Mechanisms of Peroxide Reactions: Kinetics of Reduction of Peroxomonosulphuric and Peroxomonophosphoric Acids by Iodide Ion

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The kinetics of iodide-ion oxidation by H_2SO_5 and H_3PO_5 have been investigated. The rate of the first reaction is given by equation (i) where $k = 1.73 \times 10^3$ dm³ mol⁻¹ s⁻¹ in aqueous solution at 25 °C and $I = 0.2$ mol dm⁻³.

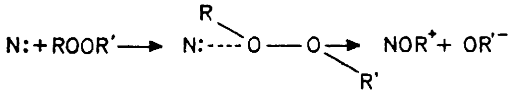
$$\text{Rate} = k[HSO_5^-][I^-] \qquad \text{(i)}$$

The rate equation for the second reaction is given by the three-term expression (ii) with $k_1 = 1.57 \times 10^3$, $k_2 =$

$$\text{Rate} = (k_1[H_3PO_5] + k_2[H_2PO_5^-] + k_3[HPO_5^{2-}])[I^-] \qquad \text{(ii)}$$

57.5, and $k_3 = 0.418$ dm³ mol⁻¹ s⁻¹ under the same conditions. The effect of electrolyte addition has been investigated. An inverse linear dependence of the logarithms of the rate constants on the basicity of the leaving group has been found. The mechanism is consistent with nucleophilic attack by I^- on the external peroxidic oxygen leading to breaking of the oxygen–oxygen bond.

It is known that certain reactions involving oxidation by peroxides are essentially polar in nature despite the fact that free radicals can arise from the facile homolysis of the oxygen–oxygen bond.[1] The polar mechanism of these reactions was first recognized by Swern [2] in a study of the nucleophilic behaviour of olefins in their reactions with peroxides, and since 1947 many articles have been published [3] dealing with nucleophilic displacements on peroxidic oxygen. Edwards and his co-workers [4] explored this type of reaction by systematic experiments and explained their results and those available in the literature on the basis of the simple model (1), where N: represents a nucleophile.



(1)

In order to extend the knowledge of the mechanism of reduction reactions of oxo- and peroxo-compounds in the homogeneous phase [5] and at the electrode,[6] we have measured the rates of reduction of peroxomonosulphuric, H_2SO_5, and peroxomonophosphoric acids, H_3PO_5, by iodide ion.

EXPERIMENTAL

Caro's acid, H_2SO_5, was prepared by acid hydrolysis of $K_2[S_2O_8]$ as described by Gleu.[7] Peroxomonophosphoric acid was prepared by acid hydrolysis of $Na_4[P_2O_8]$ according to a procedure previously described.[8] Both methods have the advantage of yielding solutions which are free from the starting disubstituted peroxide and from H_2O_2, as we checked by polarographic analysis.[9,10] Stock solutions of the peroxo-acids were kept in a refrigerator in order to prevent decomposition, and their concentration was frequently titrated by iodimetry. The above polarographic technique was also used to perform periodic analyses of the solutions in order to detect the presence of H_2O_2 which originates from slow hydrolyses of peroxo-acids.[11] Dioxan

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[2] D. Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692.

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[4] ' Peroxide Reaction Mechanisms,' ed. J. O. Edwards, Interscience, New York, 1962, p. 67.

[5] (*a*) A. Indelli, F. Ferranti, and F. Secco, *J. Phys. Chem.*, 1966, **70**, 1966; (*b*) F. Secco and M. Venturini, *J.C.S. Perkin II*, 1972, 2305.

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[7] K. Gleu, *Z. anorg. Chem.*, 1931, **195**, 61.

[8] C. J. Battaglia and J. O. Edwards, *Inorg. Chem.*, 1965, **4**, 552.

[9] G. Raspi and M. Venturini, *Chimica e Industria* 1968,**50**, 536.

[10] M. Venturini, A. Indelli, and G. Raspi, *J. Electroanalyt. Chem.*, 1971, **33**, 99.

[11] F. Secco, M. Venturini, and S. Celsi, *J.C.S. Perkin II*, 1973, 1544.

was purified by the usual procedure [12] and care was taken to ensure the absence of peroxide impurities. Conductivity water was used to prepare the solutions and as a reaction medium. The remaining chemicals were of analytical grade.

The acidity was adjusted by adding appropriate amounts of the buffers sodium chloroacetate–chloroacetic acid, sodium acetate–acetic acid, $Na_2[HPO_4]$–$Na[H_2PO_4]$, and, when necessary, perchloric acid. Sodium, barium, and magnesium perchlorates were used to adjust the ionic strength and to study salt effects. The kinetic runs were performed with a Durrum stopped-flow apparatus by measuring the decrease in transmittance at 460 nm caused by the iodine produced. The agreement between replicate runs was within 10%. The temperature was constant to within ±0.1 °C.

RESULTS

Peroxo-acids, ROOH, oxidize iodide ion to iodine according to equation (2), which is quantitative and furnishes the

$$ROOH + 2I^- + 2H^+ \longrightarrow ROH + I_2 + H_2O \quad (2)$$

basis for the iodimetric determination of peroxides.[13]

Reaction of Peroxomonosulphuric Acid and Iodide.—Pseudo-first-order conditions were attained by working in the presence of at least a ten-fold excess of iodide ion with respect to the peroxide concentration, and the observed rate constants, $k_{obs.}$, were derived from plots of log $(D_\infty - D)$ against time. The plots were linear for more than 80% completion of reaction and the agreement between replicate runs was *ca.* 10%.

The pseudo-first-order rate constants increased linearly with the iodide-ion concentration, which was varied widely (5×10^{-4}—2×10^{-2} mol dm^{-3}), but were independent of the initial concentrations of peroxide and of H^+ in the explored range of acidities ($2 \leqslant pH \leqslant 6.5$) where the peroxide is present as HSO_5^- (pK 9.4).[14] These results enable us to write the rate equation (3). The same behaviour was observed in water–dioxan mixtures. In Table 1 are reported

$$\text{Rate} = k[HSO_5^-][I^-] \quad (3)$$

the second-order rate constants at different temperatures in water and in water–dioxan mixtures, and the activation parameters.

TABLE 1

Second-order rate constants for the peroxomonosulphuric acid–iodide ion reaction at different temperatures in water and water–dioxan mixtures. $I = 0.2$ mol dm^{-3} ($Na[ClO_4]$); 1 cal = 4.184 J

Solvent	θ_c / °C	$10^{-3} k$ / dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$ / kcal mol^{-1}	$\Delta S^\ddagger$ / cal K^{-1} mol^{-1}
Water	15	1.08 ± 0.05	7.3	−19
	25	1.73 ± 0.04		
	30	2.09 ± 0.02		
	35	2.65 ± 0.15		
	40	3.13 ± 0.02		
Water–dioxan (13 : 7)	25	0.667 ± 0.018		
Water–dioxan (1 : 1)	18.5	0.365 ± 0.009	7.6	−21
	25	0.448 ± 0.012		
	35	0.778 ± 0.076		
	45	1.150 ± 0.030		

Reaction of Peroxomonophosphoric Acid and Iodide.—The same procedure was used to investigate this reaction. The reaction was first order with respect to the concentrations of both peroxide and iodide ion. It was also dependent on $[H^+]$, contrary to the reactions of I^- with $PhCO_3H$ [5b] and H_2SO_5. When log $k_{obs.}$ was plotted against $-\log [H^+]$ a sigmoid curve was obtained which strongly suggests that other species of peroxo-acid, differing in their degrees of protonation, are simultaneously reduced (Figure 1).

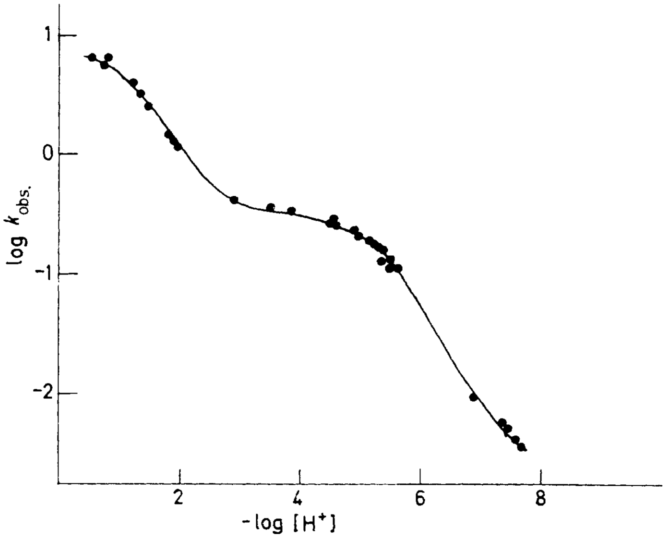

FIGURE 1 Plot of the logarithm of the pseudo-first-order constant, $k_{obs.}$, of the reaction between H_3PO_5 and I^- against $-\log [H^+]$. [NaI] = 5×10^{-3} mol dm^{-3}, 25 °C, $I = 0.2$ mol dm^{-3} ($Na[ClO_4]$)

The reaction scheme can be represented by equations (4)—(7) where HIO is rapidly converted into iodine by the

$$\begin{tikzcd}
H_3PO_5 + I^- \arrow[r, "k_1"] \arrow[d, shift right, "K_{A1}"'] & H_2PO_4^- + HIO & (4) \\
H_2PO_5^- + I^- \arrow[r, "k_2"] \arrow[u, shift right, "H^+"'] \arrow[d, shift right, "K_{A2}"'] & HPO_4^{2-} + HIO & (5) \\
HPO_5^{2-} + I^- \arrow[r, "k_3"] \arrow[u, shift right, "H^+"'] \arrow[d, shift right, "K_{A3}"'] & [PO_4]^{3-} + HIO & (6) \\
{[PO_5]^{3-} + I^-} \arrow[r, "k_4"] \arrow[u, shift right, "H^+"'] & {[PO_4]^{3-} + [IO]^-} & (7)
\end{tikzcd}$$

excess of iodide. According to the scheme the rate of the reaction is given by equation (8). On the other hand under

$$\text{Rate} = -d[PO_5]_T/dt = (k_1[H_3PO_5] + k_2[H_2PO_5^-] + k_3[HPO_5^{2-}] + k_4[PO_5^{3-}])[I^-] \quad (8)$$

our experimental conditions (excess of iodide and buffered solutions) the rate of the reaction is expressed by equation (9). By using the dissociation constants of peroxomonophosphoric acid, K_{A1}, K_{A2}, and K_{A3}, and the mass-conservation condition for phosphorus-containing species, from

$$\text{Rate} = -d[PO_5]_T/dt = k_{obs.}[PO_5]_T \quad (9)$$

equations (8) and (9) one obtains the relation between $k_{obs.}$

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

[13] A. J. Martin, in ' Organic Analysis,' Interscience, New York, 1970, vol. 4, p. 1.

[14] D. L. Ball and J. O. Edwards, *J. Amer. Chem. Soc.*, 1956, **78**, 1125.

TABLE 2

Observed and calculated pseudo-first-order rate constants of the peroxomonophosphoric acid–iodide ion reaction at different concentrations of the reactants, 25 °C, and $I = 0.2$ mol dm^{-3} (Na[ClO$_4$])

Expt. no.	pH	$10^4[\mathrm{PO_5}]_\mathrm{T}$ / mol dm^{-3}	10^3[NaI] / mol dm^{-3}	$k_{\mathrm{obs.}}$ / s^{-1}	$k_{\mathrm{calc.}}$ / s^{-1}
1	0.70	2.50	5.00	6.50	6.15
2	0.90	2.50	5.00	5.28	5.47
3	0.95	2.50	5.00	6.44	5.28
4	1.30	2.50	5.00	3.98	3.81
5	1.48	2.50	5.00	3.07	3.05
6	1.50	2.50	5.00	3.21	2.97
7	1.60	2.50	5.00	2.41	2.58
8	1.94	2.50	5.00	1.42	1.54
9	2.02	2.50	5.00	1.25	1.36
10	2.10	2.50	5.00	1.13	1.20
11	3.04	2.50	5.00	0.406	0.405
12	3.63	2.50	5.00	0.359	0.320
13	4.00	2.50	5.00	0.330	0.300
14	4.67	1.00	2.50	0.120	0.128
15	4.67	1.00	5.00	0.263	0.259
16	4.67	2.00	5.00	0.286	0.259
17	4.67	3.00	5.00	0.281	0.259
18	4.67	2.00	2.50	0.121	0.129
19	4.67	2.00	2.00	0.111	0.102
20	4.67	2.00	10.00	0.576	0.510
21	4.67	2.00	20.00	1.120	1.020
22	4.67	3.00	2.50	0.110	0.127
23	4.67	7.00	10.00	0.530	0.522
24	4.67	10.00	10.00	0.549	0.512
25	4.71	5.00	5.00	0.275	0.252
26	4.80	5.00	2.50	0.102	0.121
27	5.02	2.50	5.00	0.211	0.219
28	5.10	2.50	5.00	0.195	0.200
29	5.28	2.50	5.00	0.173	0.182
30	5.36	2.50	5.00	0.171	0.170
31	5.41	2.50	5.00	0.151	0.161
32	5.50	2.50	5.00	0.150	0.147
33	5.61	2.50	5.00	0.133	0.129
34	5.70	2.50	5.00	0.132	0.116
35	7.00	2.50	5.00	0.0091	0.011
36	7.50	2.50	5.00	0.0055	0.0050
37	7.53	2.50	5.00	0.0053	0.0048
38	7.70	2.50	5.00	0.0041	0.0039
39	7.80	2.50	5.00	0.0034	0.0035
40	7.87	2.50	5.00	0.0033	0.0034

and the hydrogen-ion concentration in the form (10). The

$$\frac{k_{\mathrm{obs}}}{[\mathrm{I}^-]} = \frac{k_1[\mathrm{H}^+]^3 + k_2K_{\mathrm{A1}}[\mathrm{H}^+]^2 + k_3K_{\mathrm{A1}}K_{\mathrm{A2}}[\mathrm{H}^+] + k_4K_{\mathrm{A1}}K_{\mathrm{A2}}K_{\mathrm{A3}}}{[\mathrm{H}^+]^3 + K_{\mathrm{A1}}[\mathrm{H}^+]^2 + K_{\mathrm{A1}}K_{\mathrm{A2}}[\mathrm{H}^+] + K_{\mathrm{A1}}K_{\mathrm{A2}}K_{\mathrm{A3}}} \tag{10}$$

second-order rate constants k_1, k_2, k_3, and k_4 were evaluated by a least-squares analysis [15] applied to the data in Table 2. For the dissociation constants of $\mathrm{H_3PO_5}$, the values obtained by Battaglia and Edwards [8] at 25 °C and I 0.2 mol dm^{-3} were used: $K_{\mathrm{A1}} = 8.0 \times 10^{-2}$, $K_{\mathrm{A2}} = 4.2 \times 10^{-6}$, and $K_{\mathrm{A3}} = 1.6 \times 10^{-13}$ mol dm^{-3}. The hydrogen-ion concentrations were calculated from the experimentally measured pH values with the aid of the Davies equation.[16]

In Table 3 are reported the results obtained by applying the statistical analysis, not only to the four-parameter equation (10) but also to equations with three, two, and one rate parameters. The corresponding percentage standard deviations are also reported and were calculated from equation (11) where N is the number of experiments and P

$$\text{Standard deviation}/\% = 100\{\Sigma[1 - (k_{\mathrm{obs.}}/k_{\mathrm{calc.}})]^2/(N - P)\}^{\frac{1}{2}} \tag{11}$$

is the number of parameters in the equation under examination. As shown in the Table, the standard deviation of the four-parameter equation is nearly identical to that of the three-parameter equation. Moreover the value of k_4 is small and negative. This allows us to rule out path (7) involving $[\mathrm{PO_5}]^{3-}$. Reaction schemes with two and one paths were also ruled out since their standard deviations are high and the errors are systematic. The more reliable kinetic picture involves the simultaneous reduction by $\mathrm{I^-}$ ion of the three species $\mathrm{H_3PO_5}$, $\mathrm{H_2PO_5}^-$, and $\mathrm{HPO_5}^{2-}$ [equations (4)–(6)]. This leads to the rate equation (12), which has

$$\frac{k_{\mathrm{obs.}}}{[\mathrm{I}^-]} = \frac{k_1[\mathrm{H}^+]^2 + k_2K_{\mathrm{A1}}[\mathrm{H}^+] + k_3K_{\mathrm{A1}}K_{\mathrm{A2}}}{[\mathrm{H}^+]^2 + K_{\mathrm{A1}}[\mathrm{H}^+] + K_{\mathrm{A1}}K_{\mathrm{A2}}} \tag{12}$$

been used to calculate the rate constant $k_{\mathrm{calc.}}$ in Table 2. Once it was established that equation (12) is the most appropriate to the experimental data, the statistical treatment was repeated by allowing K_{A1} and K_{A2} to vary until optimal values of the parameters were obtained; these are $K_{\mathrm{A1}} = 10.8 \times 10^{-2}$ mol dm^{-3}, $K_{\mathrm{A2}} = 4.8 \times 10^{-6}$ mol dm^{-3}, $k_1 = 1.87 \times 10^3$ dm^3 mol^{-1} s^{-1}, $k_2 = 59.6$ dm^3 mol^{-1} s^{-1}, and $k_3 = 0.456$ dm^3 mol^{-1} s^{-1} with a standard deviation of 8.8%. The agreement between these results and those reported in Table 3 is good, and moreover the values of K_{A1} and K_{A2}

TABLE 3

Second-order rate constants for possible reaction paths in the $\mathrm{H_3PO_5} + \mathrm{I^-}$ reaction and related standard deviations at 25 °C and $I = 0.2$ mol dm^{-3} (Na[ClO$_4$])

Species	10^3k_1 / dm^3 mol^{-1} s^{-1}	$10\,k_2$ / dm^3 mol^{-1} s^{-1}	$10^{-1}k_3$ / dm^3 mol^{-1} s^{-1}	10^2k_4 / dm^3 mol^{-1} s^{-1}	Standard deviation / %
$\mathrm{H_3PO_5}$	1.80				10^5
$\mathrm{H_2PO_5}^-$		6.37			21×10^2
$\mathrm{HPO_5}^{2-}$			8.52		10^5
$\mathrm{H_3PO_5}$ $\mathrm{H_2PO_5}^-$	1.55	6.08			40
$\mathrm{H_3PO_5}$ $\mathrm{HPO_5}^{2-}$	1.80		8.52		56×10^2
$\mathrm{H_2PO_5}^-$ $\mathrm{HPO_5}^{2-}$		6.05	3.94		21×10^2
$\mathrm{H_3PO_5}$ $\mathrm{H_2PO_5}^-$ $\mathrm{HPO_5}^{2-}$	1.57	5.75	4.18		9.51
$\mathrm{H_3PO_5}$ $\mathrm{H_2PO_5}^-$ $\mathrm{HPO_5}^{2-}$ $\mathrm{PO_5}^{3-}$	1.57	5.75	4.20	−1.94	9.50

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[15] F. Secco, A. Indelli, and P. L. Bonora, *Inorg. Chem.*, 1970, **9**, 337.

[16] C. W. Davies, *J. Chem. Soc.*, 1938, 2093.

TABLE 4

Salt effects on the reactions of H_2SO_5 and H_3PO_5 with iodide ion in aqueous solution at 25 °C and [NaI] = 2.50×10^{-3} mol dm^{-3}

Expt. no.	$10^4[HSO_5^-]$ / mol dm^{-3}	$[NaClO_4]$ / mol dm^{-3}	$[Mg(ClO_4)_2]$ / mol dm^{-3}	pH	$k_{obs.}$ / s^{-1}
1	2.5			4.7	5.28
2	2.5	0.02		4.7	6.05
3	2.5	0.07		4.7	7.04
4	2.5	0.12		4.7	7.42
5	2.5	0.17		4.7	8.93
6	2.5		0.01	4.7	5.35
7	2.5		0.02	4.7	6.12
8	2.5		0.04	4.7	6.79
9	2.5		0.06	4.7	7.48
10	2.5	0.17	0.01	4.7	8.36
11	2.5	0.14	0.02	4.7	8.56
12	2.5	0.08	0.04	4.7	7.72
13	2.5	0.03	0.06	4.7	7.08
	$10^4[PO_5]_T$ / mol dm^{-3}		$[Ba(ClO_4)_2]$ / mol dm^{-3}		
14	2.5		0.01	4.7	0.165
15	2.5		0.023	4.7	0.179
16	2.5		0.04	4.7	0.193
17	2.5		0.06	4.7	0.238
18	2.5		0.033	1.0	6.06
19	2.5		0.043	1.0	6.02
20	2.5		0.06	1.0	6.38
21	2.5		0.077	1.0	6.18

obtained in this kinetic study are in agreement with the spectrophotometric results of Battaglia and Edwards.

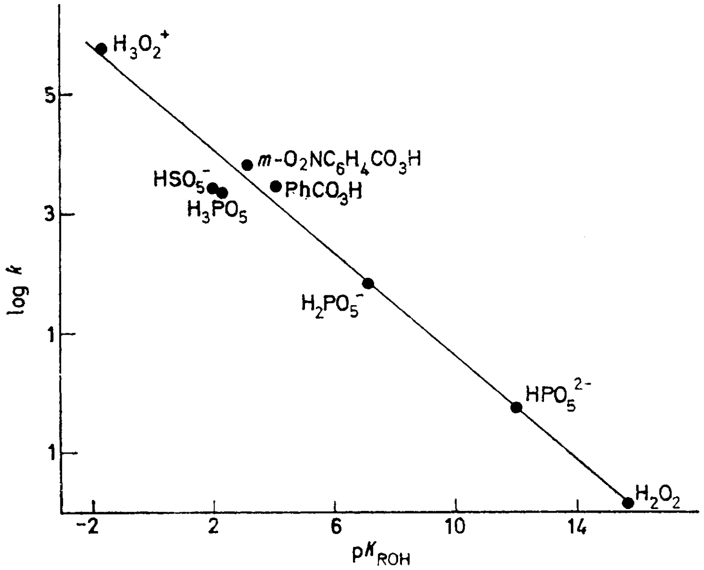

FIGURE 2 Plot of the logarithm of the second-order rate constants of reactions between I^- and different peroxides against the basicity of the leaving group (pK_{ROH}). Data for hydrogen peroxide were taken from ref. 4 and for perbenzoic acids from ref. 5b

Salt Effects.—In Table 4 are reported rate data obtained in the presence of sodium, magnesium, and barium perchlorates. The reaction of H_2SO_5 and I^- was accelerated by increasing the concentration of added salt, as expected for a reaction between two anions,[17] and the effect was specific and dependent on the cation concentration rather than on the ionic strength. In fact runs 10—13, in the presence of different mixtures of $Mg[ClO_4]_2$ and $Na[ClO_4]$ at constant ionic strength, exhibited different rates.

As far as the reaction between H_3PO_5 and iodide ion is concerned we should expect (on the basis of the rate law) k_1 to be insensitive to salt addition, whereas k_2 should increase with the concentration of added electrolytes.[17] These predictions were verified by runs at pH 1.0 where H_3PO_5 gives the major contribution to the overall rate, and at pH 4.7 where, on the other hand, $H_2PO_5^-$ ion is the prevailing active species.

DISCUSSION

The results obtained in this study show that the reactivities of H_3PO_5 and HSO_5^- are similar, and for H_3PO_5 the rate strongly increases with the number of protons bound to the peroxide. This leads to the exclusion of the hypothesis that only electrostatic interactions are responsible for the differences in reactivity. In this case in fact the rate of the HSO_5^- reduction should be lower than that of H_3PO_5. Moreover, if the reactions of $H_2PO_5^-$ and HPO_5^{2-} with I^- ion, *i.e.* (5) and (6), are compared on the basis of electrostatic theory[18] it is necessary to assume a value of the reaction distance of 1.5 Å in order to obtain a value of k_2/k_3 equal to the experimental value of 131. This is unreasonable if one considers that the ionic radius of iodide ion alone is 2.19 Å.[19] Assuming, more probably, a value of 7.8 Å for the reaction distance between iodide and peroxide (see below), the diminution of electrostatic repulsion accounts for a k_2/k_3 value of *ca.* 2.5.

These results confirm that one of the main factors affecting this kind of reaction is the basicity of the leaving group.[4] Figure 2, in which our and literature data are given,[4,5b] shows that there is a good linear relation between the rates of reduction by iodide of peroxides of different nature and the basicities of the corresponding leaving anions (pK_{ROH}). This is in agreement with the

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[17] P. Debye and E. Hückel, *Z. phys. Chem.*, 1923, **24**, 185.

[18] A. Indelli and P. L. Bonora, *J. Amer. Chem. Soc.*, 1966, **88**, 924.

[19] J. A. A. Ketelaar, 'Chemical Constitution,' 2nd edn., Elsevier, Amsterdam, 1958, p. 28.

polar mechanism in equation (1), and the gradient of -0.5 indicates that the breaking of the oxygen–oxygen bond is quite advanced in the transition state.[20]

In Table 1 data are given that were determined with the purpose of obtaining evidence for the inclusion of protic solvent molecules in the transition state. The formation of an activated complex in which water molecules are linked to the peroxide by hydrogen bonds should contribute in lowering the activation entropy.[4] This hypothesis has been verified in studies of peroxide reductions by iodide [5b] and organic sulphides.[21] In our study the changes in the activation parameters were small. However, a noticeable decrease in rate was observed on changing the dielectric constant of the medium from 78.5 (D_1) of water to that of 33 (D_2) of water–dioxan (1 : 1). This can be ascribed to increased repulsion of the two negatively charged reactants due to the decreased dielectric constant. According to the equation [22] $(k_{D_1}/k_{D_2}) = (Z_A Z_B e^2/\mathbf{k}Tr)[(1/D_2) - (1/D_1)]$ the calculated value of (k_{D_1}/k_{D_2}) corresponds to the experimental one of 0.55 when the reaction distance r is set equal to 7.8 Å, which is a reasonable value.

It is also confirmed that a second important factor in these reactions is the polarizability of the nucleophile.[4] Our results and those of Fortnum *et al.*,[23] who studied the reduction of H_2SO_5 by Cl^- and Br^-, show that the rate constants increase from the less polarizable chloride to the more polarizable iodide in the order $Cl^- : Br^- : I^- = 1 : 10^3 : 10^6$. The same sequence has been observed in reactions of hydrogen peroxide.[4]

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[22] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, p. 123.

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