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Coulometric Study of the Reaction of Diphenylpicrylhydrazyl and Bromide Ion[1]

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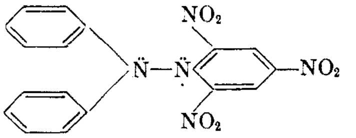
The rate of the reaction of diphenylpicrylhydrazyl (DPPH) and bromide ion in an acetonitrile medium was studied using the technique of controlled potential coulometric analysis. The rate of the reaction was second order with respect to both DPPH and bromide ion. A mechanism for the reaction was proposed and an integrated rate equation based on this mechanism was derived.

The electrochemistry of diphenylpicrylhydrazyl (DPPH), a stable free radical, has been described.[3] The study showed that acetonitrile solutions of DPPH containing tetra-*n*-butylammonium perchlorate (TBAP) were stable, and that DPPH was reduced at a platinum electrode in a reversible, one-electron, reaction ($E_{1/2} = 0.20$ v. *vs.* s.c.e.)



DPPH

$$R\cdot + e \rightleftarrows R:^- \qquad (1)$$

where $R\cdot$ is DPPH and $R:^-$ is its reduction product. When tetra-*n*-butylammonium bromide (TBAB) was used as a supporting electrolyte, voltammetry showed that the cathodic wave height decreased and the anodic wave height increased with time (indicating a reaction resulting in conversion of $R\cdot$ to $R:^-$), until the solution, originally purple in color, became brown, and only the anodic wave remained.

Since the potential of the bromine–bromide ion couple in acetonitrile is more positive than 0.5 v. *vs.* s.c.e., an oxidation–reduction reaction between DPPH and bromide ion appeared thermodynamically unfavorable, and a study of the reaction was undertaken. No recorded reaction of DPPH and bromide ion has appeared, although several authors mention a reaction of DPPH and bromine.[4]

Results

The rate of the reaction was studied by preparing acetonitrile solutions of DPPH and TBAB and determining the concentration of DPPH at various times after mixing using controlled potential coulometry. The theoretical treatment for the controlled potential coulometric electrolysis of a species undergoing chemical reaction prior to and during the electrolysis has been given.[5] By using a high speed coulometric apparatus,[6] the electrolysis times were kept short (less than 5 min.) and the amount of reaction occurring during the coulometric analysis was practically negligible.

The measured quantity was n_{app}^0, the apparent number of electrons involved in the reduction of DPPH based upon the initial concentration of DPPH in the stock solution, C_i

$$n_{\text{app}}^0 = \frac{Q}{FVC_i} = \frac{nC}{C_i} \qquad (2)$$

where Q is the number of coulombs involved in the electrolysis, n is the number of equivalents per mole of

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[1] (a) Based on a thesis submitted by E. S. in partial fulfillment of the requirements for the degree of Ph.D., August, 1963; (b) presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

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[3] E. Solon and A. J. Bard, *J. Am. Chem. Soc.*, **86**, 1926 (1964).

[4] R. H. Poiner, E. J. Kahler, and F. Fenington, *J. Org. Chem.*, **17**, 1437 (1952); S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922); J. A. Weil, private communication.

[5] A. J. Bard and E. Solon, *J. Phys. Chem.*, **67**, 2326 (1963).

[6] A. J. Bard, *Anal. Chem.*, **35**, 1121 (1963).

electroactive species reduced (1 for the reduction of DPPH), V is the volume of stock solution taken, and C is the concentration of DPPH at the start of the electrolysis. Typical results for the reaction of 0.1 M TBAB and 11.64 mM DPPH in acetonitrile are shown in Table I. For comparison, results for a TBAP–DPPH mixture are also given. Similar trials were also carried out with other concentrations of TBAB; in all cases the concentration of TBAB was larger than that of DPPH.

Table I: $n_{\mathrm{app}}{}^0$ for Reduction of DPPH in Acetonitrile Solutions of Tetra-n-butylammonium Perchlorate (TBAP) and Bromide (TBAB)

Time elapsed after mixing stock soln., hr.	$n_{\mathrm{app}}{}^0$ TBAP, 0.1 M^a	$n_{\mathrm{app}}{}^0$ TBAB, 0.1 M^b
0.33	1.02	0.858
2.1		0.697
4.0		0.645
9.6		0.558
19.2	1.04	
24.0		0.419
44.0	1.03	
48.4		0.328
74.5	1.03	

[a] The DPPH concentration was 7.95 mM. [b] The DPPH concentration was 11.64 mM.

The order of the reaction with respect to DPPH was established by plotting various functions of $n_{\mathrm{app}}{}^0$ against the time, t. For a second-order reaction the following equation applies

$$\frac{C_i}{C} = 1 + C_i k' t \qquad (3)$$

or, using eq. 2

$$\frac{n}{n_{\mathrm{app}}{}^0} = 1 + C_i k' t \qquad (4)$$

Plots of $n/n_{\mathrm{app}}{}^0$ *vs.* t were nearly linear for all concentrations of TBAB (Fig. 1) indicating a reaction second order in DPPH. The limiting slopes of some of these plots at various concentrations of TBAB are shown in Table II. Considering

$$k' = kZ_i{}^b \qquad (5)$$

where Z_i is the initial concentration of TBAB, the data of Table II best fit eq. 5 for a value of b of 2, indicating that the reaction is second order with respect to bromide ion (or TBAB).

Voltammetry in solutions in which DPPH had reacted completely with bromide ion showed a limiting anodic current about one-half as large as that of the original cathodic limiting current due to the reduction of DPPH. This indicated that one-half of the original DPPH was converted to its reduction product (R:$^-$) in the over-all reaction.

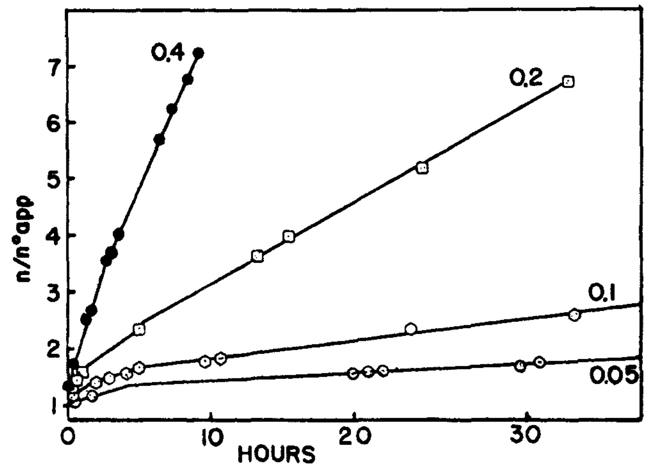

Figure 1. Variation of $n/n_{\mathrm{app}}{}^0$ with time elapsed between mixing of DPPH–TBAB stock solution and coulometric determination. Concentrations of DPPH varied between 2.57 and 21.2 mM (see Table III). TBAB concentrations (M) are given on each curve.

Table II: Values of k' for Various Concentrations of DPPH and TBAB

DPPH concn., C_i (mM)	TBAB concn., Z_i (M)	$k' \times 10^3$	$k \times 10^3$: $\frac{k'}{Z_i}$	$k \times 10^3$: $\frac{k'}{Z_i{}^2}$
20.4	0.050	0.47	9.5	188
11.6	0.10	2.2	22	220
20.4	0.20	7.0	35	176
20.2	0.40	29	72	181
			Av.	191

Discussion

A reaction scheme consistent with the above results is

$$\mathrm{R}\cdot + \mathrm{Br}^- \underset{}{\overset{K_1}{\rightleftarrows}} \mathrm{R}:^- + \mathrm{Br}\cdot \quad \text{(fast)} \qquad (6)$$

$$\mathrm{Br}\cdot + \mathrm{Br}^- \overset{K_2}{\rightleftarrows} \mathrm{Br}_2\cdot^- \quad \text{(fast)} \qquad (7)$$

$$\mathrm{R}\cdot + \mathrm{Br}_2\cdot^- \xrightarrow{k_3} \mathrm{RBr} + \mathrm{Br}^- \quad \text{(slow)} \qquad (8)$$

where K_1 and K_2 are the concentration equilibrium constants of eq. 6 and 7, respectively, k_3 is the rate constant of eq. 8, and RBr is a nonelectroactive product. The over-all reaction is as shown in eq. 9

$$2\text{R}\cdot + \text{Br}^- \longrightarrow \text{R}:^- + \text{RBr} \qquad (9)$$

in agreement with the voltammetric data.

The rate equation for the over-all process is based on the rate equation of the slow step (reaction 8)

$$\frac{-\text{d}[\text{R}\cdot]}{\text{d}t} = k_3[\text{R}\cdot][\text{Br}_2\cdot^-] \qquad (10)$$

where brackets represent concentrations. From eq. 6 and 7

$$K_1 = \frac{[\text{R}:^-][\text{Br}\cdot]}{[\text{R}\cdot][\text{Br}^-]} \qquad (11)$$

$$K_2 = \frac{[\text{Br}_2\cdot^-]}{[\text{Br}\cdot][\text{Br}^-]} \qquad (12)$$

Combination of eq. 10, 11, and 12 yields

$$\frac{-\text{d}[\text{R}\cdot]}{\text{d}t} = k_3K_1K_2\frac{[\text{R}\cdot]^2[\text{Br}^-]^2}{[\text{R}:^-]} \qquad (13)$$

An expression for $[\text{R}:^-]$ can be obtained from the over-all stoichiometry of the reaction

$$[\text{R}:^-] = (C_i - C)/2 \qquad (14)$$

Combining eq. 13 and 14 yields

$$-\frac{\text{d}C}{\text{d}t} = k\left(\frac{C^2Z^2}{C_i - C}\right) \qquad (15)$$

where Z is the bromide ion concentration and

$$k = 2k_3K_1K_2 \qquad (16)$$

The integrated form of eq. 15 is

$$C_i/C - 1 - \ln(C_i/C) = kZ_i^2t \qquad (17)$$

when the bromide ion concentration is in large enough excess to be assumed constant during the electrolysis and equal to its initial concentration, Z_i. When the bromide ion concentration is not much larger than the DPPH concentration, integration of eq. 15 can be performed using, from the stoichiometry of the reaction

$$Z = Z_i - (C_i - C)/2 \qquad (18)$$

The resulting equation is

$$(2Z_i - C_i)^2kt/4 = C_i/C + 2Z_i/(2Z_i + C - C_i) - 2 - \frac{2Z_i + C_i}{2Z_i - C_i}\ln\left(\frac{C_i(2Z_i + C - C_i)}{2Z_iC}\right) \qquad (19)$$

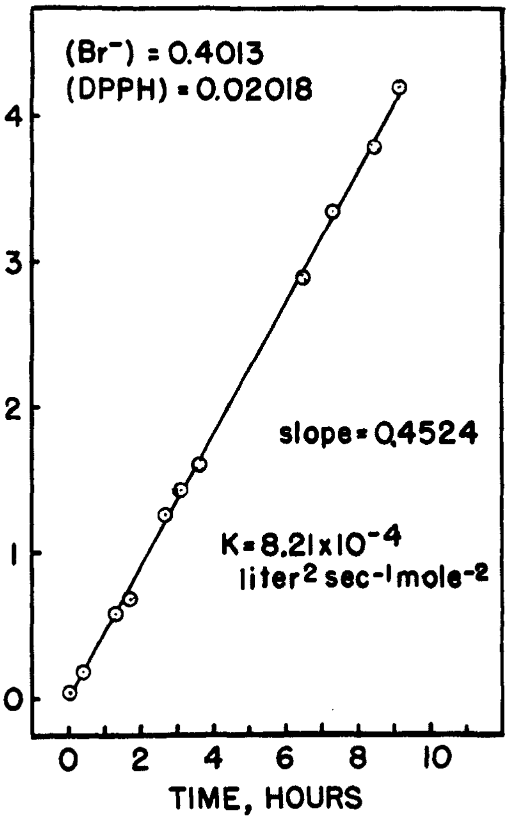

Figure 2. Plot of DPPH–TBAB reaction according to eq. 19. The ordinate is the right-hand side of eq. 19.

A plot of the right-hand side of eq. 19 *vs.* t, shown in Fig. 2, is linear, and allows calculation of k from its slope. The plots based on eq. 19 take account of the inverse order dependence with respect to $\text{R}:^-$; the deviations from linearity shown in Fig. 1 disappear when the data are plotted according to eq. 19. Values of k determined from plots such as that in Fig. 2 for different concentrations of DPPH and bromide ion are given in Table III.

Table III: Values of Over-all Rate Constant k for Various DPPH and TBAB Concentrations

DPPH concn., C_i (mM)	TBAB concn., Z_i (M)	$k \times 10^4$ (l.^{2} mole^{-2} sec.$^{-1}$)
2.57	0.05	9.3
11.8	0.05	6.3
20.4	0.05	7.4
21.2	0.10	6.1
20.4	0.20	7.7
20.2	0.40	8.2
	Av.	7.5 ± 0.7

The rate of the reaction of DPPH and bromide ion depends quite strongly upon the solvent medium. The reaction was about one order of magnitude slower when methanol rather than acetonitrile was used as the solvent. This reaction was complicated by the simultaneous reaction of DPPH and methanol itself. Addition of water to the acetonitrile also decreased the rate of the reaction. Similarly the reaction rate was very slow in a carbon tetrachloride medium.

The existence of the species Br_2^- has precedence in electrochemical studies. Llopis and Vazquez[7] in a study of the electroreduction of bromine at a platinum electrode postulated a one-electron primary step forming Br_2^-. Reaction 7 also was used in their mechanism and was assumed to be rapid compared to the electrode reaction, which had a rate constant (k^0) of about 0.05 cm./sec.

Experimental

Reagents. The acetonitrile (Matheson Coleman and Bell practical grade) was purified by several distillations from phosphorus pentoxide and a final distillation from anhydrous potassium carbonate. The TBAB and TBAP were polarographic grade (Southwestern Analytical Chemicals, Austin, Texas) and were oven-dried before use. The DPPH was obtained from Eastman Kodak Co. and was used as received.

Procedure. The general apparatus and techniques have been described.[3] Controlled potential coulometry was performed in a high speed apparatus[6]; to prevent the solution from heating up during the electrolysis ultrasonic stirring was not used. The reference electrode was an aqueous saturated calomel electrode (s.c.e.) with an agar–1 *M* potassium nitrate bridge. The auxiliary electrode, a silver wire coil, was separated from the working electrode by an agar–1 *M* KNO_3 plug and a sintered glass disk.

Stock solutions of known DPPH and TBAB concentration were prepared using acetonitrile which was previously deaerated with nitrogen and were mixed at $t = 0$. A deaerated acetonitrile solution containing TBAB in the coulometric cell was reduced at a platinum electrode at +0.015 v. *vs.* s.c.e. until the current decayed to a small background level. At time t an aliquot portion of the DPPH–TBAB stock solution was added, and the electroreduction of DPPH continued until the current decayed to the background level. The number of coulombs necessary for the electrolysis was noted and corrected for the background current. Electrolysis times were always less than 5 min.

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[7] J. Llopis and M. Vazquez, *Electrochim. Acta*, **6**, 177 (1962).