Kinetics of the Reduction of Some Perbenzoic Acids by Iodide Ions

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The kinetics of the reduction of some ring-substituted perbenzoic acids by iodide ions have been investigated in different protic solvents and in water–dioxan mixtures. The rates are independent of the ionic strength and of the hydrogen-ion concentration, and the reaction is of the first order in peroxide concentration and in iodide-ion concentration. The results are discussed in terms of the participation of protic solvents in the activated complex.

THE electrophilic behaviour of peroxides in reactions with electron-pair donors is well known.[1] Among the reactions between peroxoacids and halide ions the kinetics of the oxidation of bromide by peracetic acid, peroxomonosulphate (SO_5^{2-}), and peroxomonophosphoric acid (H_3PO_5), and of chloride ion by peroxomonosulphate ion have been investigated.[2] As far as we are aware no study of rates of oxidation of iodide ions by peracids has been reported [except the reaction [3] between peroxonitrous acid (HO·ONO) and I^-] and these reactions are classified [1] as ' very fast '. However, since the overall reaction order is higher than unity it is possible, by suitable dilution of the reactant solutions, to reduce the rates of the reaction to values which can be measured by the stopped-flow method. Within the frameworks of the investigations of iodide-ion oxidations by peroxo-compounds [4] and of the behaviour of peroxides [5] we

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[1] R. Curci and J. O. Edwards in ' Organic Peroxides,' ed. D. Swern, Wiley–Interscience, New York, 1970, vol. 1, p. 199.

[2] D. H. Fortnum, C. J. Battaglia, S. R. Cohen, and J. O. Edwards, *J. Amer. Chem. Soc.*, 1960, **82**, 778.

[3] M. N. Hughes, H. G. Nicklin, and W. A. C. Sackrule, *J. Chem. Soc.* (*A*), 1971, 3722.

[4] (*a*) A. Indelli, F. Ferranti, and F. Secco, *J. Phys. Chem.*, 1966, **70**, 631; (*b*) A. Indelli, F. Secco, and M. L. Fernandez Castañon, *Ann. Chim.*, (*Italy*), 1966, **55**, 207; (*c*) F. Ferranti, A. Indelli, F. Secco, and M. G. Lucarelli, X Congresso della Società Chimica Italiana, 1968, XIV, 19; (*d*) F. Secco, A. Indelli, and P. L. Bonora, *Inorg. Chem.*, 1970, **9**, 337; (*e*) F. Secco, S. Celsi, and G. Grati, *J.C.S. Dalton*, 1972, 1675.

[5] (*a*) F. Secco and S. Celsi, *J. Chem. Soc.* (*A*), 1971, 1092; (*b*) F. Secco and S. Celsi, *J. Chem. Soc.* (*B*), 1971, 1792; (*c*) M. Venturini, A. Indelli, and G. Raspi, *J. Electroanalyt. Chem.*, 1971, **33**, 99; (*d*) F. Secco, M. Venturini, and S. Celsi, *J.C.S. Perkin II*, 1972, 497.

report rate measurements of the reaction between iodide ions and some perbenzoic acids.

EXPERIMENTAL

Perbenzoic acids were prepared as described by Silbert *et al.*[6] and stored at 263 K in the dark. Conductivity water was used as reaction medium and to prepare the chemicals. Acetic acid (Erba RP) was purified by repeated crystallizations and dioxan (Erba RP) was purified by the usual procedure.[7] D_2O (99·7%) was a Fluka product. Benzoic acids, $NaClO_4$, NaI, and perchloric acid were Erba RP products. Stock solutions of peracids were standardized iodometrically[5b] and the absence of hydrogen peroxide, which originates from the hydrolysis of the peracids,[5b,d] was checked by polarography.[5d] The kinetic runs were performed with a Durrum stopped-flow apparatus by measuring at 460 nm the decrease of transmittancy due to the iodine developed. The temperature was controlled with water from a circulating bath (±0·1 K).

RESULTS

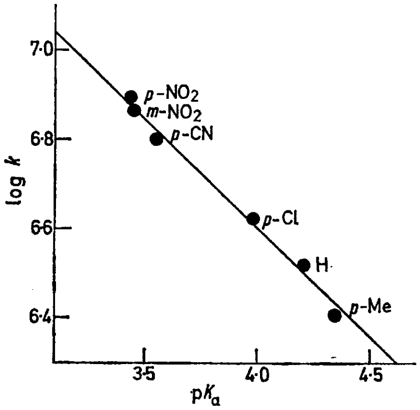
Peracids oxidize iodide ion according to reaction (1) which is used for the iodometric determination of per-

$$RCO_3H + 2I^- + 2H^+ \longrightarrow RCO_2H + I_2 + H_2O \qquad (1)$$

oxides.[8] Preliminary runs showed that the rates are not affected by light, oxygen, and impurities from the solvent or reactants unlike free-radical reactions.[5a,9,10] Iodide-ion concentrations were always kept in excess with respect to the peroxide concentrations, and good pseudo-first-order plots of log $(D_\infty - D_t)$ against time were obtained over more than 80% of the reaction according to the integrated form of equation (2). The agreement between repeated runs was

$$d[I_2]/dt = -d[RCO_3H]/dt = K_{obs}[RCO_3H] \qquad (2)$$

ca. 5%. The results in Table 1 refer to the reaction between perbenzoic acid and iodide in aqueous solution at 298 K.



Plot of the logarithms of second-order rate constants/cm^3 mol^{-1} s^{-1} for the reaction of perbenzoic acids with iodide ion against the basicities of leaving oxyanions

TABLE 1 [a]

Observed rate constants at various concentrations of the reactants at 298 K in aqueous solution

	$\frac{10^7[PhCO_3H]}{mol\ cm^{-3}}$	$\frac{10^6[I^-]}{mol\ cm^{-3}}$	$\frac{10^5[H^+]}{mol\ cm^{-3}}$	$\frac{10^3\ I^b}{mol\ cm^{-3}}$	$\frac{k_{obs\ expt}}{s^{-1}}$	$\frac{k_{obs\ calc}}{s^{-1}}$
1	2·0	2·0	15	0·2	5·87	6·64
2	2·0	5·0	15	0·2	17·3	16·6
3	2·0	7·5	15	0·2	24·0	25·7
4	2·0	10·0	15	0·2	31·2	33·2
5	2·0	20·0	15	0·2	66·0	64·0
6	2·0	50·0	15	0·2	169	166
7	0·2	10·0	15	0·2	34·7	33·2
8	0·4	10·0	15	0·2	36·5	33·2
9	1·0	10·0	15	0·2	30·1	33·2
10	3·0	10·0	15	0·2	33·0	33·2
11	10·0	10·0	15	0·2	31·7	33·2
12	5·0	5·0	0·1	0·2	17·6	16·6
13	5·0	5·0	1·0	0·2	18·0	16·6
14	5·0	5·0	5·0	0·2	16·8	16·6
15	2·0	50·0	0·5	0·2	165	166
16	5·0	5·0	20·0	0·25	16·9	16·6
17	5·0	5·0	0·5	0·01	16·8	16·6
18	5·0	5·0	0·5	0·1	16·7	16·6
19	5·0	5·0	0·5	0·4	17·1	16·6
20	5·0	5·0	0·5	1·0	16·6	16·6

[a] $k = (3·32 \pm 0·19) \times 10^6$ cm^3 mol^{-1} s^{-1} from 41 runs in which the concentrations of the reactants were widely varied [b] The ionic strength was adjusted with $NaClO_4$.

Similar data were obtained for other peracids and used in the Figure. The values of k_{obs} are independent of initial peracid concentrations which have been changed by a factor of 50. Also, the reaction rates are not affected by the H^+ concentration or by ionic strength. The observed rate constants depend on iodide-ion concentrations according to equation (3). The reaction is thus of the first order

$$k_{obs} = k[I^-] \qquad (3)$$

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[6] L. S. Silbert, E. Siegel, and D. Swern, *Org. Synth.*, 1963, **43**, 93; *J. Org. Chem.*, 1962, **27**, 1336.

[7] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, 3rd edn., 1962, p. 177.

[8] A. J. Martin, in 'Organic Analysis,' Interscience, New York, 1970, vol. IV, p. 1.

[9] W. K. Wilmarth and A. Haim, in 'Peroxide Reaction Mechanisms,' ed. J. O. Edwards, Interscience, New York, 1962, p. 200.

[10] E. J. Behrman and J. O. Edwards, in 'Progress in Physical Organic Chemistry,' eds. A. Streitwieser and R. Taft, Interscience, New York, 1967, vol. 4, p. 93.

with respect to I^- and substitution of equation (3) in (2) yields the rate law (4). The rate constant obtained from

$$-d[RCO_3H]/dt = k[RCO_3H][I^-] \qquad (4)$$

41 experimental runs is $k = (3{\cdot}32 \pm 0{\cdot}19) \times 10^6$ cm^3 mol^{-1} s^{-1} in aqueous solution at 298 K. The Figure shows a plot of log k against pK_a of the parent benzoic acids for the reaction of some ring-substituted perbenzoic acids with iodide ion. The value of the slope is $-0{\cdot}49$. The rate constant values are the average of five runs at different concentrations of the reactants. Measurements done in different solvents confirmed the rate law represented by equation (4). Table 2 reports rate constants for the reaction of $PhCO_3H$ with iodide ion in various media at different temperatures, and activation parameters.

TABLE 2

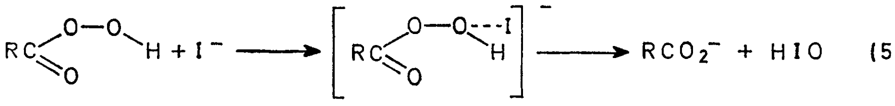
Second-order rate constants in various solvents and activation parameters

Solvent	T/K	$10^{-6}k$ / cm^3 mol^{-1} s^{-1}	$10^{-4}E_a$ / J mol^{-1}	$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	μ/D [a]
AcOH	298	42·4			6·15
D_2O	298	2·2			78·2
H_2O	291	2·14	2·84 ± 0·38	−109 ± 13	78·5
	298	3·30			
	308	4·25			
	318	5·82			
Dioxan(25) : H_2O(75) [b]	298	2·78	3·14 ± 0·42	−84 ± 13	55·7
	308	4·1			
	318	6·16			
Dioxan(50) : H_2O(50) [b]	298	3·22	3·34 ± 0·38	−75 ± 17	33·0
	308	4·4			
	318	6·50			
Dioxan(75) : H_2O(25)	298	0·451	4·77 ± 0·54	−42 ± 13	13·5
	308	0·855			
	318	1·49			

[a] Dielectric constants at 298 K (A. A. Maryott and R. E. Smith, National Bureau of Standard Circular 514, U.S. Government Printing Office, Washington, D.C., 1951); for water–dioxan mixtures (B. E. Conway, ' Electrochemical Data,' Elsevier, Amsterdam, 1952, p. 10). [b] By volume.

DISCUSSION

This reaction does not exhibit the features which are characteristic of free radical involvement. The order is unity both in peroxide and in substrate whereas for most radical reactions the reaction orders with respect to the reactants are often non-integral.[5a,9,10] Moreover the rates are not affected by the presence of radical traps such as oxygen[5a,10] or impurities[9] from solvent or chemicals. Finally the activation energy is not high and the activation entropy is quite negative as required for a bimolecular reaction with a definite orientation of the transition state. Once a radical mechanism is ruled out, a pathway in which the reducing agent acts as a nucleophile displacing a polar group of the peroxide seems to be the more reliable to explain the experimental results. This is represented by the simplified scheme (5). Iodide ion does react at the outer peroxidic oxygen and the oxygen–oxygen bond is broken. This mechanism is in line with the model suggested for the reactions of nucleophiles and peroxides in general[1,10-12] and it was advanced[2] for the reactions of some monosubstituted peracids with bromide and chloride ions. Recently[3] the kinetics of the reaction of peroxonitrous acid with SCN^-, CN^-, and I^- have been interpretated on the same basis. According to the model represented by equation (5) it would be expected that the rate of oxidation by RCO_3H should increase as the basicity of the leaving group decreases.[11,12] The results in the Figure confirm this expectation and the value of the slope ($-0{\cdot}49$), even if not high, is still of significant magnitude to indicate oxygen–oxygen and cleavage in the transition state. In addition, the value of the slope of the Figure is in satisfactory agreement with the value of *ca.* $-0{\cdot}4$ obtained by analogous plots[1,12] for halide oxidation by different peroxides bearing leaving groups of different nature, and the value of the rate constants also are in line with the values which can be inferred from such plots.



$$\mathrm{RC(=O)O{-}O{-}H} + \mathrm{I^-} \longrightarrow \left[\mathrm{RC(=O)O{-}O(H){\cdots}I}\right]^- \longrightarrow \mathrm{RCO_2^-} + \mathrm{HIO} \qquad (5)$$

The data in Table 2 show that the rates do not reflect the solvent polarity as expressed by its dielectric constant (μ). In fact the rate in acetic acid (μ 6·15 D) is *ca.* 14 time higher than in water (μ 78·5 D). Also the dielectric constants of water and D_2O are nearly identical, but the ratio $k_{H_2O} : k_{D_2O}$ is 1·5. On the other hand the rates in AcOH, H_2O, and D_2O increase with the protic character of the solvent which can be assumed as a measure of its hydrogen-bonding ability.[10] This dependence on the chemical nature of the solvent does indicate that protic media are involved in the activated complex.

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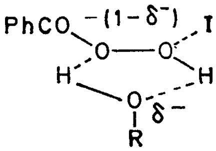
[11] J. O. Edwards, ' Inorganic Reaction Mechanism,' Benjamin, New York, 1965, ch. 5, p. 73.

[12] J. O. Edwards, ref. 9, p. 67.

The magnitude of the solvent isotope effect is in agreement with a mechanism involving proton transfer between solvent and peroxide.[12,13] Solvent isotope effects of the same order (1·4—1·7) as in this reaction have been observed in the reactions between H_2O_2 and iodide ion,[13] between peroxides and organic sulphides,[14] and very recently in the hydrolysis of *OO′*-benzylidenecatechol.[15] In all these cases mechanisms involving hydrogen-bonding between solvent and substrate in the transition state have been advanced. In addition, the lack of rate dependence on dielectric constant and the absence of salt effects suggest that charge separation is not high in the transition state. A cyclic structure involving protic solvents as in (I) may be regarded as in satisfactory agreement with the results presented in this work and those reported by others.[3,14,16] In this way the charge separation is minimized by means of proton transfers.

Table 2 shows that the activation energy increases and $\Delta S^‡$ values become less negative as the dioxan content increases. This can be explained if interaction of the peracid with dioxan in the ground state is taken into account. From studies of i.r. spectra and dipole measurements[17] it has been inferred that perbenzoic acid interacts with dioxan through an open-chain intermolecular hydrogen bond. If the activated complex in aprotic media does not involve solvent molecules[16,18] an additional desolvation energy is necessary to go from the ground state to the transition state, and a positive entropy term due to desolvation should contribute to obtain a less negative activation entropy.



(I)

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[13] P. M. Laughton and R. E. Robertson, in ' Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Dekker, New York, 1969, p. 399.

[14] M. A. P. Dankleff, R. Curci, J. O. Edwards, and H. Y. Pyun, *J. Amer. Chem. Soc.*, 1968, **90**, 3209.

[15] B. Capon and M. I. Page, *J.C.S. Perkin II*, 1972, 522.

[16] (*a*) C. G. Overberger and R. W. Cummins, *J. Amer. Chem. Soc.*, 1953, **75**, 4250; (*b*) L. Bateman and K. R. Hargrave, *Proc. Roy. Soc.*, 1954, *A*, **224**, 389; (*c*) *ibid.*, p. 339.

[17] D. Swern and L. S. Silbert, *Analyt. Chem.*, 1963, **35**, 880; W. H. T. Davison, *J. Chem. Soc.*, 1951, 2456; J. R. Rittenhouse, W. Lobunez, D. Swern, and J. G. Miller, *J. Amer. Chem. Soc.*, 1958, **80**, 4850.

[18] G. Modena and P. E. Todesco, *J. Chem. Soc.*, 1962, 4920; *Boll. sci. Fac. Chim. ind. Bologna*, 1965, **23**, 31; R. Curci, R. A. Di Prete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, 1970, **35**, 740.