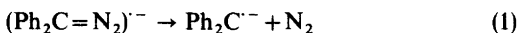


A Kinetic Characterization of the Reactions of Anion Radicals of Diazodiphenylmethane in Acetonitrile

VERNON D. PARKER^a and DONALD BETHELL^b

^a Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway and ^b The Robert Robinson Laboratories, The University, P.O. Box 147, Liverpool L69 3BX, England

Recent studies of the reduction of diazodiphenylmethane ($\text{Ph}_2\text{C}=\text{N}_2$) in *N,N*-dimethylformamide (DMF) have led to the suggestion that the anion radical rapidly evolves nitrogen to generate the carbene anion radical (eqn. 1).¹⁻³ Convincing evidence for the existence of the carbene anion



radicals in solution has not so far been presented. In fact, the cyclic voltammetric evidence which had been claimed¹ to indicate the presence of fluorenylidene anion radical was shown to be ambiguous,⁴ and subsequent kinetic studies have confirmed that the conclusion was incorrect.⁵ We now present preliminary results which indicate that in the absence of hydrogen atom and proton donors,

$(\text{Ph}_2\text{C}=\text{N}_2)^{\cdot -}$ is remarkably long-lived in solution. Thus, both heterogeneous and homogeneous kinetics studies could be conducted on the formation and reactions of $(\text{Ph}_2\text{C}=\text{N}_2)^{\cdot -}$ in acetonitrile.

Experiments in $\text{CD}_3\text{CN}-\text{Me}_4\text{NBF}_4$ (sat.) gave results incompatible with current views¹⁻³ on the ease of reaction (1). At a voltage sweep rate (ν) of 100 V s^{-1} , no reaction of the anion radical could be detected at 8°C . This is demonstrated by the voltammogram in Fig. 1 where the anion radical is generated at R and oxidized at O. The potential separation between peaks R and O was observed to be 208, 178, 142, 120 and 79.2 mV at ν of 100, 50, 20, 10 and 1 V s^{-1} , respectively. The heterogeneous rate constant calculated from the above data by the method of Nicholson⁶ was $0.041 \pm 0.003 \text{ cm s}^{-1}$. These data very convincingly show that O corresponds to the oxidation of $(\text{Ph}_2\text{C}=\text{N}_2)^{\cdot -}$ rather than of any other intermediate.

The low reactivity of $(\text{Ph}_2\text{C}=\text{N}_2)^{\cdot -}$ described above suggested that direct kinetic techniques could be used to study the homogeneous reactions of the anion radical. Double potential step chronoamperometric studies were carried out and the data were treated according to standard procedures.⁷ When the solvent was CH_3CN , the apparent first order rate constant at 8°C was of the order of 160 s^{-1} (Table 1) while the observed value in CD_3CN was

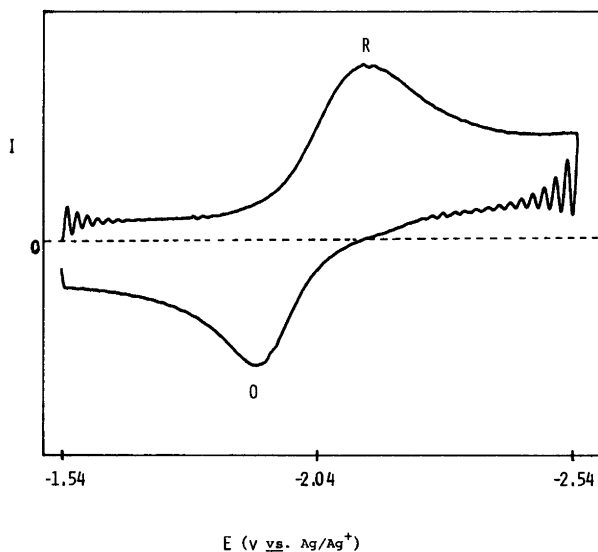


Fig. 1. Cyclic voltammogram for the reduction of diazodiphenylmethane in CD_3CN containing Me_4NBF_4 (sat.) at 8°C and 100 V s^{-1} .

Table 1. The rate of the reaction of diazodiphenylmethane anion radical generated in acetonitrile at a mercury electrode.^a

[Ph ₂ C=N ₂]/mM	Solvent	<i>t</i> _{1/2} ^b /ms	<i>k</i> _{app} /s ⁻¹
1.0	CH ₃ CN	2.27	181
2.0	CH ₃ CN	2.65	156
3.0	CH ₃ CN	2.82	146
4.0	CH ₃ CN	2.68	154
1.0	CD ₃ CN	78.6	5.3
2.0	CD ₃ CN	75.3	5.5

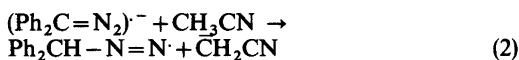
^a Measurements on solutions containing Me₄NBF₄ (sat.) at 8 °C. ^b The potential step time for the current ratio (*I*_b/*I*_r), normalized to the no reaction case, to equal 0.500. The data were treated according to Ref. 7.

5.4 s⁻¹ which indicates a deuterium kinetic isotope effect of about 30. This unusually large value is indicative of quantum mechanical tunnelling.⁸ In this respect, it is of interest to note that a value as great as 50 at -30 °C has been reported for the intramolecular hydrogen atom transfer during decomposition of tri-*tert*-butylphenyl radical.⁹

The data in Table 2 show that in spite of the fact that the voltammetric wave for the reduction of Ph₂C=N₂ is slightly broader than predicted by theory for a purely kinetic first order process, the LSV relationships¹⁰ hold. In CH₃CN with substrate concentrations ranging from 0.2 to 2.0 mM, d*E*^p/d log *v* was found to equal 31.1 ± 1.2 mV/decade and d*E*^p/d log *C*^c was observed to be 0.9 ± 1.3 mV/decade in good agreement with 29.6

and 0 mV/decade, respectively, for a rate determining first order reaction of the anion radical.¹⁰ In the presence of diethyl malonate (DEM), d*E*^p/d log *v* was found to be 29.2 ± 0.9 mV/decade and d*E*^p/d log *C*^x, where *C*^x refers to [DEM], was zero within experimental error. The latter indicates that the proton donor is not kinetically involved in the decomposition of the radical anions under the reaction conditions.

We considered three possible first order reactions as likely reaction routes for (Ph₂C=N₂)⁻. Reaction (1) involving the carbene anion radical was immediately rejected in view of the deuterium kinetic isotope effect which requires the C-H(D) bond to be broken during or before the rate determining step. Likewise, reaction (2) involving



rate determining proton transfer was eliminated on the basis of the LSV results (Table 2). Thus, the most likely rate determining step for the reaction in acetonitrile is the hydrogen atom transfer (3). The final products of the reaction, diphenylmethane and benzophenone azine could arise from reactions of Ph₂CH⁻ formed upon loss of N₂ from Ph₂CH-N=N⁻ or from competing second order reactions which are more likely under higher concentration preparative conditions.

The change in solvent electrolyte system from DMF-Bu₄NBF₄ to CH₃CN-Me₄NBF₄ obvi-

Table 2. Linear sweep voltammetric data for the reduction of Ph₂C=N₂.^a

<i>C</i> ^c /mM	[DEM] ^b /mM	- <i>E</i> ^p /mV (at <i>v</i> /V s ⁻¹)				d <i>E</i> ^p /d log <i>v</i> mV/decade
		0.100	0.200	0.400	1.000	
a. Sweep rate and concentration dependence						
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
b. Effect of a proton donor						
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

^a Measurements at an Hg electrode at 23 °C with Me₄NBF₄ (sat.) as electrolyte. The numbers in parentheses refer to the standard deviations in 5 measurements. Peak potentials are relative to a bias setting of -1.680 V vs. Ag/Ag⁺ in acetonitrile. It should be noted that the reduction process does not fulfill the requirements for purely kinetic waves, linear current potential analysis¹⁴ indicates a slope at 100 mV s⁻¹ of about 80 mV rather than 69 mV for a purely kinetic wave.

ously had a profound effect on both the heterogeneous and homogeneous kinetics during the reduction of $\text{Ph}_2\text{C}=\text{N}_2$. The former effect is most likely due to the presence of the small tetraalkylammonium ion which has been observed to significantly increase the rates of some reductions.^{11,12} On the other hand, the homogeneous reactions are probably moderated by ion association with the smaller cation as well as by the solvent change since DMF is an order of magnitude better hydrogen atom donor than CH_3CN .¹³ As far as we know, this is the first demonstration of hydrogen atom abstraction by an anion radical, intermediates well known for their basicity.

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