

Δc are small compared to c_{av} as seen in Figure 6B.

The amplitude is defined

$$\text{amplitude} = c_{\max}/c_{\min}$$

$$\text{amplitude} = (c_{av} + \Delta c_{\max})/(c_{av} - \Delta c_{\max}) = (1 + \Delta c_{\max}/c_{av})/(1 - \Delta c_{\max}/c_{av})$$

If $\Delta c_{\max} \ll c_{av}$, then

$$\text{amplitude} \sim (1 + \Delta c_{\max}/c_{av})^2$$

$$\ln(\text{amplitude}) = 2 \ln(1 + \Delta c_{\max}/c_{av}) \sim 2\Delta c_{\max}/c_{av} = 2\Delta c_0 e^{\alpha t}/c_{av}$$

or

$$\ln(\ln(\text{amplitude})) = \ln(2\Delta c_0/c_{av}) + \alpha t$$

i.e., $\ln(\ln(\text{amplitude}))$ will rise linearly with time.

Moreover, the plot of $\ln c$ vs time will rise exponentially with small oscillations:

$$\begin{aligned} \ln c &= \ln(c_{av} + \Delta c_0 \sin \omega t e^{\alpha t}) \\ &= \ln(c_{av}) + \ln(1 + \Delta c_0 \sin \omega t e^{\alpha t}/c_{av}) \\ &\sim \ln(c_{av}) + \Delta c_0 \sin \omega t e^{\alpha t}/c_{av} \end{aligned}$$

i.e., the plot of $\ln c$ vs time will rise exponentially with small oscillations with period $2\pi/\omega$ and this is exactly what is seen in Figure 6B. One should note that all the logarithmic figures are plotted on a base 10 scale.

Spectroscopic and Kinetic Characterization of Diphenyldiazomethane Radical Anion

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Diphenyldiazomethane radical anion ($\text{Ph}_2\text{CN}_2^{\cdot-}$) has been generated by radiolytic reduction of diphenyldiazomethane (Ph_2CN_2) in both protic and aprotic solvents. The absolute kinetics of formation and reactivity of $\text{Ph}_2\text{CN}_2^{\cdot-}$ were obtained by monitoring its transient absorption ($\lambda_{\max} = 355\text{--}370$ nm) following nanosecond pulse radiolysis. In isopropyl alcohol, reaction of the solvated electron with Ph_2CN_2 forms $\text{Ph}_2\text{CN}_2^{\cdot-}$ ($\lambda_{\max} = 355$ nm), which subsequently protonates to form $\text{Ph}_2\text{CN}_2\text{H}$, as detected by a sharp absorption band at 330 nm. In aprotic solvents and in the absence of added quenchers, $\text{Ph}_2\text{CN}_2^{\cdot-}$ decays primarily by pseudo-first-order reaction with Ph_2CN_2 . With added weak organic acids protonation of $\text{Ph}_2\text{CN}_2^{\cdot-}$ also occurs. $\text{Ph}_2\text{CN}_2^{\cdot-}$ reacts with molecular oxygen with a near diffusion-controlled rate; however, it demonstrates no reactivity toward hydrogen atom donors, and no evidence of thermal loss of N_2 to produce diphenylcarbene radical anion was observed.

Introduction

Over the past decade there has been considerable interest in generating radical ions of diazo compounds. This is primarily due to their potential as precursors to the exotic carbene radical ion species.¹ Early work focused on the electrochemical reduction of aryldiazomethanes in aprotic solvents.² Of particular interest was the fate of the diphenyldiazomethane radical anion ($\text{Ph}_2\text{CN}_2^{\cdot-}$) generated by one-electron reduction of diphenyldiazomethane (Ph_2CN_2). Initially, there was considerable debate as to whether $\text{Ph}_2\text{CN}_2^{\cdot-}$ was sufficiently long lived to undergo chemical reactivity or if $\text{Ph}_2\text{CN}_2^{\cdot-}$ rapidly extruded N_2 to form the diphenylcarbene radical anion ($\text{Ph}_2\text{C}^{\cdot-}$). McDonald and Hawley³ initially concluded that the unimolecular reaction of $\text{Ph}_2\text{CN}_2^{\cdot-}$ was too fast to be studied by cyclic voltammetry, and the only reaction competitive with loss of N_2 was protonation in the presence of good proton donors. Meanwhile, Bethell and Parker⁴ contended that loss of N_2 was unimportant and that $\text{Ph}_2\text{CN}_2^{\cdot-}$ reacted primarily by hydrogen atom abstraction from solvent with some competitive reactivity with the parent diazo compound and molecular oxygen. Ultimately, it was determined that unimolecular loss of N_2 was not facile in diaryldiazomethane radical anions,^{1a,5} and kinetic

study of these reactive intermediates was possible. Unfortunately, the nature of electrochemical experiments precludes study in the absence of electrolytes, and interference by electrolyte counterions on diazo radical ion kinetics is well documented.^{1a,4} Furthermore, obtaining truly homogeneous kinetics by conventional electrochemical means is difficult at best.

The goal of the present study is to clarify past discrepancies and obtain meaningful kinetic and mechanistic information on diazo radical anion reactivity in homogeneous solution. Therefore, pulse radiolysis has been chosen to rapidly generate $\text{Ph}_2\text{CN}_2^{\cdot-}$, and time-resolved optical detection has been used to monitor the absolute reactivity of $\text{Ph}_2\text{CN}_2^{\cdot-}$ in both protic and aprotic solution.

Experimental Section

Pulse Radiolysis. The pulse radiolysis experiments were performed using a 10-ns pulse of 8-MeV electrons from the Notre Dame Radiation Laboratory linear accelerator. The LINAC pulse radiolysis apparatus has previously been described in detail.⁶ The doses used were ~ 500 rd/pulse as determined by thiocyanate dosimetry. Solutions were flowed through a 1-cm path length cylindrical Suprasil cell at a rate of 3–5 mL/min from a solution reservoir connected by either BEV-A-LINE (Cole-Parmer) or glass tubing. Unless stated otherwise, solutions were deoxygenated by bubbling with high-purity nitrogen continuously throughout the experiment. All experiments were performed at 21 ± 1 °C.

Materials. Diphenyldiazomethane was prepared by treatment of benzophenone tosylhydrazone with tetramethylguanidine according to a previously described procedure⁷ and purified by

(1) See, for example: (a) Bethell, D.; Parker, V. D. *Acc. Chem. Res.* **1988**, *21*, 400. (b) McDonald, R. N.; Gung, W. Y. *J. Am. Chem. Soc.* **1987**, *109*, 7328. (c) Parker, V. D.; Bethell, D. *J. Am. Chem. Soc.* **1987**, *109*, 5066.

(2) For a comprehensive account of this field of research, see ref 1a and references therein.

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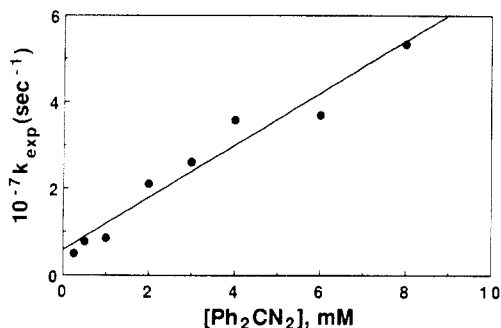


Figure 1. Plot of k_{exp} vs $[\text{Ph}_2\text{CN}_2]$ obtained by monitoring the e_{sol}^- at 700 nm in isopropyl alcohol.

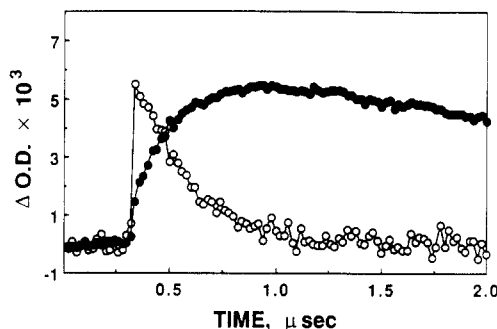


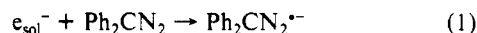
Figure 2. Time-resolved absorption traces monitored at 700 (O) and 370 nm (●) after pulse radiolysis of 5×10^{-4} M Ph_2CN_2 in isopropyl alcohol.

vacuum sublimation at room temperature. The following solvents and substrates were used as received: acetonitrile (Aldrich, spectrophotometric grade); methanol, isopropyl alcohol, and cyclohexane (Fisher, spectroanalyzed grade); ethanol (Midwest Grain Products, absolute); 2,2,2-trifluoroethanol (Aldrich, Gold Label); diethyl malonate (Aldrich). *N,N*-Dimethylformamide (DMF, Fisher) was passed through alumina prior to use.

Results

There are several organic solvents that act as excellent reducing media following ionizing radiation. It has been clearly established, for instance, that irradiation of aliphatic alcohols⁸ or acetonitrile⁹ containing certain aromatic solutes results in formation of aromatic radical anions. This occurs either by direct electron attachment to the aromatic solute or by subsequent reaction with a solvent-derived reducing species.

Reduction in Isopropyl Alcohol. Pulse radiolysis of N_2 -saturated isopropyl alcohol results in the familiar broad absorption spectrum ($\lambda_{\text{max}} = 820$ nm)⁸ of the solvated electron (e_{sol}^-). The G value for e_{sol}^- , i.e., the chemical yield/100 eV is 1.0.⁸ A pseudo-first-order reaction of e_{sol}^- with Ph_2CN_2 was readily observed by monitoring the increase in decay rate of e_{sol}^- at 700 nm with added Ph_2CN_2 .



An absolute bimolecular rate constant, k_1 , of $(6.0 \pm 0.5) \times 10^9$ $\text{M}^{-1} \text{s}^{-1}$ for reaction 1 was obtained from the dependence (eq 2)

$$k_{\text{exp}} = k_0 + k_1[\text{Ph}_2\text{CN}_2] \quad (2)$$

of the rate of decay of e_{sol}^- , k_{exp} , on the Ph_2CN_2 concentration (see Figure 1), where k_0 represents the decay of e_{sol}^- in the absence of Ph_2CN_2 . With addition of Ph_2CN_2 a transient species was also observed to be formed at 370 nm with pseudo-first-order growth kinetics that were kinetically correlated to the decay of e_{sol}^- (see Figure 2). A bimolecular rate constant of $(5.9 \pm 0.6) \times 10^9$ M^{-1}

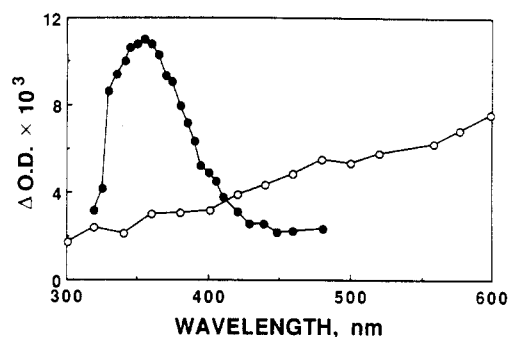


Figure 3. UV-visible spectra observed 200 ns after pulse radiolysis of isopropyl alcohol (O) and isopropyl alcohol containing 1.18×10^{-3} M Ph_2CN_2 (●).

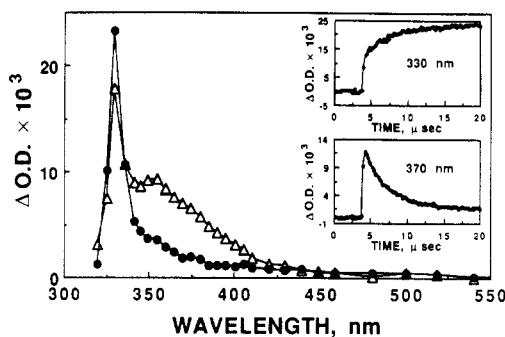


Figure 4. Time-resolved absorption spectrum observed 2 (Δ) and 10 μs (●) after pulse radiolysis of 1.18×10^{-3} M Ph_2CN_2 in isopropyl alcohol. Inserts demonstrate the time dependence observed at 330 (top) and 370 nm (bottom).

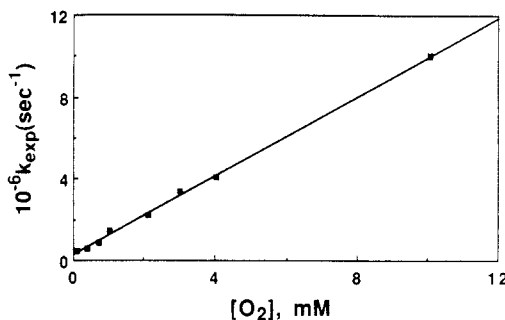
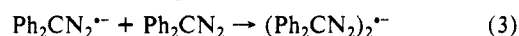


Figure 5. Plot of k_{exp} vs $[\text{O}_2]$ obtained by monitoring at 370 nm after pulse radiolysis of 1.18×10^{-3} M Ph_2CN_2 in isopropyl alcohol.

s^{-1} measured at 370 nm for the generation of this species coincides with the bimolecular rate constant for the reaction of e_{sol}^- with Ph_2CN_2 and demonstrates direct electron attachment to form $\text{Ph}_2\text{CN}_2^{\bullet -}$.

The absorption spectrum of e_{sol}^- (Figure 3) was replaced by one consisting primarily of $\text{Ph}_2\text{CN}_2^{\bullet -}$ ($\lambda_{\text{max}} = 355$ nm; bandwidth (fwhm) = 60 nm) 200 ns after pulse radiolysis of isopropyl alcohol containing 1.18×10^{-3} M Ph_2CN_2 (see Figure 3). The absorption monitored at 370 nm was found to decay with first-order kinetics, even at the lowest concentration (5×10^{-5} M) of Ph_2CN_2 needed to observe this band under the conditions described. The rate of decay of $\text{Ph}_2\text{CN}_2^{\bullet -}$ was dramatically dependent on Ph_2CN_2 concentration and a bimolecular rate constant, k_3 , of $(5.0 \pm 0.5) \times 10^7$ $\text{M}^{-1} \text{s}^{-1}$ was determined for solutions of Ph_2CN_2 ranging from 5×10^{-5} to 1×10^{-2} M. No new absorption was observed between 300 and 750 nm that could be correlated with Ph_2CN_2 concentration, i.e., as a consequence of reaction 3. A secondary



product is observed, however, after pulse radiolysis of the 1.18×10^{-3} M solution of Ph_2CN_2 in isopropyl alcohol at longer times, e.g., 2 and 10 μs (Figure 4). The overlapping sharp absorption band ($\lambda_{\text{max}} = 330$ nm) is formed at the expense of $\text{Ph}_2\text{CN}_2^{\bullet -}$ (see inserts, Figure 4).

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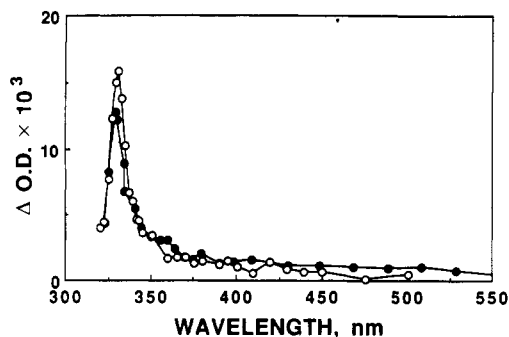


Figure 6. Absorption spectra observed 400 ns after pulse radiolysis of 1.12×10^{-3} and 1.09×10^{-3} M Ph_2CN_2 in ethanol (●) and methanol (○), respectively.

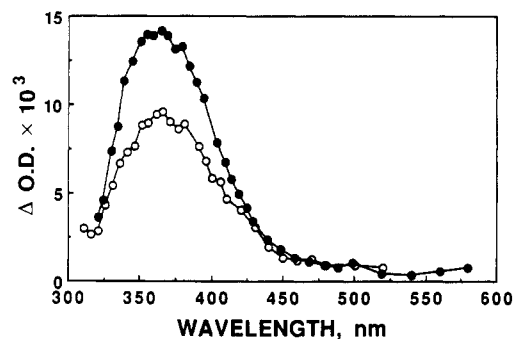
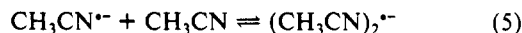
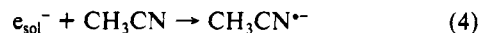


Figure 7. UV-visible absorption spectra observed 400 ns after pulse radiolysis of 3.0×10^{-4} and 3.1×10^{-4} M Ph_2CN_2 in CH_3CN (●) and DMF (○), respectively.

The 355-nm transient reacted rapidly with molecular oxygen and interrupted formation of the 330-nm secondary absorption. Degassing with various O_2/N_2 mixtures resulted in a bimolecular quenching plot (Figure 5) and a rate constant of $(9.65 \pm 0.15) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of $\text{Ph}_2\text{CN}_2^{\bullet-}$ with O_2 .

Reduction in Ethanol and Methanol. The reductive nature of irradiated ethanol and methanol are well-known, yielding G values for e_{sol}^- of 1.7¹⁰ and 1.1,¹¹ respectively. Pulse radiolysis of thoroughly degassed ethanol and methanol containing 1.12×10^{-3} and 1.09×10^{-3} M Ph_2CN_2 completely "quenched" the absorption of e_{sol}^- and yielded absorption spectra having sharp maxima at 330 nm, 400 ns after the irradiation pulse (see Figure 6).

Reduction in Acetonitrile. Liquid acetonitrile has also proven to be an excellent reducing medium following pulse radiolysis. An equilibrium between monomeric and dimeric solvent derived reductive species (reactions 4 and 5) is believed to be responsible



for the resultant reducing G value of 1.03.⁹ Pulse radiolysis of N_2 -saturated "dry" acetonitrile containing 3.01×10^{-4} M Ph_2CN_2 resulted in an absorption spectrum (Figure 7) nearly identical with that observed at 200 ns in isopropyl alcohol ($\lambda_{\text{max}} = 370$ nm; bandwidth (fwhm) = 70 nm). Although there was no direct detection of the reductive species of reaction 4 and 5, the absolute rate of reduction of Ph_2CN_2 in acetonitrile was obtained ($3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) by monitoring the rate of growth of $\text{Ph}_2\text{CN}_2^{\bullet-}$ at 370 nm with varying Ph_2CN_2 concentrations (1×10^{-4} – 1×10^{-2} M). As in isopropyl alcohol, the lifetime of $\text{Ph}_2\text{CN}_2^{\bullet-}$ is dependent on Ph_2CN_2 concentration and a bimolecular rate constant of $(2.6 \pm 0.1) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ was measured in acetonitrile. Again no additional absorptions were observed as a result of this reaction.

In dramatic contrast to the results in the aliphatic alcohols, the time-resolved absorption spectrum observed after pulse radiolysis

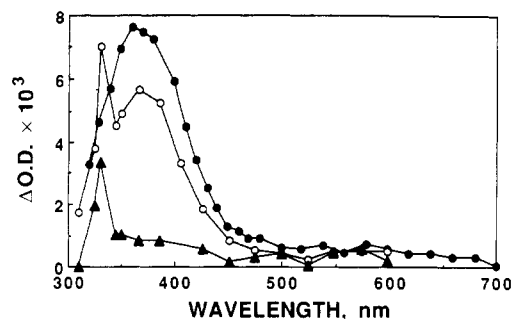


Figure 8. Time-resolved absorption spectrum observed 1 (●), 4 (○), and 80 μs (▲) after pulse radiolysis of 8×10^{-4} M Ph_2CN_2 in CH_3CN containing 1×10^{-2} M DEM.

of Ph_2CN_2 in acetonitrile changes only with time, i.e., no secondary products are observed. A nearly identical spectrum was also observed (Figure 7) after pulse radiolysis of 3.1×10^{-4} M Ph_2CN_2 in DMF, that is, there was no 330-nm band or other secondary absorptions.

A comparison of the pseudo-first-order rates of decay of $\text{Ph}_2\text{CN}_2^{\bullet-}$ in 5×10^{-3} M Ph_2CN_2 solutions of acetonitrile and isopropyl alcohol, 1.9×10^5 and $1.8 \times 10^7 \text{ s}^{-1}$, respectively, demonstrates the inert nature of $\text{Ph}_2\text{CN}_2^{\bullet-}$ toward acetonitrile. Therefore, acetonitrile was chosen as the primary solvent to investigate the absolute reactivities of $\text{Ph}_2\text{CN}_2^{\bullet-}$.

Reactivity of $\text{Ph}_2\text{CN}_2^{\bullet-}$ in Acetonitrile. In addition to the reactivity toward the parent diazo compound, $\text{Ph}_2\text{CN}_2^{\bullet-}$ reacted rapidly with oxygen. A bimolecular rate constant of $(3.6 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was obtained in acetonitrile, and again no oxygen derived products were observed.

No reactivity, i.e., $< 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, was observed for the reaction of $\text{Ph}_2\text{CN}_2^{\bullet-}$ with hydrogen-atom donors. No changes in the rate of decay of $\text{Ph}_2\text{CN}_2^{\bullet-}$ was observed at 370 nm with added aliphatic hydrocarbons, even in acetonitrile solutions containing up to 1 M cyclohexane, i.e., a saturated solution.

$\text{Ph}_2\text{CN}_2^{\bullet-}$ was, however, found to react with proton donors. Addition of the weak proton-donor diethyl malonate (DEM) quenched the 370-nm absorption with a bimolecular rate constant of $1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. As DEM was added, a secondary transient absorption was observed to "grow-in" at 330 nm. A time-resolved absorption spectrum (see Figure 8) observed after pulse radiolysis of acetonitrile with 8×10^{-4} M Ph_2CN_2 and 1×10^{-2} M DEM demonstrates the formation of the product band.

$\text{Ph}_2\text{CN}_2^{\bullet-}$ also reacted with 2,2,2-trifluoroethanol with a bimolecular rate constant of $3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ with formation of the same 330-nm absorption band.

Discussion

Evidence against Carbene Formation. An initial concern of using pulse radiolysis to generate $\text{Ph}_2\text{CN}_2^{\bullet-}$ was the potential of instigating unimolecular decomposition of diazo to form diphenylcarbene (Ph_2C). However, the evidence is overwhelming against this possibility:

(i) There was no evidence of destruction of the diazo moiety after the irradiation pulse in any solvent, under all conditions studied. This is in contrast to laser flash photolysis (LFP) studies,¹² where bleaching of the diazo band is readily observed.

(ii) The absorption of ground-state triplet Ph_2C was not observed. It is well documented that LFP of Ph_2CN_2 in solution yields the characteristic absorption spectra of Ph_2C : (315 nm) and subsequently diphenylmethyl radical (334 nm).¹² Additionally, the inability of Ph_2C to form nitrile yields¹³ rules out the possibility of the diphenylcarbene acetonitrile ylide for the 370-nm band in acetonitrile.

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(iii) Even if small amounts of $\text{Ph}_2\text{C}^\cdot$ were generated, this would be detected by the strong absorption ($\lambda_{\text{max}} = 410 \text{ nm}$) of the diphenylcarbonyl oxide,^{12b} formed at near diffusion control ($5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) with O_2 . No such absorption was observed even in O_2 -saturated solutions.

(iv) In aliphatic alcohols, $\text{Ph}_2\text{C}^\cdot$ inserts into the O-H bond to form the corresponding ethers at rates far too fast to allow competitive formation of carbene-derived products in neat alcohols, e.g., $\text{Ph}_2\text{C}^\cdot$ reacts with methanol and isopropyl alcohol at 2.4×10^7 and $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$,¹⁴ respectively.

Formation and Reactivity of $\text{Ph}_2\text{CN}_2^{\cdot-}$. One of the benefits of using nanosecond time-resolved pulse radiolysis to study diazo radical anions is the ability to directly monitor the formation and reactivity of the species of interest. By direct observation of the reaction of e_{sol}^- with diazo to form $\text{Ph}_2\text{CN}_2^{\cdot-}$ there is little doubt that the kinetically correlated growth at 370 nm in isopropyl alcohol is due to direct electron attachment of e_{sol}^- to Ph_2CN_2 . Although the reducing species were not directly detected in all of the solvents studied, the similarity of the absorption bands ($\lambda_{\text{max}} = 355\text{--}370 \text{ nm}$) and the chemical reactivity observed ensures that $\text{Ph}_2\text{CN}_2^{\cdot-}$ is initially formed in each solvent.

In the absence of efficient quenchers, such as O_2 , the primary reaction pathway of $\text{Ph}_2\text{CN}_2^{\cdot-}$ decay is by reaction with Ph_2CN_2 . It is not surprising, therefore, that the cyclic voltammetric anodic wave for the oxidation of $\text{Ph}_2\text{CN}_2^{\cdot-}$ was never observed³ (vide supra), considering the magnitude of k_3 ($\sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$). The lifetime of $\text{Ph}_2\text{CN}_2^{\cdot-}$ in millimolar solutions of diazo compound is approximately 1–10 μs , whereas electrochemical detection, as described,^{1a,3–5} would require a lifetime of at least 0.1 ms.¹⁵

The near diffusion-controlled reaction rate of $\text{Ph}_2\text{CN}_2^{\cdot-}$ with O_2 combined with the lack of detection of an O_2 -incorporated intermediate strongly suggests that an electron-transfer mechanism, as presented in reaction 6, occurs. There was, however, no



detection of superoxide ($\text{O}_2^{\cdot-}$), $\lambda_{\text{max}} = 245 \text{ nm}$,¹⁶ due to the absorption of the diazo precursor below 300 nm. Evidence of such a mechanism has been reported,¹⁷ although, for the reaction of 9-diazofluorene radical anions, generated by γ -irradiation of 9-diazofluorene in 3:2:1 v/v water:isopropyl alcohol:acetone, with O_2 . Under these conditions, no loss of diazo compound was observed following irradiation in the presence of O_2 , as opposed to 65% loss in N_2 -saturated solution. This demonstrated a mechanism for regeneration of diazo compound after formation of the corresponding radical anion.

Protonation of $\text{Ph}_2\text{CN}_2^{\cdot-}$. Clearly, in the aliphatic alcohols studied, the transient at 330 nm is formed from the reaction of $\text{Ph}_2\text{CN}_2^{\cdot-}$. Furthermore, its formation in acetonitrile occurring *only* as a consequence of the addition of proton donors confirms that the 330-nm absorption is due to the protonated form of $\text{Ph}_2\text{CN}_2^{\cdot-}$. There is precedence for these observations. It has been

demonstrated^{8a,18} that arene radical anions radiolytically generated in neutral aliphatic alcohols react by direct proton transfer from the alcohol. Similar to the present study, the arene radical anion formation was kinetically correlated with the e_{sol}^- decay and subsequently led to the growth of the free radical formed by protonation. Furthermore, as in the present study, methanol and ethanol were found to react more efficiently than isopropyl alcohol. For example, the radical anion of biphenyl reacted with bimolecular rate constants^{8a} of 0.55×10^4 , 2.6×10^4 , and $6.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ with isopropyl alcohol, ethanol, and methanol, respectively.

The similarity of the sharp absorption spectrum of the 330-nm band with the spectrum of diphenylmethyl radical (334 nm) indicates protonation of $\text{Ph}_2\text{CN}_2^{\cdot-}$ occurs on the terminal nitrogen to form $\text{Ph}_2\text{CN}_2\text{H}$. Protonation of the 9-diazofluorene radical anion (vide supra) also gave a resultant radical absorption spectrum ($\lambda_{\text{max}} = 510 \text{ nm}$, shoulder = 480 nm) that dramatically resembled fluorenyl radical.¹⁷

Product Studies. The groups of Bethell and Parker and McDonald and co-workers have both used product analysis of the one-electron reduction of Ph_2CN_2 under various conditions to decipher the reaction mechanisms involved. Although these results are enlightening, one must remain cautious when dealing with a system where a multitude of reaction pathways exist that may lead to the same products or very similar product ratios. Overall, however, the reactivities reported support the absolute kinetics observed in this work.

For instance, up to 85% of the products observed upon preparative electrolysis of Ph_2CN_2 in DMF or acetonitrile are due to diphenylmethane (Ph_2CH_2) and benzophenone azine ($\text{Ph}_2\text{CN}_2\text{CPh}_2$) with minor amounts of $\text{Ph}_2\text{C}=\text{NNH}$, Ph_2CO , and $\text{Ph}_2\text{CHNHN}=\text{CPh}_2$.^{3,4} Under the most inert conditions, azine is the major product and is increased with increased concentrations of Ph_2CN_2 . A dramatic increase in Ph_2CH_2 and $\text{Ph}_2\text{C}=\text{NNH}_2$ was observed in the presence of diethyl malonate or trifluoroethanol, and analysis of the $\text{Ph}_2\text{CH}_2/\text{Ph}_2\text{C}=\text{NNH}_2$ ratio demonstrated that protonation of $\text{Ph}_2\text{CN}_2^{\cdot-}$ occurred exclusively on the terminal nitrogen.^{3c}

Conclusion

The radiolytic reduction of Ph_2CN_2 in suitable organic solvents to form $\text{Ph}_2\text{CN}_2^{\cdot-}$ has allowed for a direct kinetic study of this intermediate without the interfering effects observed in electrochemical studies. The use of nanosecond pulse radiolysis also allows for the differentiation between the reactivity of primary and secondary intermediates. In an inert homogeneous solution $\text{Ph}_2\text{CN}_2^{\cdot-}$ preferentially reacts with the diazo precursor, ultimately producing benzophenone azine. In the presence of proton donors, $\text{Ph}_2\text{CN}_2^{\cdot-}$ will protonate with all indications of terminal protonation. Contrary to previous reports, $\text{Ph}_2\text{CN}_2^{\cdot-}$ shows no evidence of undergoing hydrogen-atom abstraction reactions⁴ or unimolecular loss of N_2 .³

The use of this and similar methods are currently being employed to investigate other diazo systems.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Contribution No. NDRL-3277 from the Notre Dame Radiation Laboratory.

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