Voltammetric Study of Some Perbenzoic Acids. Mechanism of Reduction at a Platinum Electrode

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A voltammetric study of the reduction of some substituted perbenzoic acids in aqueous solution has been performed by using a platinum microelectrode with periodical renewal of the diffusion layer. The acids give a cathodic wave corresponding to the irreversible process (i). Analysis of the reduction waves shows that the potential-determining

$$\mathrm{RCO{\cdot}OOH} + 2\mathrm{H}^+ + 2\mathrm{e}^- \longrightarrow \mathrm{RCO{\cdot}OH} + \mathrm{H_2O} \qquad \text{(i)}$$

step involves a molecule of undissociated peracid and one electron. The effect of substituents on the half-wave potential has also been investigated and the mechanism of electroreduction of peroxyacids is compared with the mechanism of their reduction by iodide ions.

ORGANIC peroxides, including peroxyacids are electroreduced according to the overall equation (1).[1] At the dropping mercury electrode (DME) the reduction in

$$\mathrm{RCO_3H} + 2\mathrm{H}^+ + 2\mathrm{e}^- \longrightarrow \mathrm{RCO_2H} + \mathrm{H_2O} \qquad (1)$$

aqueous solutions takes place at a potential slightly less positive than the potential of anodic dissolution of the mercury and the waves are therefore incomplete consisting only of the more negative part.[1,2] Complete reduction waves have been obtained at the DME for peroxyacids in nonaqueous solvents.[3] The use of a platinum electrode with periodical renewal of the diffusion layer (DLPRE) [4] allows us to extend the range of the potentials in aqueous solutions toward more positive values and to obtain complete reduction waves.[5a] We therefore considered it useful to investigate the voltammetric characteristics of perbenzoic acids in aqueous solution at the DLPRE under the same conditions in which the reduction by iodide ions has been studied.[6]

EXPERIMENTAL

Peroxyacids were prepared according to the procedure of Sielbert *et al.*[7] Their solutions were standardized iodometrically,[8] kept in a refrigerator, and used within one day. This procedure is necessary to avoid the possible presence of H_2O_2 arising from the hydrolysis of peroxyacids.[5] The polarographic currents were recorded by a three-electrode system using a Polarecord E 261 Metrohm connected with a IR compensator E 446 Metrohm. Both the reference and auxiliary electrodes were of mercury(I) sulphate joined to the cell by bridges made with a solid mixture of silica gel and sodium sulphate (3 : 2). The runs were performed at 25 ± 0·1 °C with a platinized platinum electrode and the solutions were deaerated by a stream of pure nitrogen.

RESULTS

At the platinum electrode perbenzoic acids are reduced to the corresponding carboxylic acids with transfer of two faradays per mole [equation (1)] as shown by coulometric measurements performed at a constant potential corresponding to the limiting current. Figure 1 represents the reduction wave of $PhCO_3H$ (10^{-3}M) in 5×10^{-3}M-$HClO_4$ and 0·195M-$NaClO_4$. All the waves were recorded toward more positive potentials after having pre-electrolysed the solution for 1 min at 2 V in order to keep constant the conditions of the electrode surface. The limiting current is proportional to the depolarizer concentration which ranged between 5×10^{-4} and 5×10^{-3}M. The temperature coefficient of the limiting current (i_d) is 1·4% K^{-1}. This suggests that the limiting current is diffusion controlled.[7] The oscillographic analysis of single oscillations also supports this assumption.[4] The electroreduction of peroxyacids [equation (1)] is an irreversible process. Plots of the potential E against $\log\,[(i_d - i)/i]$ yield straight lines with slopes between 0·120 and 0·106 V instead of *ca.* 0·03 V expected for a reversible process. Equation (2) was used to perform the logarithmic analysis [8] on several polarograms recorded at different pH. From the above mentioned

$$E = E_{\frac{1}{2}} + 2{\cdot}3RT \log\,[(i_d - i)/i]/\alpha nF \qquad (2)$$

slopes, values for αn of 0·48—0·55 are obtained. This means that since the most probable value for α is 0·5, only one electron is involved in the potential determining step ($n = 1$). The height of the waves does not change in the range of $[H^+]$ explored. Figure 2 represents the dependence of half-wave potential of $PhCO_3H$ upon $-\log\,[H^+]$. In the

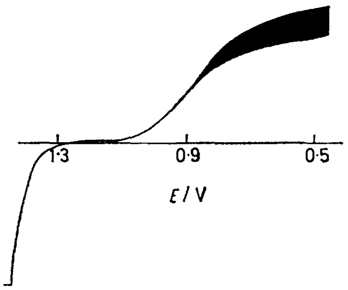

FIGURE 1 Polarogram for perbenzoic acid reduction in aqueous solution containing 5×10^{-3}M-$HClO_4$ and 0·195M-$NaClO_4$

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[1] H. Brushweiler and G. J. Minkoff, *Analyt. Chim. Acta*, 1955, **12**, 186; D. Swern, in 'Organic Peroxides,' ed. D. Swern, Wiley-Interscience, New York, 1970, vol. 1, p. 475.

[2] E. J. Kutta and F. W. Quackenbush, *Analyt. Chem.*, 1960, **32**, 1069; W. E. Parker, C. Ricciuti, C. C. Ogg, and D. Swern, *J. Amer. Chem. Soc.*, 1955, **77**, 4037.

[3] I. W. Siddiqi and R. M. Johnson, *J. Electroanalyt. Chem.*, 1971, **31**, 211.

[4] (*a*) D. Cozzi, G. Raspi, and L. Nucci, *J. Electroanalyt. Chem.*, 1966, **12**, 36; (*b*) M. Venturini, A. Indelli, and G. Raspi, *ibid.*, 1971, **33**, 99.

[5] (*a*) F. Secco, M. Venturini, and S. Celsi, *J.C.S. Perkin II*, 1972, 497; (*b*) F. Secco and S. Celsi, *J. Chem. Soc.* (*B*), 1971, 1792.

[6] F. Secco and M. Venturini, *J.C.S. Perkin II*, 1972, 2305.

[7] J. Heyrovsky and J. Kůta, 'Principles of Polarography,' Academic Press, New York, 1966, p. 88.

[8] P. Zuman, *Progr. Phys. Org. Chem.*, 1967, **5**, 81.

low pH range $E_{\frac{1}{2}}$ is independent of the acidity whereas at pH > 5 the half-wave potentials decrease linearly as the pH increases. In Figure 3 is reported a plot of $E_{\frac{1}{2}}$ of some peroxyacids against σ values. The half-wave potential is shifted toward more positive values as the electron-attracting power of substituents increases. The slope of the straight line of Figure 3 yields the polarographic reaction constant ρ_π. From its value (0·117 V) and by use of equation (3) a value of +0·95 for the reaction constant ρ of the heterogeneous electrochemical reaction (4) is obtained.[9] A plot of $E_{\frac{1}{2}}$ against the logarithm of the rate constants of perbenzoic acids–iodide reactions [6] is shown in Figure 4.

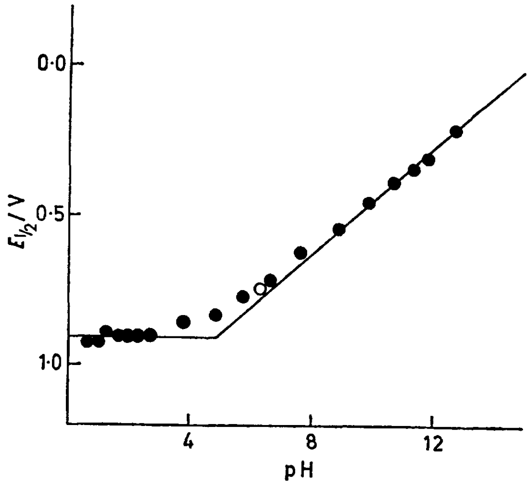

FIGURE 2 Dependence of half-wave potentials $E_{\frac{1}{2}}$ (*vs.* s.c.e.) of perbenzoic acid (10^{-3}M) on $-\log[H^+]$. Ionic strength 0·2M ($NaClO_4$). Open circle, ionic strength 1M

$$E_{\frac{1}{2}} = \rho_\pi\sigma = 2{\cdot}3\rho\sigma RT/\alpha nF \qquad (3)$$

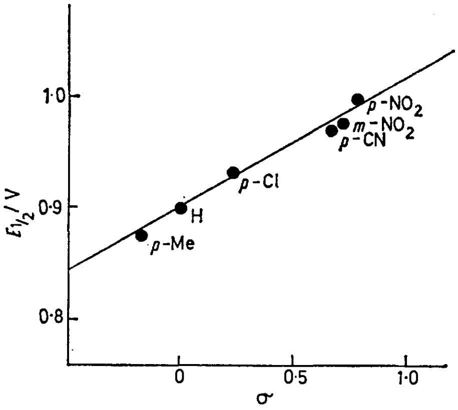

FIGURE 3 Plot of half-wave potentials $E_{\frac{1}{2}}$ (*vs.* s.c.e.) of some substituted perbenzoic acids against Hammett substituent constants

DISCUSSION

The value of αn strongly suggests that the rate-determining step of the electrochemical process involves only one electron. On the other hand the dependence of the half-wave potential upon pH together with the fact that a single wave with constant height is observed at each H^+ concentration support the hypothesis that a rapidly established acid–base equilibrium is preceding the electron-transfer step. The mechanism of the electroreduction may therefore be represented by equations (4) and (5) followed by the fast reaction (6). In acidic medium

$$RCO_3^- + H^+ \overset{\text{fast}}{\rightleftharpoons} RCO_3H \qquad (4)$$

$$RCO_3H + e^- \longrightarrow RCO_2^- + OH \qquad (5)$$

$$OH + e^- \longrightarrow OH^- \qquad (6)$$

both OH^- and RCO_2^- ions are converted to H_2O and RCO_2H respectively. The half-wave potential for the reactions (4) and (5) depends on pH according[8] to equation (7) where K_a is the acid dissociation constant.

$$E_{\frac{1}{2}} = \text{const} + 2{\cdot}3RT \log \{[H^+]/(K_a + [H^+])\}/\alpha nF \quad (7)$$

For $[H^+] \gg K_a$ the half-wave potential is pH independent. For $[H^+] \ll K_a$ $E_{\frac{1}{2}} = \text{const} - 2{\cdot}3RT(\text{pH})/\alpha nF$. The two linear portions of the plot of Figure 2 should intersect at a pH value corresponding to pK_a. However the pH at the intersection is lower than the potentiometrically determined pK_a of perbenzoic acid.[10] This difference may be attributed to the fact that the concentration quotient at the electrode surface may differ from the concentration quotient in the bulk of the solution.

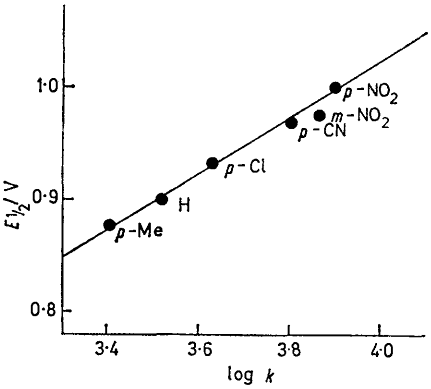

FIGURE 4 Plot of $E_{\frac{1}{2}}$ (*vs.* s.c.e.) for perbenzoic acid reduction against the logarithm of the second-order rate constants (k) for the perbenzoic acid–iodide reaction

The positive value of the reaction constant ρ confirms the nucleophilic properties of the electron, and the good ρ_π–σ correlation offers support for a polar mechanism.[9] Poor $E_{\frac{1}{2}}$–σ fits are expected for reductions proceeding *via* radical-like transition states.[11] In our opinion the electroreduction of peroxyacids occurs by a sort of S_N2 mechanism in which the negatively charged electrode acts as a nucleophile toward the outer peroxidic oxygen displacing the anion of the parent carboxylic acid. The features of this reaction are very similar to those of the peroxyacid reduction by iodide ions [6] in which the rate-determining step involves a molecule

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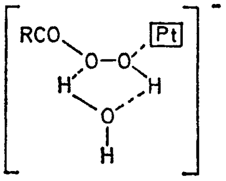
[9] C. L. Perrin, *Progr. Phys. Org. Chem.*, 1965, **3**, 165.

[10] J. F. Goodman, J. F. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, 1962, **58**, 1846; F. Secco, unpublished results.

[11] G. Klopman, *Helv. Chim. Acta*, 1961, **44**, 1908; A. Streitwieser, jun., and C. Perrin, *J. Amer. Chem. Soc.*, 1964, **86**, 4938.

of peroxyacid, a molecule of protic solvent, and one iodide ion. The linear relation between $E_{\frac{1}{2}}$ and the logarithm of rate constant of the RCO_3H–I^- reaction (Figure 4) suggests of analogous transition state which may be depicted as (I) where $\boxed{\text{Pt}}$ indicates participation of the negatively charged electrode. The five-membered ring facilitates the proton transfer, charge separation is minimized, and reduction is facilitated. The hypothesis of protic solvent involvement in the transition state is also in agreement with results[3] for the electroreduction of some peroxyacids in methanol–benzene and in dimethylformamide. The half-wave potentials become more positive by changing from dimethylformamide to methanol–benzene. Moreover addition of increasing amounts of water to dimethylformamide solutions produces a shift toward more positive values of $E_{\frac{1}{2}}$.



(I)

The similarity between peroxide reductions at an electrode and by iodide ions has been also observed in the case of peroxodiphosphate and peroxodisulphate ions.[4] These examples offer further support for the analogy between reduction processes at an electrode and in the homogeneous phase.[8,12]

[2/1490 *Received, 26th June, 1972*]

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[12] A. Giacomelli and A. Indelli, *Trans. Faraday Soc.*, 1968, **64**, 548.