The Kinetics and Mechanism of the Acid and Alkaline Hydrolyses of Some Perbenzoic Acids

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The rates of hydrolysis of some ring substituted perbenzoic acids have been measured in both acidic and alkaline solutions. The results are consistent with a bimolecular mechanism involving nucleophilic attack of water and hydroxide ion at the carbonyl carbon atom of the peroxide. Measurements performed in the presence of acetic acid–acetate ion buffers gave evidence for the formation of a tetrahedral intermediate.

PREVIOUS kinetic [1,2] and tracer [3] studies have shown that the hydrolysis of organic peroxyacids involves cleavage of the acyl–oxygen bond leading to the parent carboxylic acids and hydrogen peroxide as products in acidic [1,3] and alkaline [2] solutions, whereas in the pH range 7—9 (close to the pK of the peroxyacids) oxygen is produced [3,4] instead of H_2O_2. The kinetic features of the hydrolysis paths were explained on the basis of bimolecular mechanisms analogous to ester and amide hydrolyses.

We report here rate measurements of the decomposition of some substituted perbenzoic acids in acidic and alkaline aqueous solutions.

EXPERIMENTAL

Peroxyacids were prepared as reported by Silbert *et al.*[5] and stored at −10 °C in the dark. Conductivity water was used to prepare reagents and solutions and as a reaction medium. All the chemicals were of AnalaR grade. Stock solutions of peroxyacids were standardized iodometrically [1,2,6] and the absence of hydrogen peroxide was checked by polarography.[2,7] Reaction rates were measured by removing, at various times, suitable amounts of the reacting mixtures from flasks immersed in a bath at constant temperature (±0·1 °C). The peroxyacid was titrated by the iodometric method previously described.[1,2]

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[7] M. Venturini and F. Secco, *J.C.S. Perkin II*, 1973, 491.

RESULTS

All the kinetic runs were performed at an ionic strength of 0·2M which was kept constant with $NaClO_4$. Plots of the logarithm of the peroxyacid concentration against time were linear over >80% reaction and the accuracy of the measurements was of ±5%. The rate laws for the acid[1] and alkaline[2] hydrolyses are represented by equations (1) and (2) respectively. In the range of hydroxide ion con-

$$\begin{aligned} -\mathrm{d}[XC_6H_4CO_3H]/\mathrm{d}t &= k_{\mathrm{obs}}[XC_6H_4CO_3H] \\ &= \{k_{1\mathrm{A}} + k_{2\mathrm{A}}[H^+]\}[XC_6H_4CO_3H] \qquad (1) \\ -\mathrm{d}[XC_6H_4CO_3^-]/\mathrm{d}t &= k_{\mathrm{obs}}[XC_6H_4CO_3^-] \\ &= \{k_{1\mathrm{B}} + k_{2\mathrm{B}}[OH^-] + k_{3\mathrm{B}}[OH^-]^2\}[XC_6H_4CO_3^-] \qquad (2) \end{aligned}$$

centrations explored (⩽0·075M) the contribution to the overall velocity of the term proportional to $[OH^-]^2$ is negligible[2] and thus only the paths $k_{1\mathrm{A}}$, $k_{2\mathrm{A}}$, $k_{1\mathrm{B}}$, and $k_{2\mathrm{B}}$ were considered. The rate constants $k_{1\mathrm{A}}$ and $k_{2\mathrm{A}}$ were obtained from intercepts and slopes of plots of k_{obs} against $[H^+]$. Analogous plots of k_{obs} against $[OH^-]$ yielded $k_{1\mathrm{B}}$ and $k_{2\mathrm{B}}$. The results obtained at 25 °C are reported in Table 1.

TABLE 1

Values of rate constants for the acidic and alkaline hydrolyses of some ring substituted perbenzoic acids in aqueous solution [temperature 25 °C, ionic strength 0·2M ($NaClO_4$)]

Substituent	$10^7 k_{1\mathrm{A}}$ / s^{-1}	$10^6 k_{2\mathrm{A}}$ / $l\ mol^{-1}\ s^{-1}$	$10^6 k_{1\mathrm{B}}$ / s^{-1}	$10^4 k_{2\mathrm{B}}$ / $l\ mol^{-1}\ s^{-1}$
p-CH_3	1·7	4·40	3·0	1·14
H	2·8	5·14	4·8	3·32
p-Cl	3·9	5·40	8·5	4·15
p-CN	12·6	6·65	21·0	21·9
m-NO_2	15·0	7·50	25·0	27·8
p-NO_2	18·6	9·20	28·0	48·0

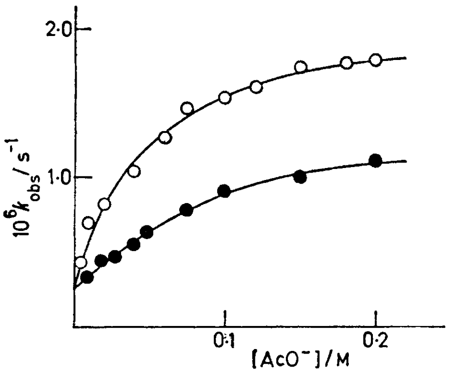
TABLE 2

Experimental and calculated rate constants k_{obs} for the hydrolysis of perbenzoic acid at different concentrations of acetate ion and acetic acid {temperature 25 °C, ionic strength 0·2M ($NaClO_4$), $[PhCO_3H]_0 = 1·5 \times 10^{-3}$M}

No.	[HOAc] / M	[Ac⁻] / M	$10^6 k_{\mathrm{obs\ expt}}$ / s^{-1}	$10^6 k_{\mathrm{obs\ calc}}$ / s^{-1}
1	0·02	0·005	0·430	0·448
2	0·02	0·01	0·650	0·590
3	0·02	0·02	0·810	0·813
4	0·02	0·04	1·04	1·11
5	0·02	0·06	1·26	1·31
6	0·02	0·075	1·51	1·41
7	0·02	0·10	1·52	1·54
8	0·02	0·12	1·60	1·62
9	0·02	0·15	1·75	1·70
10	0·02	0·18	1·76	1·77
11	0·02	0·20	1·78	1·80
12	0·1	0·00134	0·31	0·291
13	0·1	0·01	0·32	0·351
14	0·1	0·02	0·363	0·417
15	0·1	0·0286	0·458	0·470
16	0·1	0·04	0·550	0·536
17	0·1	0·05	0·609	0·590
18	0·1	0·075	0·765	0·710
19	0·1	0·10	0·920	0·813
20	0·1	0·15	0·985	0·982
21	0·1	0·20	1·09	1·11
22	0·2	0·0019	0·27	0·29
23	0·2	0·02	0·342	0·351

All the reaction paths appear to be sensitive to the effects of substituent and the reaction constants, given by plots of the logarithm of k against the Hammett σ value, are: $\rho(k_{1\mathrm{A}}) = 1·07$ ($r = 0·997$); $\rho(k_{2\mathrm{A}}) = 0·230$ ($r = 0·978$); $\rho(k_{1\mathrm{B}}) = 1·01$ ($r = 0·999$); and $\rho(k_{2\mathrm{B}}) = 1·56$ ($r = 0·987$), where r is the correlation coefficient. The data for the *p*-NO_2 substituted peroxyacid were not included in the correlation line for $\rho(k_{2\mathrm{A}})$.

Table 2 reports the rates of hydrolysis of perbenzoic acid in the presence of sodium acetate–acetic acid buffer at 25 °C and ionic strength 0·2M ($NaClO_4$). The acidity range is so low that the acid-catalysed path, $k_{2\mathrm{A}}$, does not contribute to the values of k_{obs}. At constant concentration of acetic acid (0·02M) the rate gradient decreases with increasing acetate ion concentration until a limiting value is reached. The same trend is shown when the concentration of acetic acid is 0·1M but the magnitude of the catalytic effect is reduced (Figure). The dependence of k_{obs} on [HOAc] and [OAc⁻] is represented by equation (3)



Dependence of k_{obs} for the hydrolysis of perbenzoic acid on acetate ion concentration at two concentrations of acetic acid: 0·1M (full circles) and 0·02M (open circles) [temperature 25 °C, ionic strength 0·2M ($NaClO_4$)]

$$k_{\mathrm{obs}} = \frac{2·8 \times 10^{-7}[HOAc] + 8·47 \times 10^{-7}[OAc^-]}{[HOAc] + 0·386[OAc^-]} \qquad (3)$$

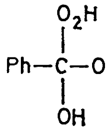
with a standard deviation of 6·1%. The parameters of this equation were obtained by least-squares treatment of the data of Table 2.

DISCUSSION

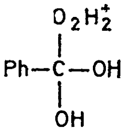
On the basis of results previously obtained[1,2] we suggested that the hydrolysis of perbenzoic acid involved nucleophilic attack by water ($k_{1\mathrm{A}}$,$k_{2\mathrm{A}}$,$k_{1\mathrm{B}}$) and hydroxide ion ($k_{2\mathrm{B}}$) at the acyl carbon atom of the peroxide, which is in turn present in various protonated forms depending on the acidity of the medium. The different pathways involve formation of tetrahedral intermediates (I)—(IV) analogous to the intermediate (V) suggested by Goodman *et al.*[3] for the hydrolysis of perbenzoic acid at pH = p*K* = 7·8. In this last case the nucleophilic attack is performed by the peroxide anion on the un-ionized peroxyacid.

The results obtained in the presence of acetic acid–acetate ion buffer enable us to give kinetic proof for the existence of an addition intermediate. This is apparent from the levelling off of the dependence of k_{obs} upon the acetate concentration shown in the Figure. The experimental results are explained by the Scheme. The assumption that a steady state concentration of the tetrahedral intermediate (I) is present gives the rate law (4) which corresponds to the experimental equation (3). The ratio $k_1k_2/(k_{-1} + k_2) = 2{\cdot}8 \times 10^{-7}$ s^{-1} is the rate constant of the uncatalysed path (k_{1A}), the value of which was also obtained by extrapolating the k_{obs} value measured for different concentrations of $HClO_4$ to $[H^+] = 0$.[1] From the parameters of equation (3) one obtains $k_{-1}/k_2 = 6{\cdot}8$. This means that the decomposition of the tetrahedral intermediate is rate-determining.[8] Similar behaviour has been found in the alkaline hydrolysis of amides.[9]

$$k_{obs} = \frac{\dfrac{k_1k_2}{k_{-1} + k_2}[HOAc] + \dfrac{k_1k_3K}{k_{-1} + k_2}[OAc^-]}{[HOAc] + \dfrac{k_3K}{k_{-1} + k_2}[OAc^-]} \qquad (4)$$


$Ph{-}C(O_2H)(OH){-}OH$

(I)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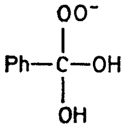
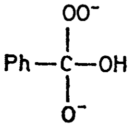
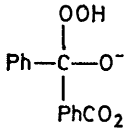
(II)


$Ph{-}C(OO^-)(OH){-}OH$

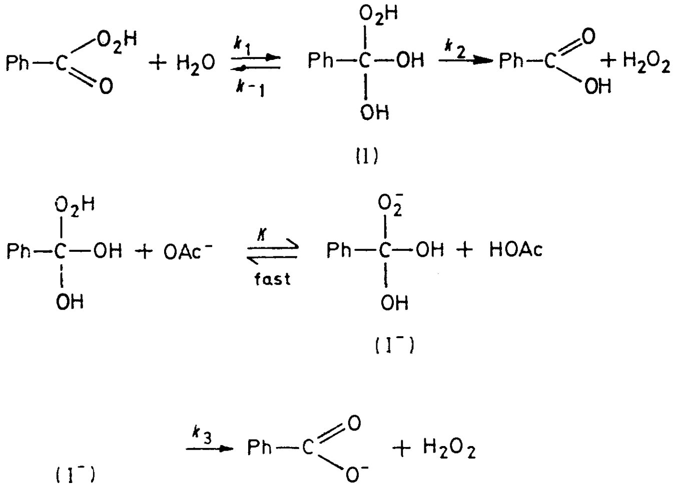
(III)


$Ph{-}C(OO^-)(O^-){-}OH$

(IV)


$Ph{-}C(OOH)(PhCO_2){-}O^-$

(V)



SCHEME

It is noteworthy that the existence of a path proportional to $[OH^-]^2$ [see equation (2)] was taken[2] as kinetic proof for formation of the intermediate (IV). However, since such a step becomes important at $[OH^-] > 0{\cdot}3$M, the possibility arises that changes in the activity coefficient could be responsible for the results at high hydroxide ion concentrations. The results here obtained at lower ionic strength (0·2M) eliminate such a doubt.

The positive values of the reaction constants ρ are in agreement with bimolecular mechanisms and suggest that bond formation predominates over bond breaking in the transition states.[10] The small ρ value (0·23) for the acid-catalysed path may be ascribed to the equilibrium for peroxyacid protonation preceding the nucleophilic reaction, the former being hindered by electron-accepting substituents.[11] The predominance of bond making in the transition state is also revealed by a comparison of substituent effects on paths k_{1B} ($\rho = 1{\cdot}01$) and k_{2B} ($\rho = 1{\cdot}56$). The greater ability of hydroxide ion to form a bond with the acyl carbon atom relative to water is reflected in the higher value of the reaction constant.[10]

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