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The Polarography of Alkyl Hydroperoxides in an Aqueous Solution

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The polarographic behavior of alkyl hydroperoxides was studied. *n*-Propyl, *n*-butyl, *n*-hexyl, and *n*-octyl hydroperoxide in an aqueous solution all show diffusion-controlled irreversible waves. The effect of the pH on the $E_{1/2}$ and $n\alpha$ values is very small. The length of the alkyl group has a marked effect on $E_{1/2}$ and $n\alpha$. The longer the chain length of the alkyl group, the larger the value of $n\alpha$ and the more positive the $E_{1/2}$. The linear free-energy relationship was found for the four alkyl hydroperoxides examined. The relation of Taft's polar substituent coefficient to $E_{1/2}$ has a negative reaction constant, which indicates a reaction promoted by high electron density in the reactive group. The electrode process seems to be the rupture of the -O–O- bond, followed by the protonation of the ions produced on the electrode.

Polarography is a versatile electrometric method that offers one of the best techniques for peroxide analysis. As most organic peroxides are polarographically reducible, their polarographic behavior has been studied for twenty years.[1–6] The electrode process may be a two-electron transfer, which leads to the rupture of the -O–O- bond, thus forming an OH group:[7]

$$\mathrm{ROOR} + 2e + 2\mathrm{H} \rightarrow \mathrm{ROH} + \mathrm{ROH}$$

The details of the above reaction have been discussed recently,[8,9] but have not yet been confirmed. The available data about the reaction of alkyl hydroperoxides provided by different authors are not sufficient for systematic discussion.

This paper will describe the polarographic behavior of the lower alkyl hydroperoxides (*n*-propyl, *n*-butyl, *n*-hexyl, and *n*-octyl hydroperoxides) synthesized in our laboratory and will discuss the electrode process in relation to the polarographic data and the organic structure. The relation of Taft's substituent coefficient to the $E_{1/2}$ values of the four compounds shows a linear line, the slope of which has a negative sign.

Experimental

All the alkyl hydroperoxides examined, *n*-propyl, *n*-butyl *n*-hexyl, and *n*-octyl hydroperoxide, were synthesized by the use of alkylmethane sulfonates.[10] The active oxygen values were determined by iodometric titration. The hydrogen peroxide and contaminated peroxides were checked by thin-layer chromatography.

Britton-Robinson's buffer solution was deaerated by N_2 bubbling for about 30 min; an alcoholic solution of a hydroperoxide was added to it with a microsyringe or a micropiette, and then N_2 was again bubbled in for a few minutes. The alcohol content was within 10 vol%.

A YEW POL-11-type polarograph (Yokogawa Denki Co.) was used for recording the d.c. polarograms. The pH of the solution was measured with a Toa Dempa PM-5A pH meter. The dropping electrode had the following characteristics: m=2.07 mg/sec, t=3.58 sec (in pure water, open circuit). No decomposition of the sample could be detected during the measurements. All the measurements were carried out at 25°C.

Results and Discussion

1) Shape of Polarographic Waves. With the four hydroperoxides examined, ill-defined waves were obtained. The wave shape indicates the irreversible nature of the step; this was confirmed by low peak height of the a.c. polarography. In both acid and alkaline solutions, the limiting currents were proportional to the hydroperoxide concentration. The half-wave potential was constant for hydroperoxide concentrations of 10^{-5}—10^{-4} M. The limiting current has a linear relation-

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[1] F. A. Bovey and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **69**, 2143 (1947).

[2] D. Swern, H. B. Knights C. O. Willits and C. Ricciuti, *Anal. Chem.*, **24**, 785 (1952).

[3] H. Brüschweiler and G. J. Minkoff, *Anal. Chim. Acta*, **12**, 186 (1955).

[4] D. A. Skoog and A. B. H. Lauwzecha, *Anal. Chem.*, **28**, 825, (1956).

[5] R. M. Johnson and I. W. Siddigi, *J. Polarograph. Soc.*, **11**, 72 (1965).

[6] H. Luck and R. Maak, *Fette, Seifen und Austrichmittel*, **68**, 305 (1966).

[7] E. J. Kutta and F. W. Quackenbush, *Anal. Chem.*, **32**, 1069 (1960).

[8] M. Schulz and K. H. Schwarz, *Monatsber. Deut. Akad. Wis.* (Berlin), **6**, 515 (1964).

[9] E. S. Levin and A. U. Yamshchikov, *Elektrochim.*, **4**, 54 (1968).

[10] H. R. Williams and H. S. Mosher, *J. Amer. Chem. Soc.*, **76**, 2984 (1954).

ship with the square root of the Hg height. The temperature coefficient of the limiting current is about 1% between 15—35°C. These results indicate that the limiting current is diffusion-controlled.

2) Dependence of Apparent $E_{1/2}$ on pH. The apparent $E_{1/2}$ values at various pH values are shown in Fig. 1. All the compounds shift with the half-wave potential more negative as the pH increases, but the effect of the pH is very small. As the number of carbon atoms increases, the half-wave potential shifts toward a more positive potential.

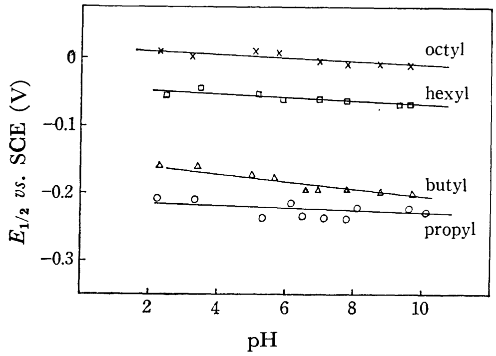

Fig. 1. Relation of $E_{1/2}$ to pH.

3) Dependence of $n\alpha$ Values on pH. As the hydroperoxides show irreversible polarographic waves, the slopes of log-plots gave $n\alpha$ values. The values of $n\alpha$ calculated at various pH are plotted in Fig. 2. Each compound seems not to change in its $n\alpha$ value with the pH of the solution. The tendency for a large alkyl group to have a large $n\alpha$ value indicates that if n=constant, a large alkyl group diminishes in polarographic irreversibility: this accords with the fact that the waves for the higher homologues are steep and well-defined.[8]

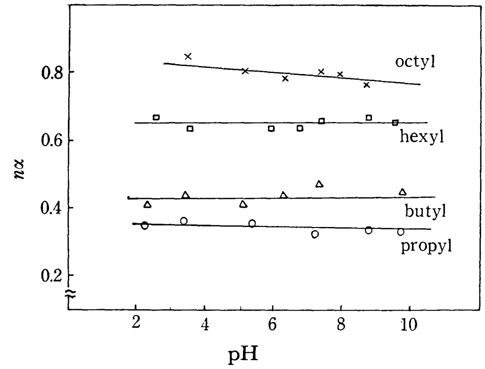

Fig. 2. Relation of $n\alpha$ to pH.

4) Effect of the Alkyl Group on $E_{1/2}$ and $n\alpha$. $E_{1/2}$ and $n\alpha$ are affected by the length of the alkyl group of the hydroperoxides. The plots of the half-wave potential and $n\alpha$ values against the chain length show a linear relation with the C_3—C_8 compounds (Figs. 3,4). The $E_{1/2}$ of C_1—C_2 hydroperoxides, quoted from Ref. (8), has a steeper slope than that of C_3—C_8.

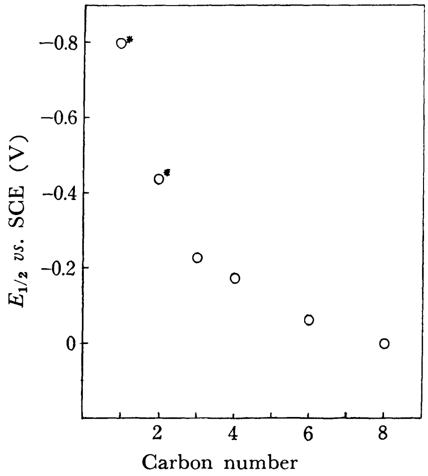

Fig. 3. Relation of $E_{1/2}$ (at pH=7) to chain length.
○*: from Ref. 8.

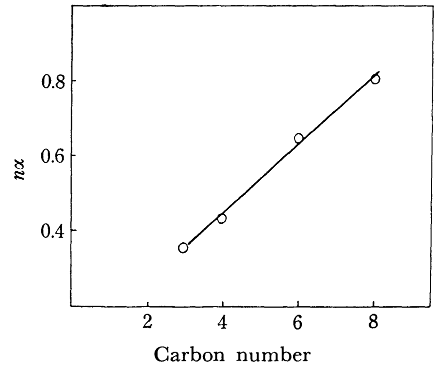

Fig. 4. Relation of $n\alpha$ to chain length.

5) The Electrode Reaction of Alkyl Hydroperoxides. The relation of the half-wave potential to Taft's polar substituent constant, σ_x^*, is shown in Fig. 5. The half-wave potential of the irreversible electrode process is expressed as follows:[11]

$$E_{1/2} = E_0 + \frac{RT}{n\alpha F} \ln 0.87\, k_f^{\circ} \sqrt{\frac{t_1}{D}} \tag{1}$$

$$\frac{\partial E_{1/2}}{\partial \mathrm{pH}} = -\frac{2.3RT}{\alpha F}$$

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[11] J. Heyrovsky and J. Kuta, "Principle of Polarography," Academic Press, New York (1966), p. 257.

where E_0 is the standard oxidation-reduction potential; $\boldsymbol{R}$, the gas constant; T, the absolute temperature; α, the transfer coefficient; n, the number of electrons transferred in the electrode process; $\boldsymbol{F}$, the faraday; $k_f{}^0$, the rate constant of the electrode process; t_1, the drop time, and D, the diffusion coefficient. From this equation, the linear free-energy relationship can be said to be valid when it is assumed that the value of the $dE_{1/2}/dpH$ slope and that of the transfer coefficient determined from the shape of the wave remain unchanged for all the members of the reaction series under study.[12] Therefore, strictly speaking, only with the large alkyl-group hydroperoxides which may have almost the same α values can a linear correlation be expected.

Recently Zuman has reported[13] that, in some instances, $dE_{1/2}/dpH$ and $\boldsymbol{R}T/\alpha nF$ are approximately linear function of the substituent constant, $\sigma_x{}^*$. In some other cases, plots of $(E_{1/2}\cdot dE_{1/2}/dpH)$ or $(E_{1/2}\cdot \boldsymbol{R}T/\alpha nF)$ against $\sigma_x{}^*$ show a better correlation than the $E_{1/2}-\sigma_x{}^*$ plots. On the other hand, in alkyl hydroperoxides, plots of $E_{1/2}\cdot \boldsymbol{R}T/\alpha n\boldsymbol{F}$ against $\sigma_x{}^*$ do not show any better correlation.

From the negative reaction constant in Fig. 5, it can be assumed that the reaction is promoted by high-electron density on the reaction group. The independence of the half-wave potential on pH suggests that the proton does not directly participate in the electrode process. The fact that in such aprotic solvent as acetonitrile and dimethylformamide the waves elongate and become ill-defined, can be interpreted in terms of the increased irreversibility in aprotic solvents. This indicates a proton contribution to the overall reaction.

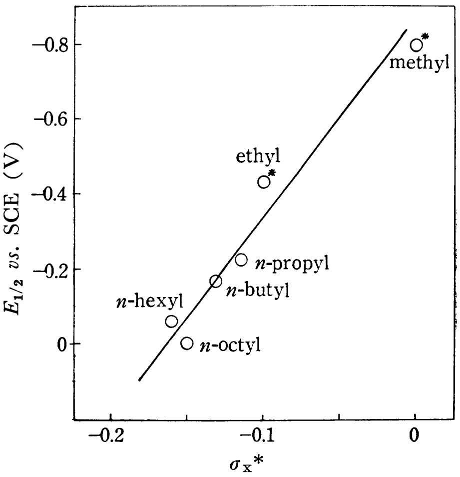

Fig. 5. Relation of $E_{1/2}$ to Taft polar substitution constant $\sigma_x{}^*$.
○*: from Ref. 8.

From the facts described above, it seems likely that the electrode process is as follows:

$$\mathrm{ROOH} + 2e \xrightarrow{\text{slow}} \mathrm{RO}^- + \mathrm{OH}^-$$

$$\mathrm{OH}^- + \mathrm{RO}^- + 2\mathrm{H} \xrightarrow{\text{fast}} \mathrm{ROH} + \mathrm{H_2O}$$

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[12] P. Zuman, "Substitution Effects in Organic Polarography," Plenum Press, New York (1967), p. 12.
[13] *ibid.*, p. 196.