

## VOLTAMMETRY WITHOUT BACKGROUND ELECTROLYTE: REDOX PATTERN OF DPPH IN NON-AQUEOUS MEDIA\*

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**Abstract**—The voltammetric behaviour of diphenylpicrylhydrazyl (DPPH), a stable organic free radical, which has been found to give reversible oxidation and reduction waves at platinum in 0.1 M NaClO<sub>4</sub> solution in acetonitrile, was investigated at platinum and graphite electrodes in several media under a variety of conditions. The reported acetonitrile data were confirmed; comparison with data obtained in acetonitrile in the absence of background electrolyte has shown that voltammetry in such absence is quite feasible when using a three-electrode IR compensation circuit. Variation of polarization rate, polarization direction, electrode rotation rate, background electrolyte (0.1 M NaClO<sub>4</sub>; 0.1 M (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub>), indicating electrode (platinum; pyrolytic graphite) and solvent (acetonitrile; pyridine; sulphur dioxide) revealed, *ia*, semi-reversible behaviour of DPPH dependent on the presence of background electrolyte, adsorption of the neutral organic free radical on pyrolytic graphite, and a lack of stability for the compound in normally available reagent grade pyridine and in liquid sulphur dioxide (one product in both cases was diphenylpicrylhydrazine). The stability of DPPH in pyridine increased with purity of the solvent, which is of significance in connexion with the postulation of free radical intermediates in organic electrode processes.

**Résumé**—Le comportement voltamétrique du diphenylpicrylhydrazyl (DPPH), radical libre organique stable, qu'on a trouvé donnant des vagues d'oxydation et de réduction réversibles sur platine dans une solution à 0,1 M de NaClO<sub>4</sub> dans l'acétonitrile, a été étudié sur électrodes de platine et graphite dans plusieurs milieux et selon toute une variété de conditions. Les données concernant l'acétonitrile ont été confirmées; la comparaison avec les résultats obtenus dans l'acétonitrile en absence d'électrolyte de base a montré que la voltamétrie est tout à fait possible dans ces conditions lorsqu'on utilise un circuit de compensation à trois électrodes IR. Les variations de la vitesse de polarisation, du sens de polarisation, de la vitesse de rotation de l'électrode, de l'électrolyte de base (0,1 M NaClO<sub>4</sub>; 0,1 M (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub>), en spécifiant l'électrode (platine; graphite pyrolytique) et le solvant (acétonitrile; pyridine; anhydride sulfureux) révèlent en particulier que le comportement semi-réversible du DPPH dépend de la présence de l'électrolyte de base, de l'adsorption du radical libre organique neutre sur le graphite électrolytique et du manque de stabilité du composé dans la pyridine et dans l'anhydride sulfureux liquide, à un degré de réaction normalement utilisable (un produit dans les deux cas était la diphenylpicrylhydrazine). La stabilité du DPPH dans la pyridine augmente avec la pureté du solvant, ce qui est significatif, en liaison avec la postulation de radicaux libres intermédiaires dans les processus inhérents aux électrodes organiques.

**Zusammenfassung**—Das voltametrische Verhalten von Diphenyl-Pikryl-Hydrazil (DPPH), einem beständigen, freien organischen Radikal, welches an Platin in 0,1 M NaClO<sub>4</sub>-Lösungen in Acetonitril reversible Oxydations/Reduktionswellen liefert, wurde an Platin- und Graphitelektroden unter verschiedenen Bedingungen und in mehreren Medien untersucht. Die Literaturdaten für Acetonitril konnten bestätigt werden; der Vergleich mit Werten, welche in Acetonitril ohne Leitelektrolyt ermittelt wurden, zeigt, dass unter diesen Bedingungen voltametrische Messungen ohne weiteres durchgeführt werden können, falls eine 3-Elektrodenanordnung zur Kompensation des Ohm'schen Spannungsabfalles verwendet wird. Veränderung der Polarisationsgeschwindigkeit, der Polarisationsrichtung, der Rotationsgeschwindigkeit der Elektroden, des Leitelektrolyten (0,1 M NaClO<sub>4</sub>; 0,1 M (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub>), der Art der Indikatorelektrode (Platin bzw. pyrolytischer Graphit) und des Lösungsmittels (Acetonitril, Pyridin, Schwefeldioxyd) ergab ua halbversibles Verhalten des DPPH, abhängig von der Gegenwart von Leitelektrolyt, eine Adsorption des neutralen freien Radikals auf den Graphit und fehlende Stabilität der Verbindung in üblicherweise erhältlichem Pyridin (R.G.) und in flüssigem Schwefeldioxyd (ein Reaktionsprodukt war in beiden Fällen Diphenyl-Picryl-Hydrazin). Die Stabilität des DPPH in Pyridin stieg mit zunehmender Reinheit des Lösungsmittels. Diese Tatsache ist bedeutsam im Hinblick auf die Postulierung von freien radikalischen Zwischenprodukten, bei organischen Elektrodenreaktionen.

\* Manuscript received 27 December 1966.

## INTRODUCTION

THE VOLTAMMETRY of organic compounds in non-aqueous media in the presence of controlled proton concentration has become increasingly important in the study of electrode mechanisms. Electrolytic investigations in the non-protonic solvent, liquid sulphur dioxide, has, to date, had to be done in the absence of a background electrolyte.<sup>1-4</sup> Due to the lack of adequate voltammetric data for a well-characterized redox system in the absence and presence of background electrolyte, no comparison of liquid-sulphur-dioxide studies to those normally obtainable has been possible. Consequently, the stable organic free radical, diphenylpicrylhydrazyl (DPPH) (Fig. 1) was studied at platinum and graphite electrodes in acetonitrile in the presence and absence of background electrolyte; the results were compared with those of Solon and Bard,<sup>5</sup> who provided voltammetric data for DPPH at platinum in acetonitrile in the presence of 0.1 M NaClO<sub>4</sub>.

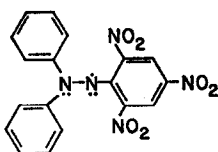


FIG. 1. Diphenylpicrylhydrazyl.

The electrolytic behaviour of DPPH in pyridine and in sulphur dioxide was also investigated; the data obtained are actually for the voltammographic behaviour of the products of a reaction(s) which DPPH undergoes in these solvents; one electro-active product is diphenylpicrylhydrazine.

Particular attention was given to the effect of lack of background electrolyte on the reversibility of electrode processes, the effectiveness of automatic *IR*-drop compensation, and the effects of polarization rate, polarization direction, and electrode rotation rate on the shape of the voltammetric curves. Since DPPH is a neutral species, the effect of migration current in the absence of supporting or background electrolyte is not involved.

## EXPERIMENTAL TECHNIQUE

*Chemicals*

Acetonitrile (Eastman), diphenylpicrylhydrazyl (DPPH) (Eastman), diphenylpicrylhydrazine (Eastman), pyridine (Baker & Adamson, reagent grade) and tetraethylammonium perchlorate (Eastman) were used as received, except where otherwise noted. Anhydrous grade sulphur dioxide (Matheson; stated purity: 99.98%) was treated to remove H<sub>2</sub>O, SO<sub>3</sub> and non-condensable gases.<sup>1</sup> Sodium perchlorate (G. Fredrick Smith Chemical Co.) was dried at 110°C for 4 h before use.

*Apparatus*

In the acetonitrile studies, two three-compartment electrolytic cells were used, in which sintered glass disks separated the compartments (the indicating electrode compartment was between the reference- and counter-electrode compartments). One cell contained a platinum-disk indicating electrode (0.7-mm diameter) connected to a 600 rpm Sargent synchronous rotator, a platinum spiral counter-electrode immersed in the sample solution, and an aqueous saturated calomel electrode (sce) with a 1 M

potassium nitrate in agar salt bridge. The sce gave results comparable to those of Solon and Bard<sup>5</sup> and was therefore assumed to be stable. (Over extended periods of time, the acetonitrile test solutions leached what is assumed to be potassium nitrate crystals through the sintered glass disk.) Solutions were de-aerated with purified and dried nitrogen for at least 10 min prior to a run; de-aeration periods of up to 20 min were used with no significant change in the voltammetric pattern.

The second cell utilized a 4-mm diameter pyrolytic graphite disk indicating electrode (pge) which could be used either rotating (600 rpm) or stationary, a platinum-spiral counter-electrode immersed in a 0.1 M  $\text{Et}_4\text{NClO}_4$  solution in acetonitrile and a silver/0.1 M silver-nitrate electrode with acetonitrile as solvent;<sup>6</sup> a methylcellulose gel in 0.1 M  $\text{Et}_4\text{NClO}_4$  (dimethylformamide as solvent) was used in the bridges between compartments (dimethylformamide was used since acetonitrile did not lend itself to being used in this type of gel). Due to the rapid diffusion of oxygen from the counter- and reference-electrode compartments, it was necessary to de-aerate all three compartments for at least 20 min.

All voltammograms in acetonitrile were recorded at  $25^\circ \pm 0.2^\circ\text{C}$ .

The three-compartment cell used for the pyridine studies contained a rotating (600 rpm) or stationary pge (2- or 4-mm diameter), a platinum-spiral counter-electrode immersed in a 0.1 M background electrolyte solution, and a Ag/1 M  $\text{AgNO}_3$  reference electrode with pyridine-methylcellulose. De-aeration was accomplished by a 20-min purge with argon. The supporting electrolyte was 0.1 M  $\text{Et}_4\text{NClO}_4$ . Voltammograms were run at  $27^\circ \pm 0.2^\circ\text{C}$ .

The previously described<sup>1</sup> electrolytic cell used in sulphur dioxide studies contained a pge (2-mm diameter) sealed in glass tubing<sup>8</sup> in place of the platinum-disk electrode previously used, a Ag/AgBr helix reference electrode, a platinum-spiral electrode of an area equal to or greater than that of the indicating electrode, which was used for short-circuiting the indicating electrode, and a double helix Ag/AgBr counter-electrode. All runs were made at  $-20^\circ \pm 0.5^\circ\text{C}$  in a  $\text{CO}_2$ -2-propanol bath.

Current/potential curves were recorded by a Sargent Model XV polarograph equipped with a Sargent Model A *IR* Compensator.

Cyclic voltammetry was carried out with an operational amplifier unit, whose construction and operational procedure have been described<sup>2</sup>. The potential excursions previously noted have been eliminated by removal of the double-pole-double-throw switch in the feedback network and the installation of a single-pole-single-throw switch between the working electrode and the current amplifier, which is used as the cell "in-out" switch.

Solution resistance in all cases was measured with a Jones-type conductivity bridge.

### *Esr procedure*

The esr measurements in the case of the sulphur dioxide studies were taken on solid material recovered from the cell on evaporation after the colour of the DPPH solution changed from violet to yellowish-brown. These were compared to the signal obtained for solid DPPH.

Measurements on the 1 mM DPPH in pyridine solution were taken when the solution colour was still deep violet and then when it had changed to reddish-brown.

TABLE 1. VOLTAMMETRY OF DIPHENYLPICTRYLHYDRAZYL IN ACETONITRILE WITH AND WITHOUT BACKGROUND ELECTROLYTE

DPPH Concn mM	Back- ground M	Electrode <sup>a</sup>	Soln resist- ance K $\Omega$	Cathodic pattern <sup>b</sup>				Anodic pattern <sup>c</sup>					
				$E_{h/2}$ V	Slope mV	$i_t$ $\mu$ A	Discharge V	$E_{a/2}$ V	Slope mV	$i_t$ $\mu$ A	Discharge V		
0.0	0.0 <sup>a</sup>	r	600				-1.50						
1.0	0.0 <sup>a</sup>	s	600	0.23 (0.18)	72 (60)	0.5		0.78 (0.81)	72 (74)	0.5			1.80
1.0	0.0 <sup>a</sup>	r	600	0.15 (0.17)	102 (120)	3.4		0.84 (0.81)	111 (108)	3.6			
0.0	0.1 <sup>a</sup>	r	4				-1.74						1.80
1.0	0.1 <sup>a</sup>	r	4	(0.17)	(55)	2.4		0.70	58	3.1			
1.0	0.0 <sup>b</sup>	s	20 $\rightarrow$ 10	-0.13	70	9.0		0.46					
1.0	0.0 <sup>b</sup>	r	20 $\rightarrow$ 10	-0.28 (-0.38)	200 (330)	72.4		0.69 (0.57)	80	8.2			
1.0	0.1 <sup>b</sup>	s	0.9	-0.07 (-0.14)	49 (54)	9.5		0.40 (0.45)	320 (220)	74.4			
1.0	0.1 <sup>b</sup>	r	0.9	-0.10	62	64.6		0.43 (0.43)	46 (57)	10.4			
1.0	0.1 <sup>c</sup>	r		0.178				0.693					
0.47	0.1 <sup>c</sup>	r		0.20				0.71					

<sup>a</sup> Background electrolyte: NaClO<sub>4</sub>. Electrode: platinum, 0.7 mm.

<sup>b</sup> Reference electrolyte: aqueous sec.

<sup>c</sup> Background electrolyte: Et<sub>4</sub>NClO<sub>4</sub>. Electrode: pgs, 4 mm.

Reference electrode: Ag/0.1 M AgNO<sub>3</sub> in acetonitrile.

<sup>d</sup> Background electrolyte: NaClO<sub>4</sub>. Electrode: platinum, 1 mm.

Reference electrode: aqueous sec. Direction of polarization not indicated. Data taken from Solon and Bard.\*

<sup>e</sup> s, stationary electrode; r, rotating (600 rpm) electrode.

\* Values in parentheses refer to those obtained on reverse polarization, *i.e.* polarization from a given positive or negative potential to zero; values not in parentheses were obtained on normal polarization.

### Potential-drop calculations

Ohm's Law was used to calculate the expected change in half-height potential between solutions with and without background electrolyte in the absence of  $IR$ -drop compensation. The resistance value used was the difference between the resistances of the two solutions. The current was that at the half-height potential of the wave for DPPH in the absence of background electrolyte.

## RESULTS

### Acetonitrile solution

The following discussion, until the section on adsorption of DPPH on graphite, deals with the data obtained at a platinum electrode, which was also used by Solon

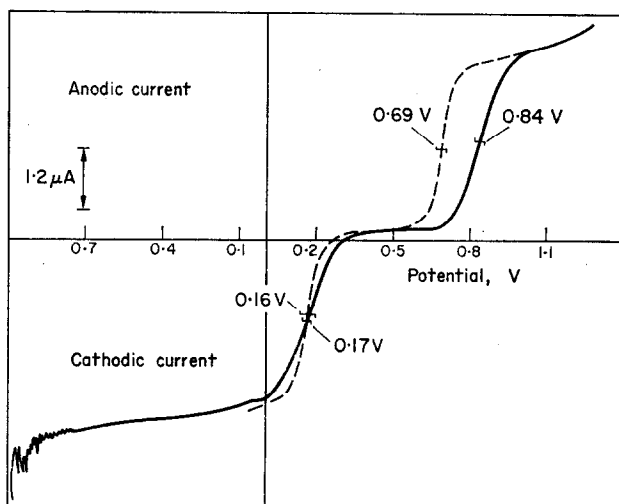


FIG. 2. Voltammetry of DPPH in acetonitrile with a rotating (600 rpm) platinum indicating electrode *vs* sce.  
Solid line, 1 mM DPPH in acetonitrile.  
Dashed line, 1 mM DPPH and 0.1 M NaClO<sub>4</sub> in acetonitrile.

and Bard,<sup>5</sup> whose data on DPPH in acetonitrile solution were satisfactorily reproduced. Slope,  $ie(E_{3/4} - E_{1/4})$ , data of 55 and 58 mV for the rotating platinum electrode (Table 1; Fig. 2) and cyclic voltammetry with a stationary platinum electrode (Fig. 3) in 0.1 M NaClO<sub>4</sub> solution indicate a one-electron reversible oxidation-reduction of DPPH as reported.<sup>5</sup>

Interestingly enough, when current/potential curves were run on acetonitrile alone and on a 0.1 M NaClO<sub>4</sub> solution in acetonitrile (Table 1), generally similar anodic curves were obtained; discharge potentials obtained by extrapolation of the vertical current portion of each curve to intersection with the potential axis were identical, 1.80 V. If current/potential curves were run on an electrode that had been subjected to anodic discharge and not reconditioned by wiping with an ethanol-saturated tissue and washing with acetonitrile, extraneous waves were observed, indicating the deposition of products on the platinum and/or chemical alteration of the electrode surface.

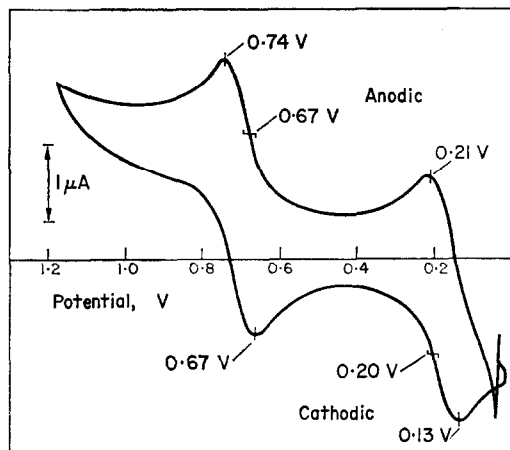


FIG. 3. Cyclic voltammetry of 1 mM DPPH in acetonitrile (0.1 M NaClO<sub>4</sub>) with a stationary platinum indicating electrode *vs* sce in acetonitrile.

**Voltammetry.** The slow-scan cathodic half-height potentials,  $E_{h/2}$ , for DPPH in the absence and presence of supporting electrolyte are comparable within experimental error (Table 1; Fig. 2), even though, *eg* the calculated half-height potential shift is 1.0 V more negative in the case of the rotating electrode. The results for cyclic voltammetry are also quite comparable (Table 2; Figs. 3 and 4). It is consequently apparent that, even though there is a very large difference in resistance between the solution with background electrolyte (4 K $\Omega$ ) and that without (600 K $\Omega$ ), the *IR* compensation is sufficient to give dependable results.

It should be noted that the slope values for the rotating electrode with and without background of 55 and 120 mV, respectively, indicate that the background electrolyte apparently plays an important role in the reversibility of the wave, the reduction being more reversible in the presence of background electrolyte (here, specifically 0.1 M NaClO<sub>4</sub>).

The slow-scan anodic  $E_{h/2}$  values show some discrepancy between solutions with and without background, *viz* 0.14 V for the rotating electrode (the calculated potential

TABLE 2. CYCLIC VOLTAMMETRY OF DIPHENYLPICRYLHYDRAZYL IN ACETONITRILE WITH AND WITHOUT BACKGROUND ELECTROLYTE

DPPH Concn mM	NaClO <sub>4</sub> M	Elec- trode <sup>a</sup>	Soln. resist- ance K $\Omega$	Potl. span V	Cathodic pattern <sup>b</sup>			Anodic pattern <sup>b</sup>			
					$E_{h/2}$ V	$E_p$ V	$i_p$ $\mu$ A	$E_{h/2}$ V	$E_p$ V	$i_p$ $\mu$ A	
1.0	0.0	s	$\geq 600$	-0.8 to 1.2	I	—	0.64	—	0.24	0.39	—
					II	0.14	0.00	1.8	0.88	1.03	2.0
1.0	0.0	s	$\geq 600$	0.8 to -1.2		0.17	0.02	2.0	0.25	0.40	2.1
1.0	0.0	r	$\geq 600$	-0.8 to 1.2		0.19	—	3.3	0.90	—	3.4
1.0	0.1	s	4	0.0 to 1.2	I	—	0.66	—	—	0.21	—
					II	0.20	0.13	1.8	0.67	0.74	1.9
1.0	0.1	r	4	0.0 to 1.2		0.18	—	3.1	0.69	—	3.3

<sup>a</sup> Platinum electrode, 0.7 mm. diameter; s, stationary; r, rotating at 600 rpm. Polarization rate: 0.12 V/s.

<sup>b</sup> Potentials are *vs* aqueous sce.

difference is 1.07 V). The stationary and rotating data in absence of background electrolyte show a difference of 0.06 V. These results may be attributed to one or more of the following: (a) insufficient *IR* compensation (b) effect of background on reversibility of the system and (c) effect of electrode rotation on a system, which may show partial irreversibility due to the increased rate of supply of the electro-active material (*cf* subsequent discussion).

The concordance of the cathodic data indicate that the *IR*-compensation system is functioning properly.

The difference of 0.14 V in  $E_{h/2}$  for the rotating electrode with and without background is probably due to the effect of background on the reversibility of the oxidation.

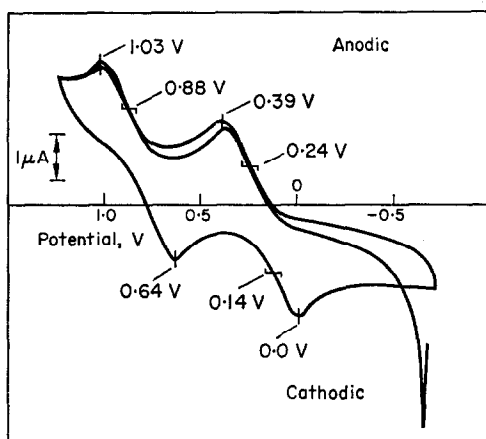


FIG. 4. Cyclic voltammetry of 1 mM DPPH in acetonitrile (no background electrolyte) with a stationary platinum indicating electrode *vs* sce.

However, the discrepancy of 0.06 V between  $E_{h/2}$  values for the rotating and stationary electrodes in absence of background may reflect an increased rate of supply of electro-active material on rotation since, for a semi-reversible electrode process, as discussed by Nickolson and Shain,<sup>9</sup> increased rate of polarization will shift potential in the positive direction for an oxidation which, above a certain rate of polarization or of supply of electro-active species to the electrode, is semi-reversible; the same is true for increased rate of electrode rotation.<sup>10</sup> This is indeed shown on comparison of slow scan and cyclic voltammetric potentials in the absence of background (Tables 1 and 2); the difference in anodic  $E_{h/2}$  is 0.06 V for the rotating electrode with the cyclic values being more positive, and 0.10 V for the stationary electrode with the cyclic values being again more positive.

**Cyclic voltammetry.** Since the cathodic  $E_{h/2}$  values on cyclic voltammetry (Table 2) are again close, *IR* compensation may be assumed to be adequate. The decreased difference of 0.02 V in anodic  $E_{h/2}$  between the rotating and stationary electrodes in absence of background, compared to 0.06 V for the slow-scan data, reflects an equalizing effect of the increased rate of polarization with respect to the effect of rotation.

The cyclic  $E_{h/2}$  values for rotating and stationary electrodes in presence of background, as compared to those without background, again show the effect of the electrolyte in increasing the reversibility of the oxidation.

**Adsorption of DPPH on graphite.** The large difference of 0.10 V in slow scan cathodic  $E_{h/2}$  values (Table 1) for forward and reverse directions of polarization at the rotating pge (no background) has associated with it slope values of 200 and 330 mV for the forward and reverse sweeps, respectively (Fig. 5). These discrepancies in  $E_{h/2}$  and slope values may be due to chemisorption of DPPH on the graphite electrode, *ie*, during forward polarization the concentration of DPPH at the electrode surface before electrolytic decomposition is equal to the bulk concentration and chemisorption of the DPPH is possible, but, on reverse polarization, the concentration of DPPH at the electrode surface during tracing of the limiting current plateau is essentially zero,

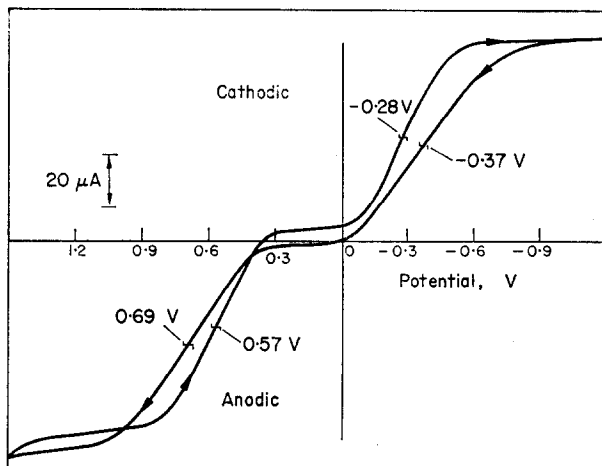


FIG. 5. Voltammetry of 1 mM DPPH in acetonitrile at the rotating (600 rpm) pge vs 0.1 M Ag/AgNO<sub>3</sub> in acetonitrile as reference electrode; both forward and reverse polarization.

eliminating the possibility of adsorption and resulting in a different  $E_{h/2}$  value. Adsorption of DPPH on the pge is supported by Spackman's<sup>11</sup> study of the chemisorption of DPPH on various carbon blacks.

An *IR*-compensation failure as the cause of the potential shift is difficult to support, because the  $E_{h/2}$  values should be reproducible, even if not properly corrected for *IR* drop, in a system in which only the direction of polarization has been changed. The same argument can be applied to the differences in potentials for the anodic process (Table 1).

In both the anodic and cathodic cases, the differences in potential between forward and reverse polarization with background are smaller than for those without background. In addition, the slope values in presence of background electrolyte also approach the value of 56 mV associated with a one-electron reversible process; this value is found in the oxidation and reduction of DPPH in acetonitrile (0.1 M NaClO<sub>4</sub>) at a platinum indicating electrode.<sup>5</sup> It can, therefore, be concluded that in the presence of background electrolyte (here specifically 0.1 M Et<sub>4</sub>NClO<sub>4</sub>), the association of charged species with the DPPH molecule and/or the pre-emption of adsorption sites by the background electrolyte competes with the chemisorption of DPPH.

Due to the differences in supporting electrolyte and reference electrode, the data obtained at platinum and graphite electrodes cannot be compared in detail; however,



TABLE 3. VOLTAMMETRY OF DIPHENYLPICRYLHYDRAZYL IN PYRIDINE WITH AND WITHOUT BACKGROUND ELECTROLYTE

DPPH Concn., mM	Et <sub>4</sub> NClO <sub>4</sub> M	Elec- trode <sup>a</sup>	Soln. resist- ance KΩ	Cathodic pattern <sup>c</sup>				Anodic pattern <sup>c</sup>				
				E <sub>h</sub> /s V	i <sub>c</sub> μA	i <sub>c</sub> /AC μA/mm <sup>2</sup> mM	Discharge V	E <sub>h</sub> /s V	i <sub>a</sub> μA	i <sub>a</sub> /AC μA/mm <sup>2</sup> mM	Discharge V	
1.0	0.0	s <sup>b</sup>	100	I -0.62 II -1.22 III -1.50 IV -1.80 V -2.20	0.9 0.7 0.6 1.1 1.8	0.29 0.22 0.19 0.32 0.57		I 0.32 II 0.79 III 1.02	1.4 1.4 1.9	0.45 0.45 0.61		
0.0	0.1	s	3.2				-1.78					1.23
1.0	0.1	s	3.2	I -0.54 II -1.24 III -1.47	3.1 5.2 6.3	0.25 0.41 0.50		I 0.27 II 0.72	4.4 14.2	0.35 1.13		
0.0	0.1	r	3.2				-1.79					2.13
1.0	0.1	r	3.2	I -0.59 II -1.27 III -1.54	27.1 27.2 7.2	2.15 2.15 0.53		I 0.31 II 0.86	26.4 94.5	2.10 7.50		

<sup>a</sup> Pyrolytic graphite electrode, 4 mm diameter except as otherwise noted; s, stationary; r, rotating at 600 rpm.

<sup>b</sup> Pge, 2 mm diameter.

<sup>c</sup> Potentials are vs Ag/1 M AgNO<sub>3</sub> in pyridine.

TABLE 4. VOLTAMMETRY OF DIPHENYLPICRYLHYDRAZYL IN SULPHUR DIOXIDE WITHOUT BACKGROUND ELECTROLYTE

DPPH Concn. C mM	Cathodic pattern			Anodic pattern				
	$E_{h/2}$ V	$i_i$ $\mu\text{A}$	$i_i/AC$ $\mu\text{A}/\text{mm}^2 \text{ mM}$	$E_{h/2}$ V	$i_i$ $\mu\text{A}$	$i_i/AC$ $\mu\text{A}/\text{mm}^2 \text{ mM}$		
0.16 <sup>a</sup>	I	0.48	0.25	0.50	I	0.92	0.45	0.90
	II	0.06	0.15	0.30	II	1.28	0.72	1.44
	III	-0.64	0.50	1.00	III	2.29	0.95	1.80

<sup>a</sup> Electrode: stationary pge 2-mm diameter. Solution resistance: 40 K $\Omega$ .

<sup>b</sup> Potentials are *vs* Ag/AgBr in sulphur dioxide.

the shifts in potential, *eg* in going from stationary to rotating electrode, are in the same direction and of generally comparable magnitude.

#### Pyridine and sulphur dioxide solutions

Discussion of the voltammetric patterns (Table 3 and 4; Figs. 6 and 7) in pyridine and sulphur dioxide has to take account of the fact that DPPH undergoes a chemical change in both solvents. Since, in the case of sulphur dioxide, no precautions were taken to shield the sample solutions from ordinary laboratory lighting, photochemical decomposition of DPPH to the hydrazine, a nitro-substituted hydrazine and a polymer as described by Suzuki, Takahashi and Shiomi<sup>12</sup> would seem to account for the observed chemical behaviour.

A study<sup>13</sup> of the behaviour of DPPH in various grades of pyridine obtained, *via* fractional crystallization of the commercial reagent-grade solvent received, has

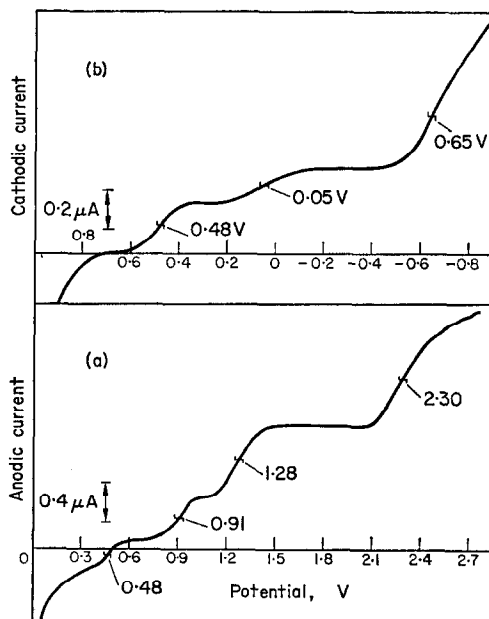


FIG. 6. Voltammetry of 0.16 mM DPPH in sulphur dioxide at the stationary 2-mm pge *vs* Ag/AgBr reference electrode. (a) anodic pattern. (b) cathodic pattern.

shown—through visual observation of the dissipation of the characteristic violet colour of the DPPH solution—that the stability of the free radical is dependent upon the concentration of impurities in the pyridine when the sample solutions are shielded from radiation. Thus, on dissolving 5 mg DPPH in 50 ml reagent-grade pyridine, the violet colour changed almost instantaneously to a reddish-brown; however, a similar solution in the same lot of pyridine, which had been fractionally crystallized twice, still showed some violet colour after 7 h.

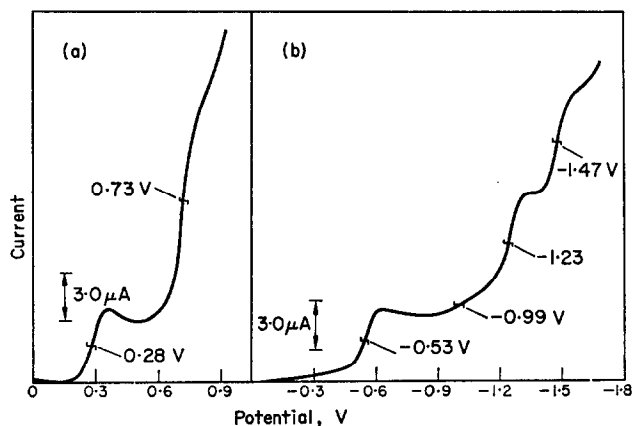


FIG. 7. Voltammetry of 1 mM DPPH in pyridine (0.1 M  $\text{Et}_4\text{NClO}_4$ ) at a stationary 4-mm pge vs nAge in pyridine. (a) anodic pattern. (b) cathodic pattern.

In the case of both solvents, esr established the decomposition of the DPPH by the disappearance of its free radical signal.

*Diphenylpicrylhydrazine.* Identical decomposition products were isolated from both solvent systems. A 7 mM DPPH solution in sulphur dioxide was allowed to stand until the colour turned yellowish-brown; the sulphur dioxide was then boiled off and the system flushed three times with dry nitrogen. A solid consisting of two visibly distinguishable solid phases (one black and one reddish-brown) was obtained; the brown solid, on exposure to air, was converted to the black solid. An ir spectrum (KBr pellet) was taken of the brown solid.

A pyridine solution containing 0.5 g DPPH per 100 ml argon-de-aerated reagent-grade pyridine was allowed to stand for two weeks in the absence of light; at the end of this time, some DPPH was still present, as indicated by the colour of the solution. The reaction mixture was therefore passed through a column of adsorption alumina, using chloroform as eluting agent. The DPPH remained on the column; a reddish-brown solid was obtained upon evaporation of the chloroform and its ir spectrum (KBr pellet) was taken. The ir spectra of the two isolated compounds were identical with that of diphenylpicrylhydrazine.

Diphenylpicrylhydrazine (1 mM in 0.1 M  $\text{Et}_4\text{NClO}_4$  in pyridine), when examined under the same conditions as DPPH, showed a voltammetric pattern containing the same number of anodic and cathodic waves as that of the decomposed DPPH.  $E_{n/2}$  became more positive (ca 100 mV) with increasing degree of purity of the pyridine used (Fig. 8).

*Interpretation of voltammetric patterns.* The voltammetric patterns obtained in pyridine and sulphur dioxide are generally similar, except that an additional wave is observed in the effectively greater potential range available in sulphur dioxide (Figs. 6 and 7). This, of course, would be expected in the absence of major molecular degradation of DPPH during the chemical reaction with the solvent, leaving the main carbon skeleton intact. The chemical reactions involved would not necessarily have to be the same in both solvents. Since DPPH is known to react with compounds containing an active hydrogen, *eg* phenols, mercaptans and acids, to form the hydrazine, it is reasonable to assume the possible presence of an impurity with an active

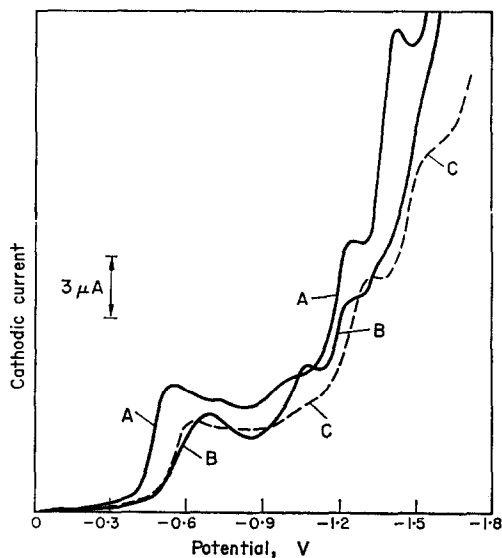


FIG. 8. Voltammetry in pyridine (0.1 M  $\text{Et}_4\text{NClO}_4$ ) at a stationary 4-mm pge vs nAg in pyridine.

- A, 1 mM diphenylpicrylhydrazine in purified pyridine.  
 B, 1 mM diphenylpicrylhydrazine in reagent grade pyridine.  
 C, 1 mM DPPH in pyridine (reddish brown in colour).

hydrogen in the pyridine, which would lead to the formation of the hydrazine even in the absence of light. However, since there are no protons in sulphur dioxide, a photochemical reaction is most probable, as already mentioned.

The observed voltammetric patterns, taking the preceding into consideration, may then be attributed to the hydrazine in the case of pyridine, and to the hydrazine and, perhaps, to the nitro-substituted hydrazine and/or the polymer in sulphur dioxide.

#### CONCLUSIONS

Voltammetry without background electrolyte is quite feasible when a reliable three-electrode *IR* compensation system is used.

However, care must be taken in comparing data obtained with and without background electrolyte to allow for effects of the latter on the reversibility of the system under study, *eg* as mirrored in the wave slope. The supporting electrolyte may have an additional pronounced effect on neutral organic molecules, *eg* in prevention of the chemisorption of neutral organic molecules, here specifically DPPH, on the pyrolytic

graphite electrode surface, where the DPPH is apparently chemisorbed in its absence.

Finally, although the voltammetric studies carried out in pyridine and sulphur dioxide contribute little to the main theme of the paper, the fact that, even in the absence of background electrolyte, the half-life of the DPPH free radical in pyridine showed a great dependence on the purity of the solvent is of significance when free-radical intermediates are proposed for electrode mechanisms in pyridine.

*Acknowledgement*—The authors thank the U.S. Atomic Energy Commission and the National Science Foundation for helping to support the work described, and Dr. Julian Gendell for his assistance with the esr measurements.

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