (at 30.0°), 5.28 (at 40.0°). ^e 50:50, by volume. ^f At 26.0°.

different and suggests the occurrence of specific solvent-solute interactions.

Sulfide and Alkene Oxidations.—The similarity of the sulfide and olefin cases suggests that the variations in rate with change of solvent should be related to a transition-state effect, or to a ground-state effect on the peroxy acid, or to both. Indeed the sulfides and olefins are poorly basic and solvent-solute interactions are expected to be weak and in any case similar.

The slope of Figure 1 would be 1.0 if the only solvent-solute interaction involved the peroxy acid. We conclude that some solvation of transition state and/or

sulfide (or alkene, of course) must obtain. These solvations presumably are less important than peroxy acid solvation and must in some fashion parallel the peroxy acid solvation, since good linearity is obtained in the linear free-energy relationships.

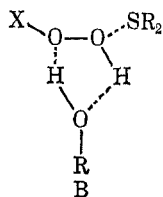
Inspection of the data given in Tables I and II shows no clear dependence of rates on solvent dielectric constant³⁴ ϵ or on the dielectric function $(\epsilon - 1)/(2\epsilon + 1)$. For example, the rates in benzene (ϵ 2.28) and in nitrobenzene (ϵ 34.8) are almost equal. Also, the rate constants differ by one power of ten in *t*-butyl alcohol and methylene chloride, which have similar dielectric constants (ϵ 10.9 and 9.08, respectively). The lack of dependence on dielectric constant indicates that a mechanism involving charge separation is unlikely.^{2,5,35} The indication is strongly supported by the fact that these oxidations depend on solvent nature in a manner only explicable by assumption of specific chemical interactions between solvent and solutes.^{2-8,35,36}

There are two alternative mechanisms, both of which avoid charge separation in the transition state, by which monosubstituted peroxides XOOH can oxidize nucleophilic substrates. The first mechanism, which should conform to the rate law

$$-\frac{d[\text{XOOH}]}{dt} = k[\text{XOOH}][\text{sulfide}]$$

with a transition state of configuration A, is expected when X is an acyl or related group. This mechanism involves an intramolecular proton transfer from the peroxidic oxygen to the carbonyl oxygen of the peroxy acid.^{6,24,35-38}

The other mechanism involves an external particle which allows proton transfer through a ring transition state of type B.



The overall data obtained in this study suggest that both mechanism types obtain for the peroxy acid oxidations depending on the nature of the solvent. The second mechanism, which has been studied in some detail for HOOH and *t*-BuOOH,²⁻⁵ has the rate law

$$-\frac{d[\text{HOOH}]}{dt} = k[\text{sulfide}][\text{HOOH}][\text{ROH}]$$

in aprotic solvents. In protic solvents where the solvent molecule can be ROH, one observes a second-order law, of course. It has also been observed that the rate is larger in protic solvents than in aprotic solvents. At least in aprotic solvents, this mechanism is ruled out for the peroxy acid oxidations, which are in every case second order with no evidence for solvent participation in the transition state.

(34) L. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964.

(35) R. Curci, R. A. DiPrete, J. O. Edwards, and G. Modena in "Hydrogen-Bonded Solvent Systems," A. K. Covington and P. Jones, Ed., Taylor and Francis Ltd., London, 1968, p 301.

(36) P. Renolen and J. Ugelstad, *J. Chim. Phys.*, **57**, 634 (1960).

(37) P. D. Bartlett, *Rec. Chem. Progr.*, **18**, 11 (1957).

(38) D. Swern, *Org. Reactions*, **7**, 378 (1953).

TABLE IV

COMPARISON AMONG RATE CONSTANTS FOR PNDS OXIDATION (k_2'), CH EPOXIDATION (k_2) BY PEROXYBENZOIC ACID, AND OD BAND INFRARED SHIFTS OF MeOD IN SOME BASIC OXYGEN SOLVENTS

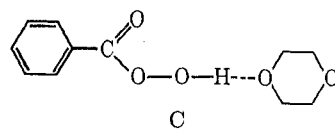
Solvent	$\Delta\nu$, cm^{-1} ^a	$10^3 k_2'$ ^b	$10^4 k_2$ ^c
Nitrobenzene	28	129.0	...
Sulfolane	77 ^d	41.5	32.7
Ethyl acetate	51	...	12.3 ^e
Dioxane	111	13.1	9.64
THF ^f	117	...	4.33 ^e
DMF	117	4.21	22.22

^a Ir shifts, mostly with CCl₄ or benzene solutions as reference. Data from E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

^b In $M^{-1} \text{sec}^{-1}$, at 25.0°. ^c In $M^{-1} \text{sec}^{-1}$, at 20.0°. ^d Ir shift for di-*n*-propyl sulfone. ^e Data from ref 36. ^f Tetrahydrofuran.

The second-order rate constants for peroxy acid as oxidant are larger in the nonbasic aprotic solvents than in basic, oxygen-containing aprotic solvents. The most evident feature is the drop in rate constants in passing from nonbasic solvents (chlorinated solvents, benzene) through a weakly basic solvent (nitrobenzene) to more basic oxygen-containing but nonprotic solvents (in order, sulfolane, dioxane, and DMF). There appears to be a general correlation of these rates with the known capability of peroxy acids to exist in either a chelate form or an open-chain, solvated configuration (see below). The relative basicities of various solvents towards a hydrogen donor should then have an influence on rates of oxidation if the chelate configuration of the peroxy acid molecule is important in the mechanism. That such is the case is seen in Table IV. When the solvent molecule is a stronger oxygen base, as indicated by the larger infrared shift, the rate of oxidation in this solvent is lower. The correlation is too clear to be fortuitous.

From infrared and dipole-moment measurements,^{15,39,40} it has been inferred that peroxybenzoic acid exists in the chelate form in solvents like carbon tetrachloride and benzene. In particular, the band at 3280 cm^{-1} attributed to an OH stretching mode does not shift with dilution; this is expected for an intramolecular hydrogen bond. However, addition of dioxane to the carbon tetrachloride causes a broadening and shift of the OH band; this behavior is consistent with a disruption of the chelate structure in favor of a structure with an open-chain intermolecular hydrogen bond between the dioxane basic center (ether oxygen) and the acidic hydrogen of the peroxy acid, as in C.



In basic solvents such as dioxane and DMF, the reaction could still proceed *via* the chelate transition state A. A shift in the ground state of the peroxy acid from the chelate (in carbon tetrachloride) to the open structure with external hydrogen bond as in C means in terms of the oxidation reaction that a desolvation process should take place before the transition state is reached in basic solvents. Such desolvation

(39) W. H. T. Davison, *J. Chem. Soc.*, 2456 (1951).

(40) J. R. Rittenhouse, W. Lobunetz, D. Swern, and J. G. Miller, *J. Amer. Chem. Soc.*, **80**, 4850 (1958).

will increase the activation free energy and decrease the rate, and this is just what is observed. With the reasonable assumption that an intermolecular hydrogen bond to a basic oxygen is energetically more stable than an intramolecular chelate, it is expected that the activation energies for reaction in basic solvents should be larger than in nonbasic solvents. This also is what is observed. (It is difficult to judge the relative entropies.⁴¹) The basis for the correlation of Table IV is clear, and the assumption that the reaction proceeds *via* mechanism 1 even in basic aprotic solvents is justified.

When analyzing the results for alcoholic solvents, it is necessary to consider the additional possibility of intervention of an external proton transfer of the type deduced for mechanism A. The rate constants for the four common alcohols are closely similar and are also of the same magnitude as the rate constant in dioxane. The latter solvent is comparable⁴² in basicity with the alcohols, but of course does not have a hydroxyl group. The alcohol acidities vary by about three pK units,^{42,43} but this seems to have no effect on the rate constants. However, rate constants which are larger by more than a factor of ten from those for the common alcohols have been observed in the solvent trifluoroethanol, which has a pK_a of 12.37.⁴⁴ The rate constants in this solvent are accompanied by significant changes in the activation parameters. The data strongly suggest that a change in mechanism (from type A to type B) has taken place in trifluoroethanol and possibly also the other alcohols. Although these results do not indicate acid catalysis (the rates are not significantly altered on the addition of stronger acids⁸), an external proton transfer related to mechanism type B is considered as to be in agreement with our data. Indeed the peroxy acid is expected to be strongly solvated in trifluoroethanol, not only as is shown in open-chain structure C but also because of proton donation by alcohol to the oxygen of the carbonyl group. Hydrogen transfer in the transition state should be very facile because of the acidity⁴⁴ of this alcohol.

The rate constant and the activation parameters indicate that the transition state is more solvated by trifluoroethanol than is the ground state. This leads to the important conclusion that the transition-state configuration is not that with an intramolecular hydrogen bond, since the energy of that transition state should not depend significantly on the solvent. In trifluoroethanol, then, mechanism A is disfavored because of the strong ground-state solvation, whereas mechanism B would be favored because of the very efficient solvation of the transition state.

In light of the above conclusions, the rates in the four more common alcohols cannot be easily interpreted, since these rate constants are consistent with either mechanism A or B, or with a combination of both. The similarity of the rate constants for these four probably

stems more from a compensation of several factors rather than from a mechanism with identical details. The suggestion of a compensation is supported by the fact that for sulfide oxidation the rate order is MeOH > EtOH > *i*-PrOH, whereas for epoxidation the rate order is *i*-PrOH > EtOH > MeOH. Of course, in both cases the rate differences are small.

Sulfoxide Oxidation.—The oxidation of sulfoxides by peroxy acids (except for alkaline oxidation, where another mechanism intrudes⁴⁵) is postulated to a nucleophilic displacement on peroxide oxygen of the kind discussed for sulfides and alkenes.^{7,46,47} The dependence on solvent nature is, however, much different, and one must now take into consideration the specific solvation of the sulfoxide ground state together with the solvation of the peroxy acid discussed above. The ability of sulfoxides to form hydrogen bonds with protic solvents is well documented and it is expected that hydrogen-bonded sulfoxides should be poorer nucleophiles than unsolvated sulfoxides; this expectation is supported by the observation that addition of acids depresses the reactivity of sulfoxides toward peroxy acids.

To analyze the ground-state solvation of sulfoxide, it is appropriate to divide the sulfide rate constant by the sulfoxide rate constant; by this procedure the influence of ground-state solvation of the peroxy acid is cancelled out. These ratios are presented in Table III. The relative rate in trifluoroethanol clearly shows the expected hydrogen bonding of solvent to the basic sulfoxide oxygen,⁴⁸⁻⁵¹ thereby lowering the reactivity of the sulfoxide molecule toward peroxy acid oxidation. The same behavior is observed in considering the reactivity ratio of the rates in carbon tetrachloride and chloroform as well as the ratio of rates in dioxane and dioxane-water mixtures. It is important to note that the rates of oxidations of sulfides and alkenes are more rapid in chloroform than in carbon tetrachloride, whereas the opposite order is observed for sulfoxide oxidations. However, it is apparent from close inspection of the data that other unknown factors intrude and must be considered in future studies.

The values of the ratio of k_1'/k_2'' deserve two further comments. (1) It is often stated that sulfides are oxidized at a much faster rate than are sulfoxides. In Table III, ratios as low as 3 or 4 are reported together with ratios as high as 900. This fact has an important synthetic utility, since the selective oxidation of sulfides to sulfoxides is feasible only in solvents where the ratio is high; these solvents are the more acidic, for example, acetic acid⁵² and trifluoroethanol. (2) The observation that sulfoxides are almost as reactive as

(45) (a) R. Curci and G. Modena, *Tetrahedron Lett.*, 1749 (1963); (b) R. Curci and G. Modena, *ibid.*, 863 (1965); (c) R. Curci and G. Modena, *Gazz. Chim. Ital.*, **94**, 1257 (1964); (d) R. Curci and G. Modena, *Tetrahedron Lett.*, No. 22, 1227 (1966).

(46) A. Cerniani and G. Modena, *Gazz. Chim. Ital.*, **89**, 843 (1959); A. Cerniani, G. Modena, and P. E. Todesco, *ibid.*, **90**, 3 (1960).

(47) G. Kresze, W. Shramm, and G. Cleve, *Chem. Ber.*, **94**, 2060 (1961).

(48) C. W. N. Cumper and S. Walker, *Trans. Faraday Soc.*, **52**, 193 (1956).

(49) D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

(50) S. Gherseti and M. Pallotti, *Gazz. Chim. Ital.*, **93**, 1000 (1963).

(51) P. Biserini, L. Lunazzi, and F. Taddei, *Boll. Sci. Fac. Chim. Ind. Bologna*, **22**, 67 (1964).

(52) J. Boeseken and E. Arrias, *Rec. Trav. Chim. Pays-Bas*, **54**, 711 (1935).

(41) In basic solvents, the greater entropy gain on solvent release should lead to more positive ΔS^\ddagger values; however, this gain should be partially compensated for in the entropy loss owing to formation of the "chelate" peroxy acid structure in the transition state from the "open" structure in the ground state.

(42) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(43) K. Bowden, *Chem. Rev.*, **66**, 119 (1966).

(44) F. A. Long and P. Ballinger, "Electrolytes," Pergamon Press, New York, N. Y., 1962, p 152.

sulfides in some solvents evidently represents another example of the α effect.⁵³

Finally, it has been observed⁵⁴⁻⁵⁶ that asymmetric induction, which is solvent dependent, obtains in systems related to the present study. Further work in this area should aid in the elucidation of solvent effects in rates of peroxide oxidation, since the optical induc-

tion can potentially give information on the solvation of the transition state.

Registry No.—*p*-Nitrodiphenyl sulfide, 952-97-6; *p*-nitrodiphenyl sulfoxide, 955-45-3; cyclohexene, 110-83-8.

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(53) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).

(54) R. C. Ewins, H. B. Henbest, and M. A. McKervey, *Chem. Commun.*, 1085 (1967).

(55) U. Folli, D. Iarossi, F. Montanari, and G. Torre, *Boll. Sci. Fac. Chim. Ind. Bologna*, **25**, 159 (1967); U. Folli, Abstracts, X Congresso Nazionale della Societa Chimica Italiana, Padova, Italy, June 1968, pp XIII-43.

(56) H. B. Henbest, *Chem. Soc., Spec. Publ.*, No. 19, 83 (1965).

The Alkaline Hydrolysis of Polynuclear Methyl β -Arylacrylates¹

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The rates of hydrolysis of 12 *trans*-methyl β -arylacrylates, ArCH=CHCOOCH₃, with Ar ranging from phenyl to 9-anthryl, were determined in 75% (by volume) aqueous acetone at 25°. The rates of seven of these compounds were also measured in 85% aqueous methanol. The compounds in which the side chain is attached to an unhindered position show only small differences in reactivity, whereas the rates of those compounds with the side chain in *peri* or *meso* positions increase with an increase in the size of Ar. The results are explained in terms of a combination of resonance and field effects. The correlation of rates with various Hückel molecular orbital reactivity parameters, as well as with parameters which express the electron-attracting field effect of aryl groups, is discussed.

Previous studies of side-chain reactivities of aromatic hydrocarbon systems, and the comparison of these reactivities with various theoretical parameters, have been hampered by the lack of exact information about the relative contributions of resonance, inductive, and steric effects. In particular, the last two effects appear to be of varying importance in determining reactivity, but neither can at present be expressed in terms of any of the available quantitative parameters.

We now wish to report data on the alkaline hydrolysis of *trans*-methyl β -arylacrylates, ArCH=CHCOOMe. This system was chosen because the reaction site is three carbons removed from the aromatic nucleus. On the basis of studies of the effect of *ortho* substituents on the dissociation constants of cinnamic acids⁴ and the rates of saponification of *ortho*-substituted ethyl cinnamates,⁵ it was thought that the methyl arylacrylate systems would be free, or almost free, from the steric effects of the *peri* hydrogen (the 1-naphthalene effect) which have influenced the work on other systems. On the other hand, in the arylacrylate system, the reaction site remains conjugated with the aromatic nucleus in the absence of steric effects, and the conjugation effects of the ring systems should be passed through the ethylenic side chain qualitatively unchanged and only slightly diminished. For this reason, the study of this system was anticipated to provide information concerning the relative importance of inductive and

resonance effects of polynuclear aromatic hydrocarbon systems.

Results and Discussion

The rates of hydrolysis of 12 *trans*-methyl β -arylacrylates in 75% by volume aqueous acetone were measured at 25°. Average rate constants are listed in Table I, in addition to rate constants for seven of the compounds which were also studied in 85% by volume aqueous methanol. The relationship between the rate constants in one solvent plotted against those obtained in the second is almost linear. The reaction is faster in the more aqueous solvent. This is due not only to the greater water content of the solvent, but also to the alkoxide-hydroxide ion equilibrium, which decreases the effective concentration of the hydroxide ions in the alcoholic solvent.⁶

In order to assess the effect of the polynuclear substituents on the rate of hydrolysis of methyl arylacrylates, it will be helpful to decide first which effects might be expected, and to what extent they manifest themselves in similar, but less complex, systems.

The saponification of ethyl cinnamates in 85% aqueous ethanol has a ρ value of 1.242.⁷ Electron-withdrawing substituents favor the reaction. Because of the separation of the ring and reaction site by the ethylenic bridge, the effect of substituents is compressed by a factor of about two, compared with the alkaline hydrolysis of ethyl benzoates under similar conditions ($\rho = 2.558$).⁷

Because of the greater electronegativity of sp² carbon compared with sp³, aryl groups attached to

(1) Relative Reactivities of Polynuclear Aromatic Systems. VI.

(2) Taken from the Ph.D. Thesis of M. K. Hoffman, Bryn Mawr College, May 1968.

(3) To whom inquiries should be addressed.

(4) G. Kortum, W. Vogel, and K. Andrussov, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworth and Co. Ltd., London, 1961; J. F. J. Dippy, *Chem. Rev.*, **25**, 151 (1939).

(5) B. Jones and J. G. Watkinson, *J. Chem. Soc.*, 4064 (1958).

(6) M. L. Bender and W. A. Glasson, *J. Amer. Chem. Soc.*, **81**, 1590 (1959).

(7) Taken from K. Bowden, *Can. J. Chem.*, **41**, 2781 (1963).