kcal./mole. This difference in activation energies should also be very close to the difference in heats of formation or combustion of bicycloheptadiene and cycloheptatriene. Of course, the preceding argument is based on the assumption that the two transition states closely resemble the reactive intermediate.[20] The energy difference $\Delta\Delta H_f°$ at 25° calculated from the heats of formations of gaseous bicycloheptadiene[21,22] and cycloheptatriene[23] is $+13.6 \pm 0.5$ kcal./mole, and this difference should be approximately the same at higher temperatures. The nonconcurrence of the experimental and theoretical energy difference strongly indicates that the assumption is incorrect and that there is not a common intermediate to the three isomerizations.

With the present state of knowledge, one cannot distinguish between the further possibilities, four distinct

(20) G. S. Hammond, J. Am. Chem. Soc., **77**, 334 (1955).

(21) A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, J. Chem. Soc., 3823 (1963).

(22) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, p. 44.

(23) H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, and G. Waddington, J. Am. Chem. Soc., **78**, 5469 (1956).

reactions (eq. 1) or the mechanism shown in eq. 10. However, we do consider the latter to be the more likely with a diradical intermediate obtained from cleavage of a $C_7–C_1$ bond. It is hard to imagine two dissimilar initial steps leading from bicycloheptadiene to cycloheptatriene and toluene. Also, as Klump and Chesick[10] have pointed out, a state quite similar to norcaradiene is required for the cycloheptatriene to toluene isomerization. Since we have shown that this reaction and the isomerizations of bicycloheptadiene to cycloheptatriene and toluene must be considered separately, such a norcaradiene state is not possible for the bicycloheptadiene isomerizations.

Kinetic experiments with substituted bicycloheptadienes and cycloheptatrienes are presently being carried out in an effort to define more closely the natures of these reactions.

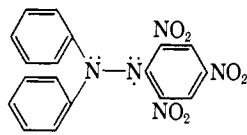# The Electrochemistry of Diphenylpicrylhydrazyl[1]

BY EMANUEL SOLON AND ALLEN J. BARD[2]

The electroreduction and oxidation of diphenylpicrylhydrazyl (DPPH), a stable free radical, at a platinum electrode in acetonitrile solutions was investigated using voltammetry, chronopotentiometry, and controlled potential coulometry. The results showed that DPPH is reduced and oxidized in reversible, one-electron reactions. A brief study of the electrode reactions in methanol, ethanol, acetone, and dimethyl sulfoxide was also made.

Diphenylpicrylhydrazyl (DPPH, I), a stable free radical first prepared by Goldschmidt and Renn,[3] has been of interest as a standard in electron spin resonance (e.s.r.) spectroscopy and as a free radical scavenger

I

and counter. The electrode reactions of DPPH are of interest because free radicals are frequently intermediates and products of electrode reactions; the electrogenerated radicals usually then react with the solvent, couple, or undergo further electrode reactions. A study of the electrochemistry of DPPH was undertaken to investigate the characteristics of electrode reactions of free radicals, to study the possibility of employing DPPH as a radical scavenger during electrode reactions, and to evaluate electroanalytical methods for the determination of DPPH. The electroreduction and oxidation of DPPH at a platinum electrode in acetoni-

(1) (a) Based on a thesis submitted by E. Solon 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.

(2) To whom correspondence and request for reprints should be directed.
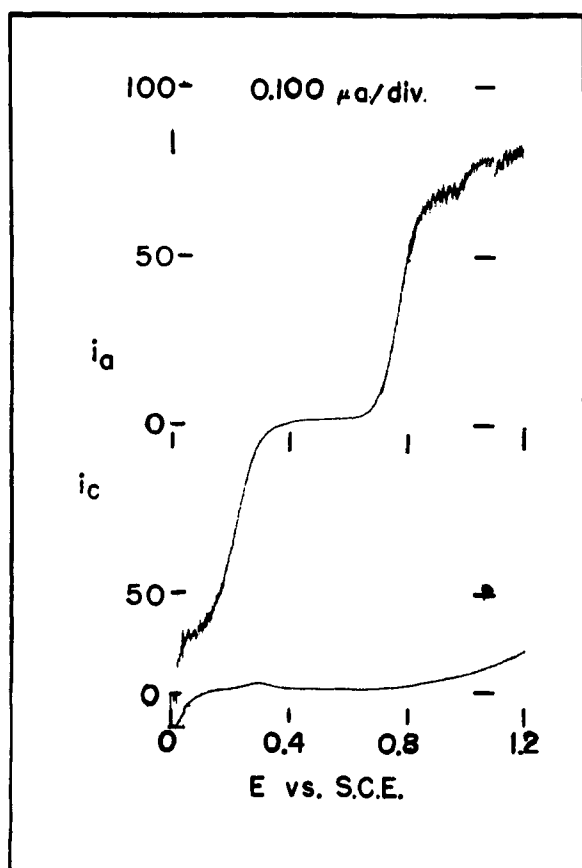
(3) S. Goldschmidt and K. Renn. Ber., **55**, 628 (1922).

trile solutions was investigated using voltammetry, chronopotentiometry, and controlled potential coulometry. A brief study of the electrode reactions of DPPH in some other solvents was also undertaken.

Results and Discussion

Voltammetry.—A typical current–potential curve for the voltammetric oxidation and reduction of DPPH at a rotating platinum electrode (r.p.e.) in an acetonitrile solution containing 0.1 M NaClO$_4$ is shown in Fig. 1. The curves showed a single cathodic wave and a single anodic wave of equal height; the half-wave potentials $(E_{1/2})$ of both waves were independent of concentration of DPPH or NaClO$_4$ (Table I). Plots of potential vs. log $[i_{lim}/(i_{lim}-i)]$, with potentials corrected for iR drop, were linear, with slopes of about 0.06 for both waves. The reversibility of both waves was shown by current–potential curves taken with solutions containing mixtures of DPPH and its oxidation product (R$^+$) or its reduction product (R:$^-$) (obtained by controlled potential electrolysis of DPPH solutions at the limiting current plateau of the waves). For both mixtures of DPPH and R:$^-$ and DPPH and R$^+$ the current–potential curves were only shifted vertically, along the current axis; $E_{1/2}$'s remained constant and the curves passed through the zero current axis without inflection. The waves correspond therefore to the following re-

Fig. 1.—Current–potential curve for reduction and oxidation of an acetonitrile solution containing 0.27 mM DPPH and 0.1 M NaClO₄ at a r.p.e. The lower curve shows the current–potential behavior in the same solution in the absence of DPPH.

versible, one-electron reactions (where R· represents DPPH).

Reduction　R· + e $\rightleftharpoons$ R:⁻　　　　(1)
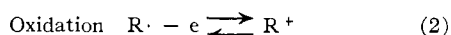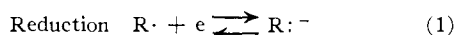
Oxidation　R· − e $\rightleftharpoons$ R⁺　　　　(2)

Chronopotentiometry.—Chronopotentiometry with current reversal[4] at a stationary, plane, shielded elec-

TABLE I

HALF-WAVE POTENTIALS FOR THE REDUCTION AND OXIDATION OF DPPH IN ACETONITRILE SOLUTIONS

DPPH concn., mM	NaClO₄ concn., M	$E_{1/2}$ (v. *vs.* s.c.e.) Cathodic	Anodic
0.47	0.100	0.20	0.72
.47	.240	.20	.71
.40	.264	.20	.71
.93	.820	.18	.68
	Av.	0.20	0.70

trode was used to confirm the results obtained with voltammetry. A typical chronopotentiogram is shown in Fig. 2 and chronopotentiometric data are given in Table II. The $E_{1/4}$ of the forward waves and the $E_{0.215}$ of the reverse waves were the same, and check well with the results obtained in voltammetry. The constancy of $i\tau^{1/2}$ and cyclic chronopotentiometric data[5] (Table II) indicate diffusion-controlled reactions. The diffusion coefficient, D, in a 0.1 M NaClO₄–acetonitrile solution, was calculated using the Sand equation

(4) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954.

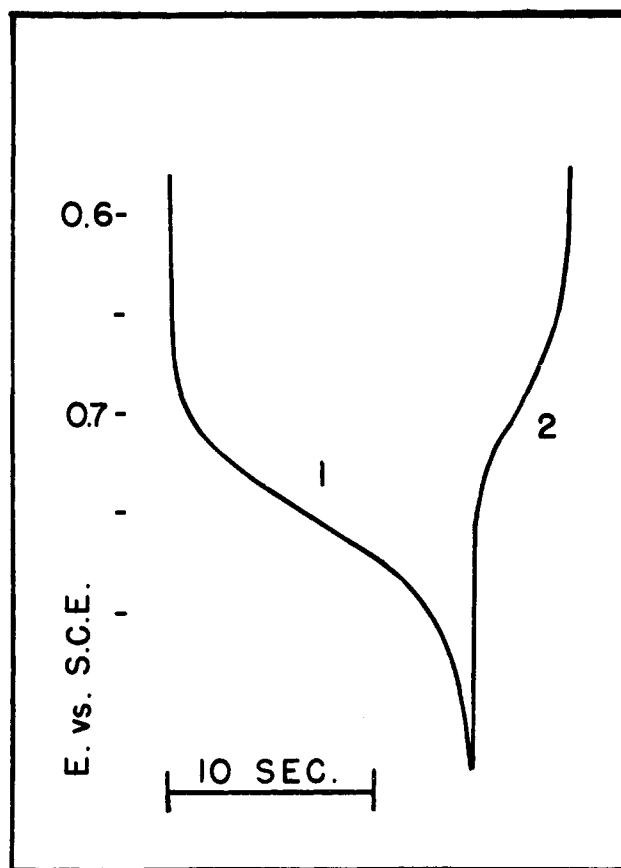(5) H. B. Herman and A. J. Bard, *Anal. Chem.*, **35**, 1121 (1963).

Fig. 2.—Chronopotentiogram of the oxidation of DPPH at 100 μa. in acetonitrile solution containing 1.04 mM DPPH and 0.1 M NaClO₄: 1, forward; 2, reverse.

to be 1.2×10^{-5} cm.²/sec. Plots of potential *vs.* log $[t^{1/2}/(\tau^{1/2} - t^{1/2})]$ were linear, with slopes of 0.060 for both oxidations and reductions.

TABLE II

CHRONOPOTENTIOMETRY OF DPPH

The acetonitrile solution contained 0.1 M NaClO₄ and 1.04 mM DPPH; the shielded platinum electrode area was 1.2 cm.²

Current, μa.	Transition time, τ, sec.	$i\tau^{1/2}$, μa. sec.$^{1/2}$	$E_{1/2}$, v. *vs.* s.c.e.	Transition time, τ', sec.	τ'/τ	$E_{0.215}$, v. *vs.* s.c.e.
		A.	Reduction			
67.7	31.8	382	0.16	9.50	0.30	0.16
100	13.6	369	.19	4.10	.30	.19
135	7.30	366	.16	2.25	.31	.18
Av.		372	0.17		0.30	0.18
		B.	Oxidation			
67.6	31.7	381	0.72	10.65	0.34	0.72
100	13.6	369	.73	4.55	.33	.72
135	7.40	368	.72	2.35	.32	.71
Av.		373	0.72		0.33	0.72

CYCLIC CHRONOPOTENTIOMETRY

The current was 100 μa.

|	Ratio of transition time to first transition time		
		Experimental	
Number	Theoretical[5]	Redn.	Oxidn.
1	1.00	1.00	1.00
2	0.33	0.32	0.33
3	.59	.57	.59
4	.35	.34	.35
5	.55	.55	
19	.49	.49	

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TABLE III

HALF-WAVE POTENTIALS FOR VOLTAMMETRIC REDUCTION AND OXIDATION OF DPPH IN VARIOUS SOLVENTS

The solutions contained 1 mM DPPH and 0.1 M NaClO$_4$; potentials in v. $vs.$ aqueous saturated calomel electrode

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Solvent	Reduction			Oxidation			Data of ref. 8		
	$E^{1/2}$	Δ^a	Slope^b	$E^{1/2}$	Δ^a	Slope^b	$E^{1/2}$	Δ^a	Slope^b
CH$_3$CN	0.178	...	0.068	0.693	...	0.059	0.860	...	0.063
CH$_3$OH	.205	0.027	.071	.727	0.034	.061	.890	0.030	.120
C$_2$H$_5$OH	.212	.034	.063	.731	.038	.065	.895	.035	.06
Acetone	.223	.045	.080	.772	.079	.074	.040	.080	.06
Dimethyl sulfoxide	.348	.170	.063	.798	.105	.065	...	...	...

^{a} $\Delta = E^{1/2}$ (solvent) $- E^{1/2}$ (CH$_3$CN). ^{b} Slope of potential $vs.$ log $[i_{lim}/(i_{lim} - i)]$ plot.

Controlled Potential Coulometry.—To determine unequivocally the number of electrons involved in the over-all electrode reactions, controlled potential coulometric reduction and oxidation of DPPH was undertaken. For a coulometric oxidation at 0.87 v. $vs.$ s.c.e. in a 0.8 M NaClO$_4$–acetonitrile solution, an apparent n of 0.98 ± 0.03 equivalent per mole of DPPH was found. For the coulometric reduction, at 0.015 v. $vs.$ s.c.e. in a 0.1 M tetrabutylammonium perchlorate–acetonitrile solution, an apparent n of 1.03 ± 0.01 was obtained. Voltammetry and coulometry of DPPH in an acetonitrile solution containing tetra-n-butylammonium bromide as the supporting electrolyte indicated a reaction between DPPH and bromide ion which will be discussed elsewhere.[6]

When DPPH was electrolyzed in a cell contained in the cavity of an e.s.r. spectrometer, using the technique of Geske and Maki,[7] the strong signal due to DPPH decreased and eventually disappeared. Electrolytic regeneration of the DPPH led to a reappearance of the DPPH e.s.r. spectrum. The product of the electro-reduction (R:$^-$) is probably II. Diphenylpicrylhydrazine is not oxidizable in these solutions, so that II is probably not protonated.

(C$_6$H$_5$)$_2$N̈–N̈–picryl   (C$_6$H$_5$)$_2$N̈–N̈–picryl   (C$_6$H$_5$)$_2$N=N̈–picryl

II   III   IV
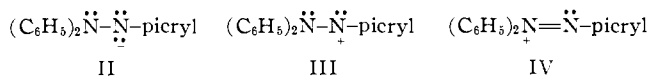
Structures III and IV probably contribute strongly to the resonance hybrid of the oxidized form (R$^+$).

Other Solvents.—The electrochemical behavior of DPPH in other nonaqueous solvents generally follows that found in acetonitrile; DPPH is insoluble in water. Voltammetric data, $E^{1/2}$'s, and potential $vs.$ log $[i_{lim}/(i_{lim} - i)]$ slopes are given in Table III. Nelson and Iwamoto[8] have determined the liquid junction potentials between an aqueous s.c.e. and various solvents containing 0.1 M LiClO$_4$ by measuring the $E^{1/2}$ for the oxidation of 4,7-dimethyl-1,10-phenanthroline iron(II); their data are included in Table III. The difference in potential between the $E^{1/2}$ in acetonitrile and $E^{1/2}$ in the other solvents for DPPH is very close to that obtained from the data of Nelson and Iwamoto and suggests that most of the shift in potential observed in different solvents originates in the liquid junction potential. The appreciable difference in the shift of $E^{1/2}$ for the anodic and cathodic wave in dimethyl sulfoxide may indicate greater solvation of R$^+$ in this medium. DPPH reacts with ethanol and methanol (after about

3 weeks the solutions become brownish), but these reactions are so slow that they do not interfere with the measurements.

Conclusions.—Because of its well-behaved reduction and oxidation in nonaqeuous solvents, DPPH is a good test system for electrochemical studies. It is a relatively poor radical scavenger for electrochemical reactions because it is stable only over a small range of potentials ($e.g.$, 0.30 to 0.58 v. $vs.$ s.c.e. in acetonitrile for less than 1% of the DPPH reduced or oxidized). Similarly, DPPH is not useful as a scavenger in the presence of strong oxidizing agents and moderate reducing agents. Voltammetry, chronopotentiometry, and controlled potential coulometry are all suitable techniques for analysis of DPPH solutions.

(6) E. Solon and A. J. Bard, $J. Phys. Chem.$, **68**, 1144 (1964).
(7) D. H. Geske and A. H. Maki, $J. Am. Chem. Soc.$, **82**, 2671 (1960).
(8) I. V. Nelson and R. T. Iwamoto, $Anal. Chem.$, **33**, 1795 (1961).

(9) A. J. Bard, $ibid.$, **33**, 11 (1961).
(10) A. J. Bard, $ibid.$, **35**, 1121 (1963).
(11) A. J. Bard and E. Solon, $ibid.$, **34**, 1181 (1962).