Kinetics and Salt Effects on the Alkaline Hydrolysis of Perbenzoate Ion

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The rates of hydrolysis of perbenzoate ion in alkaline aqueous solutions have been studied over a wide range of concentrations of the reactants at different temperatures. The rate equation is (i) where $k_1 = (4{\cdot}8 \pm 0{\cdot}8) \times 10^{-6}\ \mathrm{s}^{-1}$,

$$-\mathrm{d}[\mathrm{PhCO_3}^-]/\mathrm{d}t = \{k_1 + k_2[\mathrm{OH}^-] + k_3[\mathrm{OH}^-]^2\}[\mathrm{PhCO_3}^-] \qquad \text{(i)}$$

$k_2 = (3{\cdot}32 \pm 0{\cdot}04) \times 10^{-4}\ \mathrm{l\ mol^{-1}\ s^{-1}}$, and $k_3 = (6{\cdot}1 \pm 0{\cdot}2) \times 10^{-4}\ \mathrm{l^2\ mol^{-2}\ s^{-1}}$ at 25 °C and at ionic strength 0·5M ($NaClO_4$). The activation parameters have been measured, and the mechanism of the reaction is discussed. Added salts exert a positive effect on the rates of the reaction, except tetraethylammonium perchlorate. The rate-enhancing effect lies in the order $\mathrm{Co(NH_3)_6}^{3+} \gg \mathrm{Sr}^{2+} > \mathrm{Ba}^{2+} \gg \mathrm{K}^+ \simeq \mathrm{Na}^+ > \mathrm{N}^+$. The salt effect is discussed on the basis of the incorporation of added cations into the transition state.

THE hydrolysis and formation of peracids involve breaking of the acyl–oxygen bond.[1] The mechanism of the hydrolysis of perbenzoic acid in acidic solution is consistent with nucleophilic attack of a water molecule on the carbonyl carbon atom of the peracid.[2] Goodman *et al.*[3] studied the decomposition of several aromatic peracids in the range of pH 6—9, and found that the rate has a maximum value at a pH corresponding to the pK of the peracid, becoming very small at peracid dissociations close to 0 and 100%. They showed that the rate-determining step is the attack of the nucleophilic peracid anion on the electrophilic carbonyl carbon of the un-ionized peracid. We now report rate measurements on the alkaline decomposition of perbenzoate ion according to reaction (1)

$$\mathrm{PhCO_3}^- + \mathrm{H_2O} \xrightarrow{\mathrm{OH}^-} \mathrm{PhCO_2}^- + \mathrm{H_2O_2} \qquad (1)$$

EXPERIMENTAL

Perbenzoic acid was prepared and recrystallized by the procedure of Sielbert *et al.*[4] and standardized iodometrically.[2] Conductivity water was used as reaction medium, and to prepare and recrystallize the chemicals.

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[2] F. Secco and S. Celsi, *J. Chem. Soc.* (*B*), 1971, 1792.

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$NaClO_4$, $KClO_4$, Et_4ClO_4, and NaOH were Erba RP products. Barium and strontium perchlorates were prepared from the corresponding carbonates and perchloric acid and were recrystallized twice from conductivity water. Hexamminocobaltic perchlorate was obtained from the corresponding chloride and $NaClO_4$, and recrystallized from water. Carbon dioxide-free stock solutions of NaOH were stored under nitrogen pressure. The reaction mixtures were prepared by adding to solutions of perbenzoic acid appropriate amounts of NaOH. The $[PhCO_3^-]$ figures quoted correspond to the concentrations of peracid, and $[OH^-]$ figures refer to the excess over that required to neutralize the acid. The rates of hydrolysis were measured by removing at intervals suitable amounts of the contents of the reaction vessel, which was immersed on a constant-temperature bath (±0·1 °C), and titrating at $1 \leqslant pH \leqslant 2$ the undecomposed peracid iodometrically.[2] Several runs were studied by a polarographic technique which makes use of a platinum electrode with periodic renewal of the diffusion layer[5] connected with a Metrohm Polarecord E 261. This method enabled us to evaluate simultaneously the amounts of perbenzoate ion and H_2O_2 present at different times. The agreement between the two techniques was good as is shown by a comparison between the results of Table 2 and the corresponding data No. 21, 5, 7, 9 of Table 1 obtained by the iodometric method.

TABLE 1

Observed rate constants at different concentrations of the reactants at 25 °C

No.	$10^3[PhCO_3^-]/M$	$10[OH^-]/M$	$10^5k_{obs}/s^{-1}$
1	4·55	0·05	0·715
2	4·55	0·15	0·955
3	4·55	0·25	1·26
4	4·55	0·43	2·05
5	4·55	0·92	4·00
6	4·55	1·45	6·92
7	4·55	1·95	9·80
8	4·55	2·45	11·8
9	4·55	2·95	14·1
10	4·55	0·72	3·40
11	2·65	0·80	3·50
12	8·70	0·80	3·53
13	17·4	0·80	3·65
14	22·7	1·2	5·50
15	30·2	1·2	5·32
16	60·3	1·2	5·25
17	18·0	1·8	8·00
18	9·3	1·5	7·08
19	18·6	1·5	6·80
20	55·8	1·5	7·08
21	4·52	0·45	2·13
22	4·52	1·64	7·20
23	3·85	3·95	22·8
24	7·25	4·90	31·0
25	3·85	5·45	37·3
26	3·85	5·95	41·9
27	3·85	6·45	47·9
28	4·04	0·30	1·54
29	7·71	0·40	1·78

Ionic strength is 0·5M ($NaClO_4$) except in runs 25, 26, and 27.

TABLE 2

Observed rate constants obtained by polarographic measurements at 25 °C; $[PhCO_3^-] = 4·55 \times 10^{-3}M$

$10[OH^-]/M$	$10^5k_{obs}{}^a/s^{-1}$	$10^5k_{obs}{}^b/s^{-1}$
0·45	2·1	2·01
0·95	3·8	4·15
1·95	9·5	9·45
2·95	14·0	15·5

[a] From plots of log $[PhCO_3^-]$ against time. [b] From plots of log $[H_2O_2]\infty/([H_2O_2]\infty - [H_2O_2])$ against time.

RESULTS

Preliminary runs showed that the rates are not affected by light, oxygen, and impurities from the solvent or reactants, unlike free-radical reactions.[6,7] Polarographic measurements allow a check of the stoicheiometry of equation (1) by measurement of the rates of the reaction both as rate of disappearance of $PhCO_3^-$ and as rate of formation of H_2O_2. In fact perbenzoate ion gives at the platinized platinum electrode a cathodic wave corresponding to the irreversible reduction of $PhCO_3^-$ according to the overall reaction[8] (2), and hydrogen peroxide yields a

$$PhCO_3^- + 2e + H_2O \longrightarrow PhCO_2^- + 2OH^- \quad (2)$$

cathodic wave corresponding to the reversible reaction[9] (3). In both cases the diffusion limiting current is proportional to the concentrations of the electroactive species

$$HO_2^- + OH^- \rightleftharpoons O_2 + H_2O + 2e^- \quad (3)$$

and the steps are shifted sufficiently to allow the simultaneous determination of the concentrations of the two substances. Figure 1 represents two voltammetric curves. Curve A is obtained in the presence of a mixture of 0·05M-NaOH and 0·45M-$NaClO_4$ and curve B is obtained when a mixture of perbenzoate and hydrogen peroxide is added to the supporting electrolyte. The wave corresponding to the reduction of perbenzoate ion appears at more positive values of the applied potential, and at less positive values the redox wave of H_2O_2 is obtained. In the range of

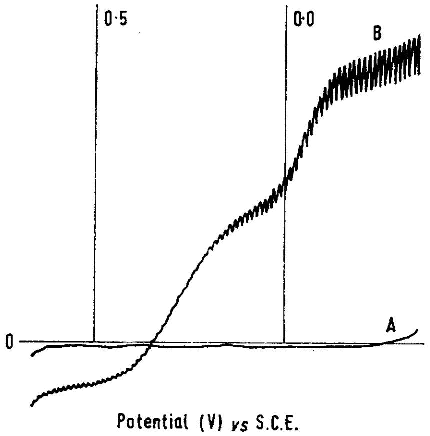

FIGURE 1 Voltammetric curves obtained in the absence (A) and in the presence (B) of $1·5 \times 10^{-3}M$-$PhCO_3^-$ and $1·0 \times 10^{-3}M$-H_2O_2; supporting electrolyte: 0·05M-NaOH + 0·45M-$NaClO_4$. The potential values are referred to satured calomel electrode

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[5] D. Cozzi, G. Raspi, and L. Nucci, *J. Electroanalyt. Chem.*, 1966, **12**, 36; G. Raspi and M. Venturini, *Chimica e Industria*, 1968, **50**, 536; M. Venturini, A. Indelli, and G. Raspi, *J. Electroanalyt. Chem.*, 1971, **33**, 99.

[6] W. K. Wilmarth and A. Haim, in ref. 1, p. 200.

[7] F. Secco and S. Celsi, *J. Chem. Soc.* (*A*), 1971, 1092.

[8] F. Secco and M. Venturini, unpublished results.

[9] G. Raspi and L. Nucci, *Ricerca sci.*, 1967, **37**, 509.

potentials between 0·35 and −0·10 V reduction of perbenzoate ion and oxidation of H_2O_2 occur simultaneously. When both are present in solution, the cathodic diffusion current of $PhCO_3^-$ compensates for the anodic diffusion current of H_2O_2. The reduction wave of $PhCO_3^-$ is therefore shifted towards the anodic portion of the polarogram proportionally to $[H_2O_2]$. By evaluating the amplitudes of the polarographic waves obtained at time intervals it is possible to measure the rates of disappearance of perbenzoate ion and the rate of formation of hydrogen peroxide. The observed rate constants obtained by first-order plots based on $[PhCO_3^-]$ and on $[H_2O_2]$ are (Figure 2) in good agreement (Table 2) meaning that other possible paths giving, say, O_2 as a product[3] are negligible in the explored range of $[OH^-]$. The reaction is of the first order in perbenzoate ion. Figure 3 represents some first-order plots obtained according to the integrated form of equation (4).

$$-d[PhCO_3^-]/dt = k_{obs}[PhCO_3^-] \qquad (4)$$

The plots are linear over 80% of the reaction and the values of k_{obs}, obtained by the slopes of straight lines as reported in Figure 3, are independent of the concentration of perbenzoate ion which is changed from $2·65 \times 10^{-3}$ to 60×10^{-3}M. The values of k_{obs} depend on the OH^- concentration, which ranges between 5×10^{-3}M and 0·645M as shown in Table 1, in which the results at 25 °C are reported. The experimental data are fitted by equation (5). The parameters of equation (5), obtained by least-squares treatment, are:

$$k_{obs} = k_1 + k_2[OH^-] + k_3[OH^-]^2 \qquad (5)$$

$k_1 = (4·8 \pm 0·8) \times 10^{-6}s^{-1}$, $k_2 = (3·32 \pm 0·04) \times 10^{-4}$ l mol^{-1} s^{-1}, and $k_3 = (6·1 \pm 0·2) \times 10^{-4}$ l^2 mol^{-2} s^{-1} at 25 °C and ionic strength 0·5M ($NaClO_4$). The standard deviation of equation (5) is 4·4% and the deviations are randomly distributed. Substitution of equation (5) into equation (4) yields the rate law (6). Table 3 reports the values of k_1,

$$-d[PhCO_3^-]/dt = (k_1 + k_2[OH^-] + k_3[OH^-]^2)[PhCO_3^-] \qquad (6)$$

k_2, and k_3 obtained at different temperatures, and the corresponding activation parameters. The results in the presence of different added salts are in Table 4.

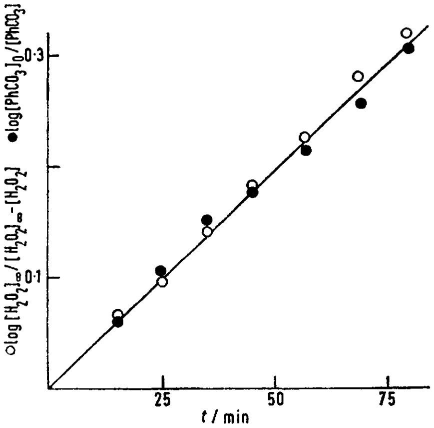


FIGURE 2 First-order plots for the alkaline hydrolysis of perbenzoate ion based on the disappearance of $PhCO_3^-$ and on the formation of H_2O_2: $[PhCO_3^-] = 4·55 \times 10^{-3}$M, $[OH^-] = 0·145$M, 25 °C (polarographic method)

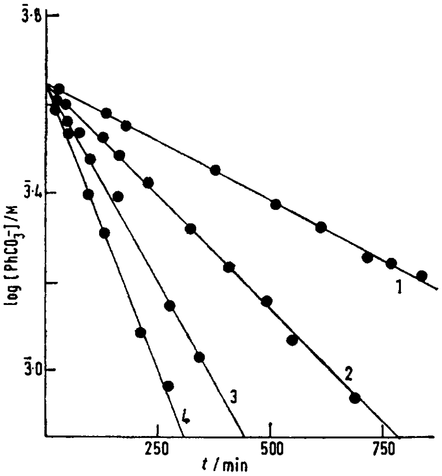


FIGURE 3 First-order plots for the alkaline hydrolysis of perbenzoate ion ($4·55 \times 10^{-3}$M) at 25 °C: $[OH^-]$ = 1, 0·043M; 2, 0·092M; 3, 0·145M; 4, 0·195M (iodometric method)

TABLE 3

Dependence of rate constants upon the temperature and activation parameters

t/°C	$10k_1$/s^{-1}	10^4k_2/l mol^{-1} s^{-1}	10^4k_3/l^2 mol^{-2} s^{-1}
20	2·5	2·68	3·5
25	4·8	3·32	6·1
35	15·8	10·7	8·5
45	48·8	31·8	11·5

	E_a/kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}
k_1	22	−12
k_2	19	−12
k_3	8	−48

TABLE 4

Observed rate constants, k_{obs}, in the presence of added salts at 25 °C

$[PhCO_3^-] = 4·45 \times 10^{-3}$M, $[OH^-] = 2·5 \times 10^{-2}$M, $k_{obs} = 11·3 \times 10^{-6}$ s^{-1} (no added salt)

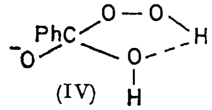
$10^2[NaClO_4]$/M	2	4	7	12	16·5
10^6k_{obs}/s^{-1}	11·6	12·1	13·2	12·5	12·7
$10^2[KClO_4]$/M	2	4	7	12	
10^6k_{obs}/s^{-1}	11·8	12·0	12·8	12·4	
$10^2[Et_4NClO_4]$/M	2	4	7	12	16·5
10^6k_{obs}/s^{-1}	11·4	11·4	11·3	11·0	10·3

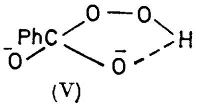
$[PhCO_3^-] = 4·45 \times 10^{-3}$M, $[OH^-] = 5 \times 10^{-2}$M, $k_{obs} = 22·0 \times 10^{-6}$ s^{-1} (no added salt)

$10^2[Ba(ClO_4)_2]$/M	0·333	1·00	1·67	2·5	3·33
10^6k_{obs}/s^{-1}	50·2	122	211	277	384
$10^2[Sr(ClO_4)_2]$/M	0·333	1·00	1·67	2·5	
10^6k_{obs}/s^{-1}	139	221	315	451	
$10^5[Co(NH_3)_6(ClO_4)_3]$	1·67	3·33	8·34	16·7	
10^6k_{obs}/s^{-1}	187	219	284	398	

DISCUSSION

The kinetic equation (6) shows that at ionic strength 0·5M the reaction occurs *via* three parallel paths, the first being of zeroth order, the second of first order, and the third of second order with respect to OH^-. The reaction does not exhibit the peculiarities characteristic of free-radical reactions.[6,7] A mechanism involving formation of tetrahedral intermediates[10] as in the Scheme might explain the form of the kinetic law (6). In the path corresponding to k_1 a molecule of water attacks the carbonyl carbon of perbenzoate ion giving the tetrahedral intermediate (I), which decomposes yielding $PhCO_2^-$ and H_2O_2. When the alkali concentration increases, an OH^- ion does compete with water in the nucleophilic attack on the carbonyl group of $PhCO_3^-$ giving the products through formation of intermediate (II) (path k_2). It is possible, on the other hand, to obtain the intermediate (II) by a reaction of intermediate (I) with an OH^- ion. At high concentrations of the alkali, a second OH^- ion might react with intermediate (II) to give the intermediate (III), which, in turn, decomposes yielding the products (path k_3). This mechanism is analogous to the ones suggested by Biechler and Taft[11] for the alkaline hydrolyses of *N*-substituted anilides, by Pearson *et al.*[12] for the hydrolysis of acetylacetone, and by Hammett[13] for the Cannizzaro reaction, the rate laws for all of which also contain a second-order term in OH^-. However the $[OH^-]^2$ term in the rate equation (6) rests essentially on results with $[OH^-] > 0{\cdot}3$M, and below this value $k_{obs} = k_1 + k_2[OH^-]$ can account equally well for the results. This makes the conclusions about the k_3 step more uncertain because effects on the activity coefficients could be responsible for the observations in the more alkaline solutions. In fact even at constant ionic strength 0·5M the activity coefficient of OH^- will certainly not be independent of the $OH^- : ClO_4^-$ ratio,[14] and this could also apply to other anions. An alternative mechanism involving attack by water or OH^- on the peroxide oxygen atom must be excluded because experiments with ^{18}O showed that there is no exchange between the peroxide group and OH^- or H_2O.[15] Attack of OH^- ion on intermediate (I) to give (II), and on intermediate (II) to give (III), is facilitated if intermediates (I) and (II) are stabilized by formation of five-membered rings[2,16] as in (IV) and (V). It is supposed, in postulating the mechanism of the reaction, that intermediates (I), (II), and (III) are in equilibrium among themselves and with the reactants. In this way the rate-determining steps correspond to the breakdown of the intermediates. However it is also possible that the intermediates are not in equilibrium with the reactants and the experimental rate constants depend on the partitioning of the tetrahedral intermediates.


(IV)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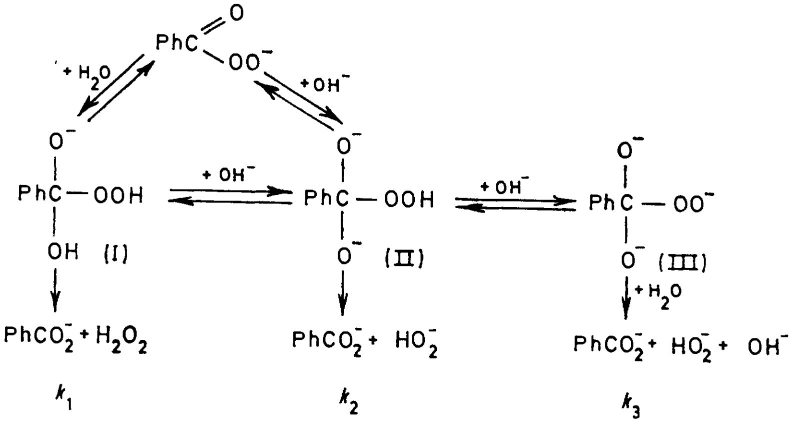

The rate of the reaction increases on increase of the concentrations of added salts. Table 4 shows that the rate-enhancing effects of cations lie in the order $Co(NH_3)_6^{3+} \gg Sr^{2+} > Ba^{2+} \gg K^+ \simeq Na^+ > Et_4N^+$. The accelerating action of hexamminocobaltic, strontium, and barium ions is much larger than the action of univalent ions, and may be regarded as a catalytic effect arising from the formation of chelate complexes between the metal ions and the negatively charged transition state. The latter is thereby stabilized and the energy barrier lowered. The greater effect of strontium than barium ions is in line with the greater stability of strontium complexes.[17] The very large effect of $Co(NH_3)_6^{3+}$ may be ascribed to the formation of a comparatively more stable chelate, owing to the formation of hydrogen bonds between the hydrogen atoms of NH_3 and the oxygen atoms of the transition state. In fact the six NH_3 molecules in the octahedral co-ordination sphere of the cation will be polarized and fractionally positively charged hydrogen atoms will be available to form hydrogen bonds with the oxygen

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atoms of the transition state. The incorporation of multivalent cations in the transition state may alternatively be described by postulating the formation of a chelate between the perbenzoate ion and the cation. The withdrawal of electrons so produced facilitates the attack of OH^- on the carbonyl carbon atoms. The hypothesis of the incorporation of cations in the form of a chelate in the transition state was advanced by Hoppè and Prue [18] to explain the catalytic effects of Tl^+, Ba^{2+}, Ca^{2+}, and $Co(NH_3)_6{}^{3+}$ on the alkaline hydrolysis of ethyl oxalate and malonate. Moreover they suggested a similar interpretation of the catalysis by heavy-metal ions on the alkaline hydrolysis of amino-acids esters,[19] and the large effect of calcium ions on the alkaline hydrolysis of acetyl- and benzoyl-citric acids.[20] The action of univalent ions can be interpreted on the basis of complexes or ion pairs between cations and transition state. The more highly charged ions form the more stable complexes,[17] but the stability constants show two kinds of behaviour in their dependence on ion size. For ligands with concentrated negative charge, such as fluoride, hydroxide, and the anions of weak oxy-acids, the stability constants increase as the cations become smaller. On the contrary, with oxy-anions of well distributed charge, the stability of the complexes shows an increase with size of cation. Perbenzoic acid is a very weak acid (pK 7·8),[3] and the negative charge in perbenzoate ion is localized on the peroxide oxygen atom. It is not surprising, therefore, that the large Et_4N^+ ion will associate less with the activated complex than do the smaller alkali-metal ions, or will not associate at all. On the other hand, the slight retarding effect produced by Et_4N^+ ion at the higher concentrations may be correlated with the large deviations from Debye–Hückel behaviour, specifically dependent on the anion, which are peculiar to tetra-alkylammonium ions.[21] This reaction is very similar, in the salt effects, to the alkaline hydrolyses of potassium alkyloxalates, alkylmalonates,[18,22] acetylsalicylate, and mandelate [23] which are sensitive to specific cation effects. Alkaline-earth cations exert a strong catalytic action, and alkali-metal ions have positive effects mainly at low salt concentrations, but tetra-alkylammonium ions exhibit a smaller effect.

We thank Professors B. Perlmutter-Hayman and A. Indelli for discussions. This work was supported by Italian C.N.R.

[1/1371 *Received, 4th August,* 1971]

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