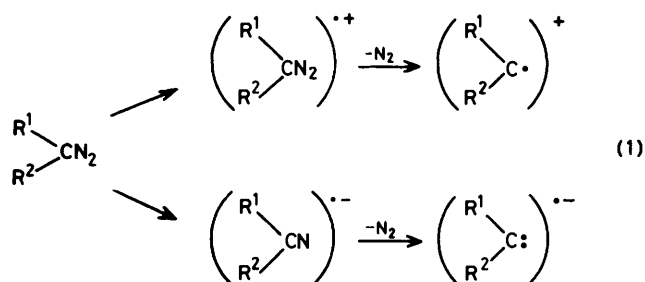# Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part 17.[1] Formation and Reaction of Diazodiphenylmethane Anion Radical in Solution

By Donald Bethell,* The Robert Robinson Laboratories, The University, P.O. Box 147, Liverpool L69 3BX
Vernon D. Parker, Laboratory of Organic Chemistry, Norwegian Institute of Technology, N-7034, Trondheim, Norway

The one-electron reduction of diazodiphenylmethane in dimethylformamide (DMF) which gives largely diphenylmethane and benzophenone azine has previously been reported to involve generation from the diazoalkane anion radical of diphenylmethylene anion radical. The reaction has now been re-examined in CH_3CN as well as DMF and the corresponding perdeuteriated solvents. It is established that at high sweep rates in both solvents one-electron reduction of Ph_2CN_2 is quasi-reversible, the heterogeneous charge charge-transfer rate being markedly influenced by the nature of the supporting electrolyte. Examination of the kinetics of disappearance of $Ph_2CN_2^{\cdot-}$ by linear sweep voltammetry and double potential step chronoamperometry shows that the reaction conforms to a first-order kinetic law. In CD_3CN, however, the rate coefficient is decreased by a factor of over 20 indicating that the solvent is involved chemically in the disappearance of $Ph_2CN_2^{\cdot-}$. Since a good proton donor, diethyl malonate, does not affect the rate, it is inferred that $Ph_2CN_2^{\cdot-}$ abstracts a hydrogen atom from the solvent. It would seem that quantum mechanical tunnelling occurs in CH_3CN, but not in DMF where the kinetic hydrogen isotope effect is only about four. A product isotope effect is also observed and interpreted in terms of competing reactions of $Ph_2CN_2^{\cdot-}$: (i) hydrogen atom abstraction from the solvent; (ii) attack on Ph_2CN_2 or $Ph_2CN_2^{\cdot-}$ giving azine, a process analogous to that observed in electrochemical decomposition of 9-diazofluorene; (iii) reaction with molecular oxygen giving benzophenone. There is no evidence for unimolecular loss of nitrogen from $Ph_2CN_2^{\cdot-}$ to give the carbene anion radical.
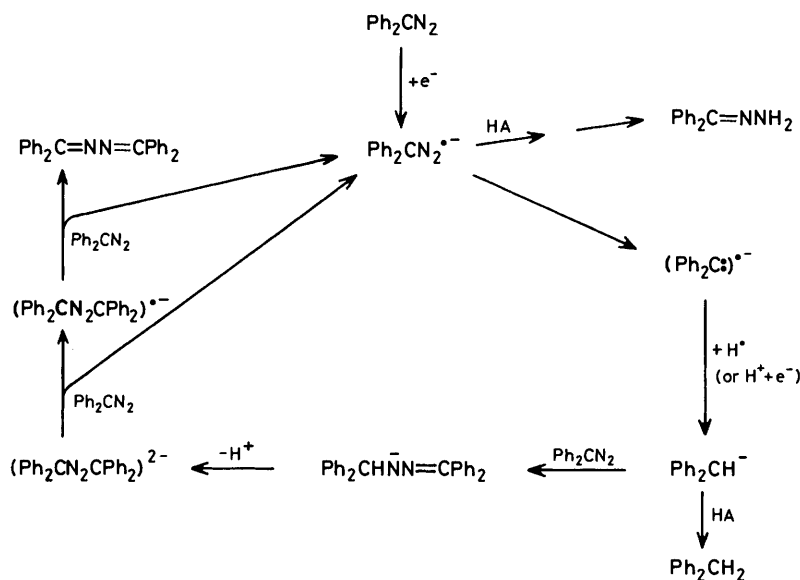
OVER the years, diazoalkanes, reactive molecules in their own right, have proved to be a rich source of a wide diversity of organic reactive intermediates, carbenium ions, carbenoids, carbenes, and derived free radicals.[2] More recently, diazoalkane radical cations[3] and anions[4] have been generated by one-electron oxidation and reduction of aryldiazoalkanes, both chemical and electrochemical, and this has raised the question of whether unimolecular loss of nitrogen from such species can occur giving rise to carbene radical cations[4a,5] and anions[5,6] [equation (1)]. Thus, for example, the methylene

(1)

radical cation, $CH_2^{\cdot+}$, was proposed as an intermediate in the methylation of pyridine when diazomethane was oxidised electrochemically in sulpholan,[5] but kinetic evidence rules out an analogous carbene radical cation in the decomposition of diazodiphenylmethane induced be $Cu(ClO_4)_2$ in acetonitrile solution.[3a] Much more substantial evidence for the formation of carbene radical anions from diazoalkanes has accumulated over the years since Webster[6] suggested the formation of such a species in the polarographic reduction of tetracyanodiazocyclopentadiene. The parent $(CH_2^{\cdot})^{\cdot-}$ has been identified

among the products of electric discharges through gaseous CH_4 and CH_2N_2,[7] and reactions of cyclopentadienylidene radical anion have recently been studied by the flowing afterglow technique.[8] Theoretical studies of the electronic structure and geometry of both these carbene anion radicals have also been reported.[8,9] In solution methylene radical anion was suggested to be responsible for the formation of ethylene and acetylene when methylene halides are treated with sodium naphthalene,[10] and diphenylmethylene anion radical has been suggested as an intermediate in the photolysis of a manganese carbene complex.[11] The most extensive investigation, however, has been that by McDonald, Hawley, and their co-workers on the electrochemical reduction of aryldiazoalkanes in aprotic solvents.

The electrochemistry of diazoalkanes has been intermittently studied, mostly in aqueous solvents, over the past 15 years or so, and the subject has been reviewed briefly by Fry.[12] Elofson et al. reported[5] that in sulpholan as solvent, diazodiphenylmethane has $E_{\frac{1}{2}}$ −1.70 V versus s.c.e. and that preparative reduction at −2 V gave diphenylmethane (40%), diphenylmethylamine (20%), and small amounts of azodiphenylmethane. A re-examination of the reaction in dimethylformamide (DMF) by McDonald et al.[13] showed that the principal initial products of the reaction are diphenylmethane and benzophenone azine. On the basis of cyclic voltammetric, coulometric, and preparative work they inferred that the diazoalkane radical anion resulting from one-electron reduction initiates a chain reaction which produces the azine and they proposed that the key step in the mechanism in the absence of proton donors is the unimolecular loss of nitrogen from $Ph_2CN_2^{\cdot-}$ yielding the carbene radical anion. The main steps of the reaction

$$Ph_2CN_2$$
$$\downarrow +e^-$$

$$Ph_2C=NN=CPh_2 \longleftarrow Ph_2CN_2^{\bullet -} \xrightarrow{HA} \longrightarrow Ph_2C=NNH_2$$

$$Ph_2CN_2 \qquad (Ph_2C\colon)^{\bullet -}$$

$$(Ph_2CN_2CPh_2)^{\bullet -}$$

$$Ph_2CN_2 \qquad +H^{\bullet} \; (or \; H^+ + e^-)$$

$$(Ph_2CN_2CPh_2)^{2-} \xleftarrow{-H^+} Ph_2CH\bar{N}N=CPh_2 \xleftarrow{Ph_2CN_2} Ph_2CH^-$$

$$\downarrow HA$$

$$Ph_2CH_2$$

Scheme

are shown in the Scheme, and the evidence may be summarised as follows.

(i) Cyclic voltammetry appeared to indicate that one-electron reduction of Ph_2CN_2 at a platinum cathode is irreversible at room temperature and scan rates up to 100 V s^{-1}. Peaks on the reoxidation scan were assigned to Ph_2CH^-, $Ph_2CH\bar{N}N=CPh_2$, $(Ph_2CN_2CPh_2)^{\bullet -}$, and $(Ph_2CN_2CPh_2)^{2-}$.

(ii) Constant-potential electrolysis shows that Ph_2CH_2 and the azine, $Ph_2CN_2CPh_2$, account for ca. 85% of the diazoalkane decomposed, with minor amounts of $Ph_2C=O$, $Ph_2C=NNH_2$, and $Ph_2CHNHN=CPh_2$. A dramatic increase in the yield of Ph_2CH_2 and $Ph_2C=NNH_2$ occurs when small concentrations of electroinactive proton donors, such as diethyl malonate and trifluoroethanol, are present.

(iii) The reaction shows an n value much less than unity when azine is the major product indicating that it is formed in an electrochemically initiated chain process.

(iv) In the electrochemical reduction of 9-diazofluorene, FIN_2, proton donors protonate the diazoalkane radical anion $FIN_2^{\bullet -}$ on nitrogen (increasing the yield of $Fl=NNH_2$) but not on carbon (the yield of FlH_2 being virtually unaffected).[14] It was then argued that in the reduction of Ph_2CN_2, the formation of Ph_2CH_2 arises by protonation of or hydrogen abstraction by $(Ph_2C\colon)^{\bullet -}$ rather than via $Ph_2CHN_2^-$, a type of intermediate accepted as involved in the Wolff–Kishner reduction of hydrazones to the corresponding hydrocarbon.[15]

Although a similar carbene radical anion mechanism was advanced for the electrochemical reduction of FIN_2,[16] evidence from low-temperature cyclic voltammetry [17] as well as ^{15}N-labelling studies on the related reduction of FIN_2 initiated by 2-ethylfluorene in strongly basic media [18] suggested that this mechanism is much less likely than in the reduction of Ph_2CN_2. Indeed, electrochemical kinetic studies using linear sweep voltam-

metry showed that $FIN_2^{\bullet -}$ is consumed by dimerisation in the vicinity of the electrode surface.[19] The evidence for $(Ph_2C\colon)^{\bullet -}$ in the reduction of Ph_2CN_2 though more substantial is still circumstantial. The nub of the mechanistic question is whether attachment of hydrogen to the diazo-carbon atom preceeds or succeeds nitrogen loss from the diazoalkane radical anion, and this can only be established by direct examination of the behaviour of $Ph_2CN_2^{\bullet -}$. In this paper we present a full account [20] of our electrochemical studies of the behaviour, especially the kinetic behaviour, of $Ph_2CN_2^{\bullet -}$. To elucidate this behaviour, it was necessary to make a fairly detailed study of the heterogeneous charge-transfer processes in which $Ph_2CN_2^{\bullet -}$ is formed. We conclude that the corresponding carbene radical anion is not an important intermediate in cathodic reduction of Ph_2CN_2.

RESULTS

Heterogeneous Charge Transfer to Ph_2CN_2.—By generating $Ph_2CN_2^{\bullet -}$ in CD_3CN in the presence of Me_4NBF_4 as supporting electrolyte, the rates of its homogeneous chemical reactions are decreased compared with other solvent–electrolyte systems; it was possible therefore to study the kinetics of the heterogeneous charge-transfer process. The cyclic voltammogram of Ph_2CN_2 under these conditions measured at 100 V s^{-1} is shown in Figure 1. The response indicates that this is a well behaved quasi-reversible system with little perturbation from the subsequent homogeneous reactions. The effect of the voltage-sweep rate (v) on the separation of the anodic and cathodic peaks (ΔE^P) together with heterogeneous charge-transfer rate constants (k_s) calculated using Nicholson's theoretical data [21] are shown in Table 1. That k_s is essentially independent of v indicates a good correspondence of the theoretical and experimental data.

It has previously been observed that in reduction of organic compounds heterogeneous charge-transfer rates are dependent on the size of the tetra-alkylammonium counter-

ion.[23] This effect is evident in the peak-separation data for Ph_2CN_2 reduction in dimethylformamide (DMF) containing various supporting electrolytes (Table 2). At 100 V s^{-1}, ΔE^P was observed to be ca. 700 mV in the presence of
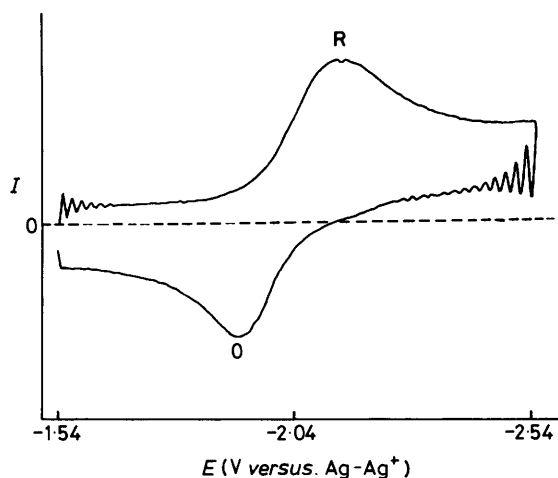

FIGURE 1 Cyclic voltammogram for the reduction of diazo-diphenylmethane at a mercury electrode in CD_3CN containing Me_4NBF_4 (saturated) at 8 °C and 100 V s^{-1}

Bu_4N^+ and to decrease progressively with decreasing cationic radius to ca. 360 mV when Me_4N^+ was present. Moreover, in the presence of Me_4N^+, ΔE^P showed the expected decrease as v was lowered. The point is further illustrated by the cyclic voltammograms in Figures 2 and 3. With Bu_4N^+ present the observed voltammogram (Figure 2a) resembles that reported earlier by McDonald et al. (Figure 1 of ref. 13a). On changing the counter-ion to $Pr_4^nN^+$ (Figure 2b)

TABLE 1

Heterogeneous charge-transfer kinetics of the reduction of diazodiphenylmethane in CD_3CN [a]

v/V s^{-1}	ΔE^P/mV [b]	ψ [c]	k_s/cm^{-1} [d]
1	79.2	1.25	0.045
10	120.4	0.35	0.040
20	142.0	0.25	0.040
50	178.4	0.17	0.043
100	208.2	0.10	0.036
			0.041 ± 0.003

[a] Measurements on a solution containing Ph_2CN_2 (1.0mM) and Me_4NBF_4 (saturated) at 8 °C. Measurements were made using derivative cyclic voltammetry as described in ref. 22. [b] The peak-potential difference for the quasi-reversible couple. [c] Dimensionless parameter relating ΔE^P to k_s, as described in ref. 21. [d] Calculated from ψ according to ref. 21.

TABLE 2

Cyclic voltammetric peak-potential separations during the reduction of Ph_2CN_2 in DMF

v/V s^{-1}	R_4N^+ [a]	ΔE^P/mV [b]
100	Bu_4N^+	698
100	Pr_4N^+	608
100	Et_4N^+	424
100	Me_4N^+	360
100	Me_4N^+ [c]	344
50	Me_4N^+ [c]	312
20	Me_4N^+ [c]	260
10	Me_4N^+ [c]	123

[a] Supporting electrolyte concentration 0.1M unless specified. [b] Potential differences between cathodic and anodic peaks measured by derivative cyclic voltammetry at 22 °C. [c] In perdeuterio-DMF saturated with Me_4NBF_4.
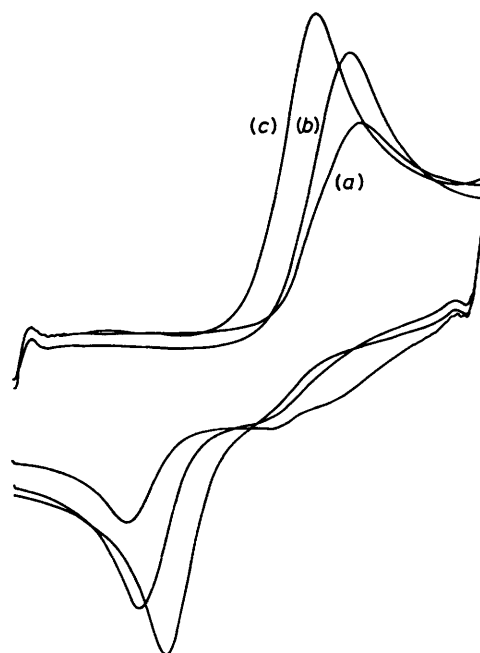

FIGURE 2 Cyclic voltammograms for the reduction of diazo-diphenylmethane at a mercury electrode in DMF at 21.5 °C. Voltage sweep rate 100 V s^{-1}; potential limits, -0.80 to -2.30 V [versus $Ag-Ag^+(CH_3CN)$]. In order of increasing current, the cations of the supporting electrolyte were (a) $Bu_4^nN^+$, (b) $Pr_4^nN^+$, and (c) Et_4N^+

and Et_4N^+ (Figure 2c), ΔE^P became smaller and the voltammograms appeared to represent well behaved quasi-reversible systems. The heterogeneous charge transfer was further enhanced, using Me_4NBF_4 as supporting electrolyte (Figure 3). However, comparison of the result in DMF at
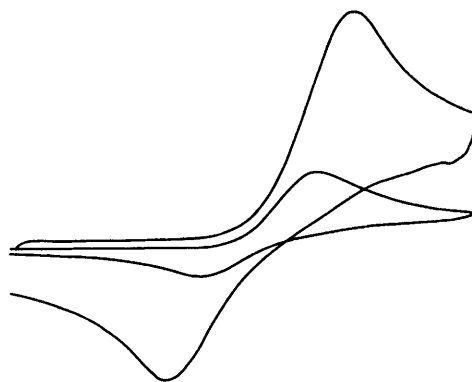

FIGURE 3 Cyclic voltammograms for the reduction of diazo-phenylmethane at a mercury electrode in [$^2H_7$]DMF containing Me_4NBF_4 (saturated) at 22 °C. Voltage sweep rates are 100 and 10 V s^{-1} and the potential limits are -1.00 to -2.00 V [versus $Ag-Ag^+(CH_3CN)$]

10 V s^{-1} with that in CD_3CN under similar conditions suggests that k_s is approximately four-fold lower in DMF than CD_3CN.

Homogeneous Kinetics.—In the cathodic reduction of Ph_2CN_2, the reactions following charge transfer were studied by (i) linear sweep voltammetry (LSV), (ii) double potential-step chronoamperometry (DPSC), and (iii) derivative cyclic voltammetry (DCV).

(i) LSV kinetic studies.[24] The reaction was studied both

in acetonitrile and DMF using Me_4NBF_4 as supporting electrolyte so as to optimise the charge-transfer kinetics. The results are summarised in Table 3. In CH_3CN, dE^P/d-log v was found to be 31.1 ± 1.2 mV decade^{-1} and dE^P/d log $[Ph_2CN_2]$ 0.9 ± 1.3 mV decade^{-1} (Table 3a). These values

in the absence of DEM are due to problems other than interference from the charge-transfer process.

LSV studies in DMF (Table 3c) gave a clear indication that the voltammetric response is partially controlled by charge transfer. Values of $dE^P/d\log v$ and $(\Delta E^P)_{exp.}$ are

TABLE 3

Linear sweep voltammetric results for the reduction of Ph_2CN_2 [a]

| [Ph₂CN₂]/mM | [DEM]/mM | $-E^P$/mV (at v/V s^{-1}) | | | | $dE^P/d\log v$ (mV decade^{-1}) |
		0.100	0.200	0.400	1.000	
a, Sweep rate and concentration dependence in CH₃CN						
0.2	0	303.1 (1.4)	305.5 (0.6)	314.3 (0.5)	329.4 (0.9)	31.9
0.5	0	300.8 (0.4)	306.8 (0.3)	315.8 (0.5)	330.0 (0.4)	29.5
1.0	0	297.5 (0.2)	305.6 (0.6)	316.0 (0.6)	329.3 (0.6)	32.1
2.0	0	301.2 (0.5)	308.3 (0.8)	318.8 (0.8)	331.6 (0.8)	30.9
Average		300.6	306.5	316.7	330.1	
$(\Delta E^P)_{exp.}$			5.9	10.2	13.4	
$(\Delta E^P)_{th.}$			8.5	8.5	12.6	
b, Effect of a proton donor (DEM) in CH₃CN						
1.0	5.0	300.8 (0.2)	308.0 (0.1)	316.7 (0.1)	329.3 (0.1)	28.7
1.0	10.0	299.7 (0.3)	307.8 (0.1)	316.8 (0.1)	329.8 (0.1)	30.2
1.0	20.0	298.9 (0.3)	307.5 (0.1)	315.3 (0.1)	327.7 (0.1)	28.6
Average		299.8	307.7	316.3	328.9	
$(\Delta E^P)_{exp.}$			7.9	8.6	12.6	
$(\Delta E^P)_{th.}$			8.5	8.5	12.6	
c, Sweep rate-dependence in DMF						
1.0	0	335.4 (0.2)	347.9 (0.7)	361.4 (0.2)	377.3 (0.3)	42.4
$(\Delta E^P)_{exp.}$			12.5	13.5	15.9	
$(\Delta E^P)_{th.}$			8.5	8.5	12.6	

[a] Measurements at a mercury electrode at 23 °C. Electrolyte: Me_4NBF_4 (saturated). Peak potentials are relative to a bias setting of -1.680 V versus $Ag-Ag^+(CH_3CN)$, and numbers in parentheses are standard deviations on five determinations.

are in fair agreement with the requirements of rate law (2) for which values of 29.6 and 0 mV decade^{-1} are predicted.[24] That the peak potential is practically independent of the

$$v = k_{obs.}[Ph_2CN_2^{\cdot-}] \qquad (2)$$

substrate concentration is particularly significant since a second-order contribution to the kinetics is ruled out.

A closer analysis of the data in Table 3a reveals some non-linearity in the semi-logarithmic sweep-rate dependence. This is shown by the comparison of experimental and theoretical values of the peak-potential differences for successive values of v [$(\Delta E^P)_{exp.}$ and $(\Delta E^P)_{th.}$ respectively]. This non-linearity together with the slightly too large value of $dE^P/d\log v$ suggests some interference of charge-transfer kinetics in the LSV analysis. The deviations from theory are, however, relatively small and this suggests that the charge-transfer rate in acetonitrile is borderline for the LSV response to be under kinetic control solely by the homogeneous follow-up reactions.

LSV studies were also carried out on Ph_2CN_2 in acetonitrile solutions containing diethyl malonate (DEM) in order to test for the involvement of proton transfer in the homogeneous kinetics (Table 3b). Peak potentials were found to be nearly independent of the presence of DEM up to concentrations of ca. 20mM; $dE^P/d\log v$ was 29.2 ± 0.9 mV decade^{-1} and $dE_P/d[DEM]$ was zero within experimental error. This result clearly indicates that DEM (pK_a ca. 13)[25] is not kinetically involved in the disappearance of $Ph_2CN_2^{\cdot-}$ under these conditions. The agreement between $(\Delta E^P)_{exp.}$ and $(\Delta E^P)_{th.}$ in these experiments is very good. This may be because DEM has some beneficial effect on the electrical double layer, enhancing charge-transfer, but it could be that the deviations of the LSV response from theory

substantially larger than the theoretical values for a first-order reaction following charge transfer. Consequently an LSV mechanism analysis is ruled out in this solvent.

(ii) *DPSC* [26] *and DCV* [22,27] *studies.* Double potential-step chronoamperometry is a convenient method of determining rate constants for homogeneous reactions coupled to charge transfer at electrodes. It is not affected by the heterogeneous charge-transfer rate. The method involves a potential step, for example from the anodic limit of the cyclic voltammogram in Figure 1 (where no current flows) to the cathodic limit where Ph_2CN_2 is reduced at a diffusion-controlled rate. After a given time τ, the potential is stepped back to the anodic limit where $Ph_2CN_2^{\cdot-}$ is oxidised at a diffusion-controlled rate. The current is measured at τ and 2τ and the ratio of the two values is used to determine the rate constant using theoretical data. In the present work we measured $\tau_{\frac{1}{2}}$, the pulse width necessary for the normalised current ratio I_N to equal 0.500, which is related to the rate constant through equation (3) which is derived from theoretical data for a first-order reaction following charge transfer.

$$k_{obs.} = 0.411 \ (\tau_{\frac{1}{2}})^{-1} \qquad (3)$$

DCV studies are carried out in an analogous fashion, the variable being the voltage sweep rate and the observable the ratio of the first derivatives of the currents on the backward and forward scans. As for the DPSC studies, the sweep rate $v_{\frac{1}{2}}$ which gives a value of the ratio of 0.5 is used to calculate the rate constant from equation (4).

$$k_{obs.} = 906.2 \ v_{\frac{1}{2}} \ T^{-1} \qquad (4)$$

DPSC results for the reactions of $(Ph_2CN_2)^{\cdot-}$ in CH_3CN and CD_3CN saturated with Me_4NBF_4 at 8 °C are in Table 4.

The average first rate coefficient in CH_3CN is 159 ± 15 s^{-1}, while in CD_3CN the value is 5.4 s^{-1}. The effect of temperature on $k_{obs.}$ is illustrated by the results in Table 5 from which Arrhenius parameters were obtained: E_a 5.5 kcal mol^{-1}, log A 6.57 (corresponding to $\Delta S^{\ddagger}$ -30.5 cal K^{-1} mol^{-1}).

TABLE 4

DPSC kinetic results for $Ph_2CN_2{}^{\bullet-}$ generated at a mercury electrode in acetonitrile [a]

[Ph_2CN_2]/ mM	Solvent	$\tau_{\frac{1}{2}}$/ms	$k_{obs.}$/s^{-1}
1.0	CH_3CN	2.27	181
1.0	CD_3CN [b]	78.6	5.3
2.0	CH_3CN	2.65	156
2.0	CD_3CN [b]	75.3	5.5
3.0	CH_3CN	2.82	146
4.0	CH_3CN	2.68	154

[a] Measurements at 8 °C on solutions containing Me_4NBF_4 (saturated). [b] CD_3CN was 99.6% D (Merck).

The activation parameters predict $k_{obs.}$ at 8 °C in CH_3CN to be 201 s^{-1}, somewhat larger than those reported in Table 4. We have no explanation for the discrepancy although we have on occasion observed similar variations from one solution of substrate and electrolyte to another. The internal consistency of measurements made on a single solution is considerably better as can be seen from the results in Table 5; the fit to the Arrhenius equation gives a correlation

TABLE 5

Effect of temperature on DPSC kinetic results for the reaction of $Ph_2CN_2{}^{\bullet-}$ in CH_3CN [a]

T/°C	$\tau_{\frac{1}{2}}$ [b]/ms	$k_{obs.}$/s^{-1}
21.8	1.356	303.1
15.2	1.560	263.5
6.2	2.118	194.1
-4.9	3.271	125.6
-13.2	4.565	90.0

[a] During the reduction of Ph_2CN_2 (2.0mM) in acetonitrile containing Me_4NBF_4 (0.05M) at a mercury electrode.

coefficient of 0.999. A somewhat similar discrepancy is seen between the results in Table 4 and those in Table 6 which shows the effects of temperature variation on the rate coefficient for the homogeneous reaction in CD_3CN (from a different supplier) measured by DCV. An Arrhenius plot of the results shows no curvature but the correlation coefficient (0.984) is poorer than that for the faster reactions in CH_3CN. This poorer correlation may be a result of some non-reproducible consumption of radicals by reaction with the electrode material which has been noted elsewhere [28] The activation parameters derived from the Arrhenius plot are E_a 6.6 kcal mol^{-1}, log A 6.15 ($\Delta S^{\ddagger}$ -32.2 cal K^{-1} mol^{-1}). The Arrhenius data for CH_3CN and CD_3CN lead to a kinetic isotope effect of 20.3 at 8 °C, somewhat smaller than that

TABLE 6

Effect of temperature on DCV kinetic results for the reaction of $Ph_2CN_2{}^{\bullet-}$ in CD_3CN [a, b]

T/°C	$v_{\frac{1}{2}}$/V s^{-1}	$k_{obs.}$/s^{-1}
0	2.2	7.3
7.5	3.4	10.9
17.4	4.1	12.8
25.5	5.75	17.4
35.9	9.5	27.9
45.1	16.0	45.6

[a] Conditions as for Table 5. [b] CD_3CN was 99.6% D (CEA).

reported previously [20] on the basis of experiments at a single temperature. While we cannot be sure of the origin of the discrepancies, we do not believe that they arise from systematic differences inherent in the DPSC and DCV methods. Although DCV is the preferred method of kinetic measurement, it could not be applied to the reduction of Ph_2CN_2 in CH_3CN because the high sweep rates necessary led to interference from the heterogeneous charge-transfer process.

Kinetic results for the reactions of $Ph_2CN_2{}^{\bullet-}$ in DMF containing Me_4NBF_4 are in Table 7. Within the experimental uncertainty, values of $k_{obs.}$ were invariant over a

TABLE 7

DPSC kinetic results for the decompositon of $PhCN_2{}^{\bullet-}$ in DMF

Run	[Ph_2CN_2]/ mM	T/°C	R_4N^+	$\tau_{\frac{1}{2}}$/ms	$k_{obs.}$/s^{-1}
1	1.0	20.4	Me_4N^+	48.8	8.4
2	2.0	20.4	Me_4N^+	45.1	9.1
3	4.0	20.4	Me_4N^+	40.2	10.2
4	8.0	20.4	Me_4N^+	40.8	10.1
5	5.0	29.7	Me_4N^+	17.4	23.6
6	5.0	19.2	Me_4N^+	47.3	8.7
7	5.0	10.4	Me_4N^+	12.0	3.4
8 *	2.0	18.6	Me_4N^+	176	2.3
9	2.0	21.5	Bu_4N^+	9.93	44.4
10	2.0	21.5	Bu_4N^+	36.2	11.4
11	2.0	21.5	Et_4N^+	22.0	18.7
12	2.0	21.5	Me_4N^+	46.8	8.8

* Perdeuterio-DMF.

range of substrate concentrations from 1 to 8mM with an average value of 9.5 ± 0.9 s^{-1} at 20.4 °C. The absence of a concentration dependence of $k_{obs.}$ rules out a significant second-order contribution to the reaction under these conditions. The effect of temperature on the reaction rate (Runs 5—7) yields E_a 16.7 kcal mol^{-1}, log A 13.4 ($\Delta S^{\ddagger}$ $+2$ cal K^{-1} mol^{-1}), correlation coefficient 1.000. Comparison of Run 8 in perdeuterio-DMF with Run 6 yields a kinetic isotope effect on the reaction $k^H{}_{obs.}/k^D{}_{obs.} = ca.$ 4. Although we have not studied the kinetic isotope effect more systematically, the difference in its magnitude between acetonitrile and DMF and the solvent effect on the rate and activation parameters is, we believe, significant. Finally, we draw attention to the effect of changing the counter-ion on $k_{obs.}$ (Runs 9—12) which indicates that the rate of the follow-up reactions is highest with $Bu^n{}_4N^+$ and lowest in the case of Me_4N^+.

Product Studies.—Constant-current coulometric experiments were carried out at a cylindrical platinum cathode in acetonitrile–Me_4NBF_4 to investigate the product-forming steps of the reaction. The experiments were carried out at room temperature and a low current density was used. Reactions were stopped well before complete disappearance of the Ph_2CN_2 initially present, residual diazo-compound being converted into diphenylmethyl acetate by addition of excess of acetic acid prior to g.l.c. analysis. The results of these experiments are in Table 8.

Four products account for the initial Ph_2CN_2 with good mass balances in both CH_3CN and CD_3CN; these are diphenylmethyl acetate and the principal products of electrolysis: diphenylmethane, benzophenone, and benzophenone azine. Of the electrolysis products diphenylmethane was always the major component but the azine yield increased markedly in CD_3CN or at high initial concentration of Ph_2CN_2. Benzophenone arises from incom-

plete removal of dissolved oxygen from the solvent, but whether oxygen reacts with $Ph_2CN_2^{\cdot-}$ or some later intermediate (e.g. Ph_2CH^-) cannot be decided on the basis of the present results. However, our conclusions are not affected. The mass balance was poorest for the reaction at highest initial concentration of Ph_2CN_2. The g.l.c. trace showed the presence of a number of additional peaks, the most important being identified as due to tetraphenylethylene. Only traces of benzophenone hydrazone could be detected.

TABLE 8

Products[a] of cathodic reduction of Ph_2CN_2 at 21 °C [b]

Solvent	CH_3CN	CD_3CN	CH_3CN
$[Ph_2CN_2]_0$/mM	4.20	4.36	16.9
% reaction	40	26	60
Products			
Ph_2CH_2	65	48	33
Ph_2CO	32	21	26
$Ph_2CN_2CPh_2$	3	31	23
$Ph_2CH_2/Ph_2CN_2CPh_2$	21	1.5	1.4

[a] % Ph_2CN_2 converted into each product. [b] Constant-current electrolysis at a cylindrical platinum cathode; current density ca. 0.1 mA cm⁻².

DISCUSSION

Electroreduction of Ph_2CN_2 *in Acetonitrile.*—We begin by discussing the reduction in acetonitrile since most of our results refer to this solvent. Moreover, our observations indicate that the heterogeneous charge transfer which initiates reaction can be made to take place sufficiently rapidly that the voltammetric behaviour of the system is almost wholly determined by the homogeneous kinetics of the follow-up reactions at low voltage-sweep rates. At high sweep rates and temperatures below room temperature, the reduction of Ph_2CN_2 is quasi-reversible. This is clearly demonstrated by the appearance of the cyclic voltammogram recorded at 100 V s⁻¹ in CD_3CN at 8 °C (Figure 1), and by the constancy of the rate coefficients (k_s) for the heterogeneous charge transfer obtained by comparison with theoretical predictions assuming quasi-reversibility. It should be noted, however, that our experiments were conducted at a mercury electrode; on platinum electrodes the same situation may not apply.

The LSV and linear current potential [29] (LCP) studies in acetonitrile suggest that the system may lie close to the borderline region where both heterogeneous charge transfer and homogeneous kinetic behaviour in the follow-up reactions combine to determine the form of the voltammetric response. Thus LCP analysis at 100 mV s⁻¹ gives a slope of 80 mV rather than the theoretical 69 mV expected of a purely kinetic wave. Further, the data in Table 3a show some evidence of curvature in the relationship between E^P and log ν. On the other hand, it is evident that, notwithstanding the difficulty of reproducing results from one reaction solution to another, E^P values are essentially independent of the concentration of Ph_2CN_2 and indicate that the consumption of $Ph_2CN_2^{\cdot-}$ is a process which is first-order in $Ph_2CN_2^{\cdot-}$. Much clearer evidence comes from the results in Table 3b in which the carbon acid diethyl malonate (DEM)

was present. The linearity of the relationship between E^P and log ν is now excellent and in good agreement with theoretical expectation, confirming the first-order form of the kinetics of the follow-up reaction. Moreover, E^P is unaffected by the presence of DEM showing that proton transfer is not an important reaction pathway for $Ph_2CN_2^{\cdot-}$ up to DEM concentrations of 20mM (5- to 20-fold excess over Ph_2CH_2). Since the pK_a value for DEM is ca. 12 units lower than that for the solvent (ca. 25),[25] DEM should be capable of competing successfully with the solvent in supplying protons despite its much lower concentration. We conclude therefore that proton abstraction is not an important route for the consumption of $Ph_2CN_2^{\cdot-}$ under our conditions.

The DPSC results in Table 4 confirm that in CH_3CN the reduction is first-order in $Ph_2CN_2^{\cdot-}$ with an average rate coefficient at 8 °C of 160 s⁻¹, essentially invariant over a four-fold range of Ph_2CN_2 concentrations. The large decrease in $k_{obs.}$ resulting from the change to CD_3CN as solvent makes it plain, however, that the solvent is chemically involved in the follow-up reaction and clearly rules out the possibility that a significant component of the disappearance of $Ph_2CN_2^{\cdot-}$ is unimolecular loss of nitrogen leading to the formation of the carbene radical anion. Since DEM has no effect on the consumption of $Ph_2CN_2^{\cdot-}$, the solvent must function as a hydrogen atom donor * and we conclude that the key step in the reaction under these conditions is (5), the product of which then gives rise to the observed products of the overall reaction, predominantly diphenylmethane at these concentrations.

$$Ph_2CN_2^{\cdot-} + CH_3CN \longrightarrow (Ph_2CN_2,H)^- + {}^{\cdot}CH_2CN \quad (5)$$
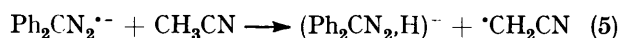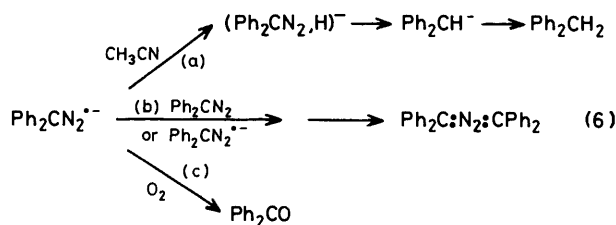
We leave open at this stage the question of whether the diazoalkane radical anion abstracts the hydrogen atom through its carbon or terminal nitrogen radical centre, giving either $Ph_2CHN:N^-$ or $Ph_2C:NNH^-$. We note, however, that the reaction is unusual; radical anions are well known for their basicity, but to the best of our knowledge this is the first properly characterised example of atom abstraction by such a species.

The magnitude of the kinetic deuterium isotope effect on the disappearance of $Ph_2CN_2^{\cdot-}$ is strongly suggestive of quantum mechanical tunnelling in the abstraction process. Tunnelling also manifests itself in non-linear Arrhenius behaviour for the undeuteriated reaction system, but this was not detected over the temperature range used in our studies. The quantum mechanical tunnelling aspect of the behaviour of $Ph_2CN_2^{\cdot-}$ merits more detailed examination (see also below) and this is in hand.

The large kinetic hydrogen isotope effect is also reflected in the reaction products (Table 8). Thus the change from CH_3CN to CD_3CN as solvent leads to a tenfold increase in the proportion of Ph_2CN_2 converted into

* Although the α-hydrogen atoms in dimethyl malonate are reported [30] to be three times more readily abstracted by phenyl radicals at 60 °C than those in CH_3CN, the ca. 1 000-fold greater concentration of the solvent means that it provides almost all the abstracted hydrogen.

benzophenone azine and a reduction in the yield of diphenylmethane and benzophenone. The azine yield is also increased by increasing the initial concentration of Ph_2CN_2. This pattern of behaviour is qualitatively consistent with the reaction scheme in (6) in which each

$$Ph_2CN_2^{\cdot-} \xrightarrow{\begin{array}{c}CH_3CN \\ (a)\end{array}} (Ph_2CN_2,H)^- \longrightarrow Ph_2CH^- \longrightarrow Ph_2CH_2$$
$$\xrightarrow[\text{or } Ph_2CN_2^{\cdot-}]{(b)\ Ph_2CN_2} \longrightarrow Ph_2C\text{:}N_2\text{:}CPh_2 \quad (6)$$
$$\xrightarrow[O_2]{(c)} Ph_2CO$$

of the three major products arises from a separate reaction pathway of $Ph_2CN_2^{\cdot-}$. On this basis, the ratio of diphenylmethane to azine (R) should be sensitive to isotopic substitution in the solvent and to the initial concentration of Ph_2CN_2. Indeed, $R(CH_3CN)/R$-(CD_3CN) is ca. 14 and a four-fold increase in $[Ph_2CN_2]$ causes $R(CH_3CN)$ to decrease by a factor of ca. 15.

Because of the complicating presence of benzophenone among the products and in the absence of a more detailed study, we do not wish to overemphasise the difference between the kinetic and product isotope effects. We do not therefore rule out the possibility that some azine arises by reaction of an intermediate on reaction path (6a) with Ph_2CN_2 or some benzophenone by reaction of Ph_2-CH^- with oxygen.[31] However, we believe that route (6) provides a qualitatively satisfactory interpretation of our observations. Route (6b) is analogous to the chain mechanisms previously discussed in relation to chemical and electrochemical reduction of 9-diazofluorene, but the preference of $Ph_2CN_2^{\cdot-}$ to abstract hydrogen from the solvent rather than to attack a second diazoalkane molecule ensures that the average chain length is very short, especially at low concentrations of Ph_2CN_2. The relative unimportance of azine formation in CH_3CN at $[Ph_2CN_2] < 5mM$ also results in close adherence of the kinetic results to a first-order kinetic law.

Electroreduction of Ph_2CN_2 in DMF and a Reassessment of the Work of McDonald and Hawley.—At sweep rates of 100 V s⁻¹, the reduction of Ph_2CN_2 at a mercury cathode in DMF containing tetra-alkylammonium ions is also quasi-reversible, but the peak separations in the cyclic voltammograms shown in Figures 2 and 3 point to a substantially lower heterogeneous charge-transfer rate than in acetonitrile as solvent. Again, tetramethyl-ammonium is the counter-ion which leads to the fastest charge transfer and tetra-n-butylammonium to the slowest. The LSV studies (Table 3c), however, show that even with Me_4N^+ the heterogeneous rate still has a large influence on the voltammetric response; although the relationship between E^P and log v is satisfactorily linear, the slope (42.4 mV decade⁻¹) is much too high.

Kinetic measurements by DPSC (Table 7) confirm that in DMF, as in CH_3CN, the disappearance of $Ph_2CN_2^{\cdot-}$ obeys a first-order kinetic law (2). The Arrhenius

parameters for the reaction in DMF (Me_4N^+) are both very different from the corresponding values in CH_3CN. They indicate that, at 25 °C, the rate coefficient for reaction of $Ph_2CN_2^{\cdot-}$ in CH_3CN is ca. 13.6 times greater than in DMF. Changing the counter-ion leads to a substantial change in the homogeneous rate coefficient in the sequence Me_4N^+ $< Pr^n_4N^+ < Et_4N^+ < Bu^n_4N^+$. Thus $Bu^n_4N^+$ has the opposite effect on the homogeneous and heterogeneous rate processes. Again, however, changing to the perdeuteriated solvent ($[^2H_7]DMF$) leads to a large rate reduction, the kinetic hydrogen isotope effect being close to 4, and this suggests that in DMF the slow step in the consumption of $Ph_2CN_2^{\cdot-}$ is again hydrogen-atom abstraction from the solvent. The magnitude of the isotope effect in this case gives no obvious indication of quantum mechanical tunnelling.

The activation parameters in DMF and CH_3CN cannot be allowed to pass without comment. Clearly, notwithstanding the difficulty of reproducing absolute values of rate constants from one solution to another, there is a remarkable difference in activation parameters in the two solvents which far exceeds experimental uncertainties. We can only speculate at this stage on the origin of the differences. Two possibilities suggest themselves.

(i) There is a difference in the chemistry of the hydrogen-abstraction process, such as direct abstraction in one solvent and pre-association followed by intracomplex reaction in the other.

(ii) Quantum mechanical tunnelling lowers the activation energy in CH_3CN sufficiently to account for the difference.

Although the rate of disappearance of $Ph_2CN_2^{\cdot-}$ in CD_3CN (where tunnelling is not very important) is quite similar to that in DMF under the same conditions, the activation parameters in CD_3CN and DMF are still widely different and possibility (ii) is ruled out. Theoretical predictions [32] suggest that direct hydrogen-atom abstraction from DMF should be fairly similar in activation energy to abstraction from CH_3CN. Thus the chemical difference in the abstraction processes seems the likeliest explanation at present. Further investigation is warranted, however.

Our conclusion from these experiments is clear and simple: in DMF, Ph_2CN_2 undergoes one-electron reduction and under the conditions of the kinetic studies the anion radical so produced abstracts a hydrogen atom from the solvent. This conclusion stands in sharp contrast to the interpretation which McDonald, Hawley, and their co-workers have placed upon their findings for the electroreduction of Ph_2CN_2 at a platinum cathode in DMF. Their view is that $Ph_2CN_2^{\cdot-}$ rapidly loses a molecule of nitrogen yielding the carbene anion radical $(Ph_2C\text{:})^{\cdot-}$ which by hydrogen-atom abstraction is converted into the key intermediate Ph_2CH^-. Attack by the carbanion on a second molecule of Ph_2CN_2 leads to chain decomposition involving benzophenone azine dianion, this route competing with protonation of the carbanion leading to diphenylmethane. Much of this explanation rests upon McDonald and Hawley's interpre-

tation of their cyclic voltammograms in terms of completely irreversible one-electron reduction of Ph_2CN_2 with a wave on the re-oxidation phase of the cycle corresponding only to Ph_2CH^-.

We believe that McDonald and Hawley's incorrect mechanistic conclusion stems from a misinterpretation of the voltammogram (Figure 1 of ref. 13a) for the reduction of Ph_2CN_2 in DMF ($Bu^n_4N^+$) at 50 V s^{-1} on a platinum cathode. The conditions of the experiment are just those that would lead to a large separation of peak potentials in cyclic voltammetry of quasi-reversible systems, and indeed larger than the 700 mV which we observed using a mercury electrode. Thus the wave attributed to oxidation of Ph_2CH^- is, we believe, merely due to the reoxidation of $Ph_2CN_2^{\cdot-}$ produced quasi-reversibly at these high sweep rates. Our kinetic evidence clearly indicates that in DMF $Ph_2CN_2^{\cdot-}$ decomposes much too slowly to be accommodated by McDonald and Hawley's mechanism.

The idea that reduction of Ph_2CN_2 is quasi-reversible at high voltage-sweep rates has some further consequences. From McDonald and Hawley's results it is possible to estimate an approximate reduction potential ($E^{rev.}$) for the diazo-compound as the voltage midway between the peak potentials on the reductive and oxidative phases of the cycle; * the value is ca. —0.9 V (versus Cd–Hg), almost identical with the first reduction potential of benzophenone azine. In consequence the electron-transfer equilibrium constant for (7) must be much larger than previously thought, although the electrocatalytic action of the azine is not correspondingly larger since it is evident from the present results that the subsequent disappearance of $Ph_2CN_2^{\cdot-}$ is much slower than had been surmised.

$$Ph_2CN_2 + Ph_2C\colon N_2\colon CPh_2^{\cdot-} \;\rightleftharpoons\; Ph_2CN_2^{\cdot-} + Ph_2C\colon N_2\colon CPh_2 \quad (7)$$
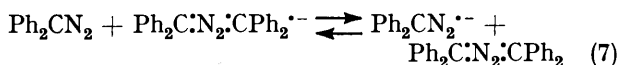
Much of the previous discussion of the mechanism of electroreduction of Ph_2CN_2 is invalidated when the correct interpretation is placed on the cyclic voltammogram of Ph_2CN_2 in DMF at high scan rates. Accordingly, we conclude that there is at present no evidence for the generation of carbene radical anions by reduction of diazoalkanes in solution.

EXPERIMENTAL

Diazodiphenylmethane was prepared and purified by a standard procedure.[33] The tetra-alkylammonium salts were of reagent grade and were used without further purification. Acetonitrile and DMF (Fluka,puriss.p.a.) were purified by passage through columns of neutral alumina immediately before use.

The cells, instrumentation, and measurement procedures for the kinetic studies were those recently reported.[22,34] Temperature control was by immersion of the cell in a large Dewar flask containing water at the appropriate tempera-

* This estimate assumes an electrochemical transfer coefficient, α, of 0.5.

ture. The electrodes were planar platinum surfaces electrolytically covered with mercury.

Product studies were carried out in a small divided cell. The working electrode was a platinum sheet (area 50 cm^2) formed into a cylinder and a constant current of 10 mA was maintained. Triphenylmethane was added to reaction mixtures to serve as the analytical standard. Product mixtures in acetonitrile were treated with a small excess of acetic acid to convert unchanged Ph_2CN_2 into Ph_2CHOAc and then poured into water. Extraction with CH_2Cl_2 yielded a mixture which was analysed by GLC (1 m column; 5% OV 17 on Celite; 60—300 °C).

APPENDIX

After submitting this paper, a note [35] appeared which strongly criticized our preliminary communication.[20] The essential point of the criticism is the claim that we have misinterpreted our voltammetry results and that the process described in Figure 1 of this paper is due to either specific adsorption or to the formation of organomercurials. In our opinion this criticism rests on a very weak basis. In the first place, the voltammogram (Figure 1) shows all the characteristics of a well behaved quasi-reversible system. The alternative interpretation requires a fast chemical process following charge transfer which results in a narrowing of the peak for the forward process, and, if surface interaction then takes place, this should result in deformation of the peak on the return scan. The latter is not observed. Secondly, the effect of sweep rate on the peak-potential separation over a 100-fold range (Table 1) gives an excellent fit to the theory for quasi-reversible charge transfer. It is highly improbable that both the forward peak and the reverse peak could be affected by either adsorption or chemical interaction with the electrode in such a way that the overall process fits the theory for quasi-reversible charge transfer. The additional voltammetry reported in this paper (Figures 2 and 3) are equally damaging to the criticism. The effect of supporting electrolyte cation is that expected for quasi-reversible reduction.[23] The smaller R_4N^+ give rise to enhanced rates of heterogeneous charge transfer and smaller peak separations during cyclic voltammetry. Of pertinent interest in this respect is that the forward and reverse peaks of the cyclic voltammograms (Figure 2) are affected nearly equally by the changes in supporting electrolyte cation. This can only be interpreted in terms of processes going on in solution having nothing to do with surface interaction. It seems that the evidence for quasi-reversible charge transfer during the reduction of Ph_2CN_2 is overwhelming.

It is also important to note that the criticism failed to mention our strongest mechanistic evidence, i.e. the large deuterium kinetic isotope effect. These data were derived from experiments using an independent technique, double potential-step chronoamperometry which does not depend upon either the rate of charge transfer or the voltammetric peak shape. The results using this technique were in complete accord with our interpretation of the cyclic voltammetry results which we considered more qualitative.[20]

Our LSV data obtained from measurements carried out in the presence of DEM were also criticized. The conditions under which the LSV peak potential was found to be independent of [DEM] were at [DEM] < 20mM. Yet, in criticizing our data [DEM] of 89mM was used. Our reason for restricting [DEM] to 20mM or less was that it does become kinetic-

ally involved at higher concentrations. Finally, we point out that different electrolytes (Me$_4$NPF$_6$) and temperatures (-37 °C) were used in the new voltammetry experiments.[35] Since the heterogeneous charge transfer becomes slower with decreasing temperature it is not surprising that the peak separation becomes greater at low temperatures. Experimentally, such a comparison must be made with great care due to the increasing importance of uncompensated resistance as the temperature is decreased.

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