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OXIDATION OF ORGANIC SULPHIDES—XVI[1]

RATES OF ALKALINE AND ACIDIC OXIDATION OF *p*-TOLYL METHYL SULPHOXIDE WITH SUBSTITUTED PEROXYBENZOIC ACIDS*

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Abstract—The effect of substitution in peroxybenzoic acid on the rates of the alkaline and acidic oxidation of *p*-tolyl methyl sulphoxide has been studied and in both cases positive values of "rho" have been found; the activation parameters of the acidic and alkaline reactions were also measured. The reaction mechanisms are discussed on the basis of the above results as well in the light of previous results.

IN PREVIOUS papers[2,3] evidence was given for the probable occurrence of two mechanisms in the oxidation of organic sulphoxides—one due to the undissociated and the other to the dissociated peroxyacid.

The substituents bonded to the SO group have opposite polar effects on the rates of oxidation at high and low pH and it suggests that a similar behaviour could be found with substituents in the peroxyacid. However, as reported in this paper, electron withdrawing groups increase the rates of both the alkaline and the acidic oxidation.

RESULTS

p-Tolyl methyl sulphoxide has been oxidized in alkaline (apparent pH $\simeq$ 12) and acidic (apparent pH 3·6–3·2) media with a series of *p*- and *m*-substituted peroxybenzoic acids in dioxan–water (40:60). The data are reported in Table 1 and graphically in Fig. 1.

p-Tolyl methyl sulphoxide is not oxidized at a significant rate by H_2O_2 and t-butyl hydroperoxide even at high pH (KOH 0·1–0·5N, in water at 25°).

The Arrhenius parameters of acidic and alkaline oxidations of phenyl methyl sulphoxide in water have been calculated by the rate coefficients measured in the temperature range 13–35°. The two reactions have almost equal energies and entropies of activation (Table 2).

The rates of oxidation in water of optically active *m*-carboxyphenyl methyl sulphoxide with peroxybenzoic acid have been measured by titration of the peroxyacid and by disappearance of optical activity. The rate coefficients agree within the experimental errors (Table 3).

DISCUSSION

The results emphasize the close similarity between acidic and alkaline oxidation which is at variance with what was previously found.

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[1] Part XV: R.Curci and G. Modena, *Tetrahedron* **22**, 1227 (1966).

[2] G. Modena *et al., Gazz. Chim. Ital.* **89**, 843 (1959); **90**, 3, 12 (1960); *Boll. Sci. Fac. Chim. ind. Bologna* **23**, 31 (1965).

[3] R. Curci and G. Modena, *Tetrahedron Letters* 1749 (1963); 863 (1965); *Gazz. Chim. Ital.* **94**, 1257 (1964).

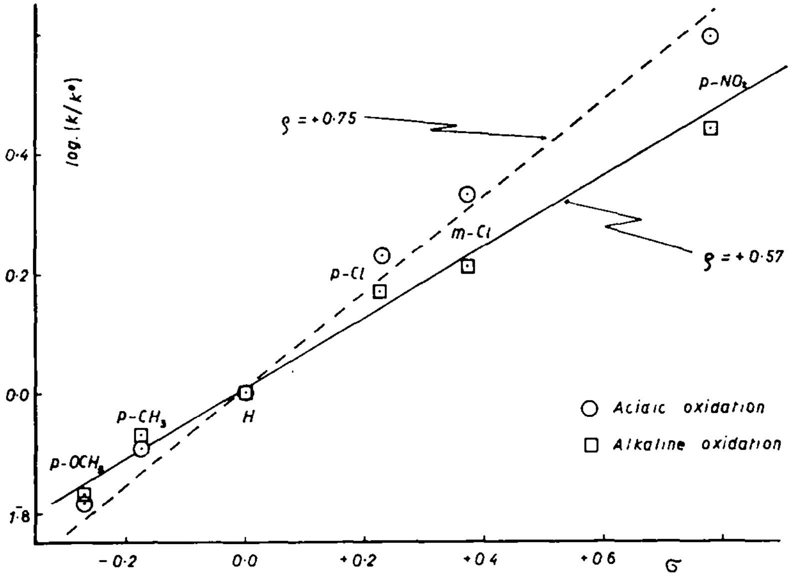


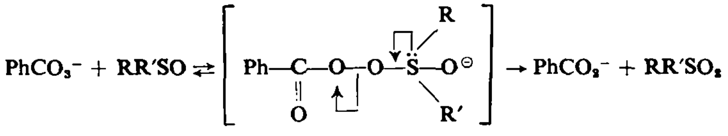
Fig. 1. Oxidation rates of *p*-tolyl methyl sulphoxide with substituted peroxybenzoic acids, in dioxan–water 40:60 at 25·0°.

In fact, in previous papers,[3] it was shown that the oxidation rates vary with pH in a typical sigmoid form, strongly indicative of the existence of two different species of oxidant: the undissociated peroxyacid and its anion. Moreover the polar effect of substituents on the sulphoxide group are opposite in the alkaline and acidic oxidations suggesting a positive character of the SO group in the transition state of the acidic and a negative character in the alkaline reaction.[2]

The steric effects likewise[1,4] suggest that the oxidation in both acidic and alkaline media is via transition states having different geometries, even if these differences are not large. On the other hand the activation parameters of the two reactions are almost equal (Table 2), but this does not contradict previous results in that the alkaline oxidation, although opposite in character to acidic oxidation regarding the polarity of sulphur, resembles the latter in many other respects.

The major point of interest is, the effect of substituents in the peroxyacid. A simple picture of the alkaline oxidation suggests that the nucleophilicity of the peroxyacid anion should be a fundamental factor and, therefore, a negative "rho" value, opposite to that of the acidic oxidation, should be found.

In fact both the acidic and alkaline oxidations give a positive "rho", its value being lower for the alkaline than for the acidic reaction. The positive value of "rho" in the alkaline reaction indicates that the cleavage of the O—O bond occurs in the transition state, which therefore may be represented as follows:



$$\mathrm{PhCO_3^-} + \mathrm{RR'SO} \rightleftarrows \left[\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}O{-}O{-}\overset{\overset{R}{|}}{\underset{\underset{R'}{|}}{\ddot{S}}}{-}O^{\ominus}}\right] \rightarrow \mathrm{PhCO_2^-} + \mathrm{RR'SO_2}$$

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[4] D. Carnimeo and R. Curci, *Boll. Sci. Fac. Chim. ind. Bologna*, in press.

The rate of formation and the equilibrium concentration of the complex should depend on the nucleophilicity of $PhCO_3^-$ (as they depend on the concentration of $PhCO_3^-$) and it must require a negative "rho" value, but this factor seems to be less important than the withdrawing of electrons from the O—O bond, which is necessary to carry the reaction to completion.[5] This is confirmed by the inability of hydrogen peroxide and alkyl hydroperoxides (where OH^- and RO^- are very poor leaving groups) to promote the oxidation in alkaline medium, in spite of their high nucleophilicity.[6–8]

On the other hand the absolute value of "rho" of the alkaline oxidation is lower than that of the acidic oxidation. This suggests that the alkaline "rho" could be the difference between a negative "rho" of the bond forming process and a positive "rho" of the O—O bond cleavage.

The bond forming step, which might be a preequilibrium, has no effect on the stereochemistry at the sulphur, because, if the substrate is optically active, the complex (I) is still asymmetric and, if it breaks down, the original sulphoxide—with unchanged conformation—should be reformed. In polarimetric runs, very close values of rate constants have been found which although not a proof is quite consistent with the suggestion.

Whereas in the acidic oxidation, an almost synchronous bond forming–bond breaking process may be hypothesized, the above formulation of the alkaline reaction stresses that in this case the S—O bond is almost fully formed in the transition state and consequently it could be shorter in the alkaline than in the acidic oxidation. The different length of the S—O bond might be, on the other hand, partially responsible for the greater steric requirements of the alkaline oxidation when compared with the acidic oxidation.

It seems probable, however, that the hypothesis purporting different geometries of the transition states in the alkaline and acidic oxidations, is more consistent with both the results reported earlier as well as those reported in the present paper.

EXPERIMENTAL

Sulphoxides

Phenyl methyl sulphoxide, p-tolyl sulphoxide and (+)-3-*carboxyphenyl methyl sulphoxide* were prepared by oxidation of the corresponding sulphides and purified as described.[2,3] The optically active sulphoxide (m.p. 132–134°, $[\alpha]_D$ +98·6 in MeOH) was obtained by resolution of the racemic 3-carboxyphenyl methyl sulphoxide (m.p. 171–172°) through its brucine salt, as reported by Phillips.[9]

Substituted peroxyacids

p-Methoxy, p-chloro and m-chloroperoxybenzoic acids were prepared as described by Overberger and Cummins.[10] They were purified by slow crystallization from conc. benzene solutions at 8–10°.

Peroxybenzoic and p-methylperoxybenzoic acids were prepared by reaction of the benzoyl chlorides with 36% H_2O_2 in alkaline EtOH–water mixture,[11] and purified by recrystallization from n-pentane, as previously described.

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[5] Similar conclusions were reached by P. Robson, *J. Chem. Soc.* 5170 (1964) on the oxidation mechanism of *o*-sulphobenzaldeide with substituted peroxybenzoic acids in aqueous alkali.

[6] W. P. Jencks and J. Carriuolo, *J. Amer. Chem. Soc.* **82**, 1778 (1960).

[7] K. B. Wieberg, *J. Amer. Chem. Soc.* **77**, 5219 (1955).

[8] J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.* **84**, 16 (1962); R. G. Pearson and D. N. Edgington, *Ibid.* **84**, 4607 (1962).

[9] P. W. B. Harrison, J. Kenyon and H. Phillips, *J. Chem. Soc.* 2079 (1926).

[10] C. G. Overberger and R. W. Cummins, *J. Amer. Chem. Soc.* **75**, 3783 (1962).

[11] A. Kerkomard and J. Bigou, *Bull. Soc. Chim. Fr.* 486 (1956).

TABLE 1. OXIDATION RATES OF *p*-TOLYL METHYL SULPHOXIDE WITH SUBSTITUTED PEROXYBENZOIC ACIDS ($X—C_6H_4—CO_3H$), IN DIOXAN–WATER 40:60 AT 25·0°

Substituent	Alkaline oxidation[a]	Acidic oxidation[b]
X = *p*-OCH_3 10^2k_2	26·3	4·06
p-CH_3 10^2k_2	33·3	4·87
H 10^2k_2	39·1	6·03
p-Cl 10^2k_2	58·0	10·2
m-Cl 10^2k_2	63·6	12·9
p-NO_2 10^2k_2	108	23·7
	$\rho = +0·57$ r = 0·995; s = 0·025	$\rho = +0·75$ r = 0·997; s = 0·024

k_2 in l mole^{-1} sec^{-1}

[a] $pH_{app} = 12·00 \pm 0·05$.

[b] $pH_{app} = 3·1 - 3·6$.

TABLE 2. OXIDATION OF PHENYL METHYL SULPHOXIDE WITH PEROXYBENZOIC ACID, IN WATER

pH	t°	10^2k_2, l mole^{-1} sec^{-1}	E_a, Kcal/mole	$\Delta H^‡$, Kcal/mole	$\Delta F^‡$, Kcal/mole	$\Delta S^‡$, e.u.
3·4–3·6	13·0°	1·11	—	—	—	—
3·4–3·6	25·0°	3·10	14·4	13·85	19·46	−18·82
3·4–3·6	35·0°	6·97	—	—	—	—
10·0	13·0°	18·0	—	—	—	—
10·0	25·0°	51·4	13·9	13·34	17·83	−15·07
10·0	35·0°	96·6	—	—	—	—

TABLE 3. OXIDATION OF *m*-CARBOXY-PHENYL METHYL SULPHOXIDE WITH PEROXYBENZOIC ACID, IN WATER, AT 25·0°

Technique	10^2[SO] (l/mole)	10^2[PBA] (l/mole)	Buffer	pH	k_2 (l mole^{-1} sec^{-1})
Titrimetric	[a]0·258	0·301	H_3BO_3–NaOH	9·92	0·266
Titrimetric	[b]1·98	2·36	H_3BO_3–NaOH	9·65	0·268
Titrimetric	[b]1·99	2·31	NaOH	12·15	0·305
Polarimetric	[a]2·05	2·39	NaOH	12·00	0·308
Polarimetric	[a]2·23	2·09	NaOH	11·95	0·322

[a] Optically active compound, $[\alpha]_D^{25} = +71·2$ (Na salt, *c* = 1 in water)

[b] Racemic compound.

TABLE 4. PEROXYBENZOIC ACIDS ($X—C_6H_4—CO_3H$)

Substituent	M.p.	Yield (%)	Purity (%)[a]	Ref.
X = *p*-OCH_3	85–86°	60	88	*b*, *c*
p-CH_3	94°	82	90	*b*, *c*
H	40–41°	82	92	*b*, *c*
p-Cl	108° (dec)	52	90	*b*, *c*
m-Cl	88–89°	62	91	*c*
p-NO_2	134–135° (dec)	85	93	*b*, *c*

[a] Tested by iodometric titration.

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

[c] B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.* 1525 (1955).

p-Nitroperoxybenzoic acid was prepared by reaction (at −20°, −10°) of *p*-nitrobenzoyl chloride with Na_2O_2 in THF, to which a few ml water were added, as reported by Vilkos.[12] The product was purified by crystallization from ether–pet. ether.

The m.ps, yields and purity of the peroxyacids used in kinetic measurements are given in Table 4.

Dioxan was purified by Vogel's method.[13]

Buffers. H_3BO_3–NaOH (AnalaR commercial grade) buffers at about 0·1 M concentration were used for the reactions at pH $\simeq$ 12.

Kinetic methods. The rate coefficients were usually evaluated by iodometric titrations of the peroxyacid concentration, as reported.[3,2] Thermostatic baths at 13·00°, 25·00° and 35·00° were used with temp. control better than ±0·05°. The oxidation rate of the optically active sulphoxide was also followed by the disappearance of optical activity: standard solutions of the sulphoxide and of the peroxyacid were mixed at zero time in the thermostatic bath, then a sample of the reaction mixture quickly transferred in a polarimetric tube (equipped with a thermostatic jacket) and the optical activity measured at proper time intervals.

All reactions follow a second order kinetic law in the range 0–70% or more, and rate constants were calculated by standard methods; they obey the Arrhenius equation, from which activation parameters were calculated in the usual way. All data collected in the Tables are mean values of two or more independent runs, which agree within the experimental errors (2–3%).

[12] M. Vilkos, *Bull. Soc. Chim. Fr.* 1401 (1959).

[13] A. I. Vogel, *Practical Organic Chemistry* p. 177, Longmans Green, London (1956).