A complementary low-temperature matrix isolation study of this system is underway. In addition further studies are planned with the objectives of determining the effect of various substituents on the reaction mechanism and of testing the predictions of Woodward and Hoffmann[14] with respect to the stereospecificity of the thermal and photochemical ring-opening and ring-closing processes.

The One-Electron Oxidation of Triplet Diphenyl-*p*-phenylenediamine by the Diimine[1]

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Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts. *Received March 31, 1967*

Abstract: The reversible photochemical conversion of N,N′-diphenyl-*p*-phenylenediamine to its semiquinone positive ion has been studied in acidified EPA, using flash photolysis, over a range of temperatures and concentrations of added diphenyl-*p*-phenylenediimine. It is shown by direct observation of all three species that the radical ion is formed primarily by reaction of the amine triplet with imine. The kinetics of the reaction suggest the possible intermediate formation of a complex between triplet amine and imine. Rate constants and activation energies are also given for the dismutation reaction of the radical ion. The question of "direct" photoionization of the amine is discussed.

The redox couple N,N′-diphenyl-*p*-phenylenediamine (DPPD) and the corresponding diimine constitutes a convenient system for the study of reversible photoredox phenomena. The two forms of the couple are readily interconvertible, and the intermediate semiquinone (positive ion) is sufficiently stable so that it may be independently characterized and followed during reaction. In previous work on this system it was demonstrated that the semiquinone ion could be obtained either by reversible photoxidation of the amine or photoreduction of the imine.[3] A kinetic study of this and related systems is now being made, using flash methods. In this paper we describe a new reaction between the triplet state of the diamine and unexcited diimine, leading to the semiquinone ion.

Experimental Section

1. Materials. Eastman DPPD was treated with Norit-A in benzene or ethanol and recrystallized several times from these solvents. The diimine was prepared by chromic acid oxidation of DPPD in glacial acetic acid[4] and recrystallized several times from ethanol and petroleum ether. The product was further purified by chromatography on silica gel, using benzene–ethyl acetate (2:5) as eluent. Isopentane (Phillips or Eastman) was washed with cold concentrated H_2SO_4 and $NaHCO_3$ solutions, stored over Drierite, and distilled from sodium. Ether was purified by distillation either from sodium or $LiAlH_4$. Ethanol was refluxed over CaO and distilled and redistilled from sodium. Acetic acid was Fisher, A.R. grade. EPA solvent was the ether–isopentane–alcohol mixture, in 8:3:5 volume ratio. A slightly acidified EPA, containing 3.5% glacial acetic acid, was much used in this work and is denoted here as EPAG.

For convenience in the following discussion, we use the notation diamine = RH_2, diimine = R, semiquinone positive ion = RH_2^+.

2. Extinction Coefficients of R, RH_2, and RH_2^+. The absorption spectra of R, RH_2, and RH_2^+ are shown in Figure 1. The molar decadic extinction coefficients of R and RH_2 in EPA or ethanol were found at their respective absorption peaks to be $\epsilon^{R}_{450} = 7.4 \times 10^3$ and $\epsilon^{RH_2}_{307} = 2.40 \times 10^4$. These values agree with previous results of Church[5] to within 2%. The semiquinone positive ion, RH_2^+, was prepared as before, by mixing ethanol or EPA solutions of amine and imine and acidifying with acetic acid.[3] To determine the extinction coefficient of RH_2^+, the reaction was carried out *in vacuo*, in an ampoule carrying suitable side arms for the spectrophotometer absorption cell and for degassing the three reagent solutions on the vacuum line before mixing.[6] The precision of this method is limited by the presence of oxidizing or reducing impurities in the solutions of R and RH_2, by uncertainties in the extent of conversion (the spectra of R and RH_2^+ overlap at 450 mμ), and by the instability of the radical. The most reproducible data were obtained using very large molar ratios (100 to 200) of RH_2/R, working at high acidities (EPA/acetic acid ratio = 1), and correcting for radical formation in blanks containing no imine. In 50% acetic acid–EPA, at these high amine–imine ratios, the reaction is essentially complete.[3] The molar decadic extinction coefficient found for RH_2^+ at 710 mμ is $\epsilon^{RH_2^+}_{710} = 1.10 \times 10^4$, with an estimated accuracy of ±10%. This is somewhat smaller than the value 1.37×10^4 given earlier.[3]

Since our flash work was carried out in EPA containing 3% acetic acid (EPAG) instead of the 50% solution used for the extinction coefficient calibration, attempts were made to obtain $\epsilon(RH_2^+)$ in more dilute acid media. However, even with 25% acid, conversion to the radical ion was quite incomplete and the intended extrapolation of $\epsilon(RH_2^+)$ to the 3.5% mixture could not be achieved. Nevertheless, the band shapes and relative peak heights of the RH_2^+ spectrum, obtained photochemically (see below), were essentially the same in EPAG as in 50% acetic acid–EPA and did not change detectably with temperature. The semiquinone extinction coefficients were therefore taken to be independent of medium and temperature variation, over the range used here. Table I summarizes the values of the extinction coefficients of DPPD, the diimine, and radical ion at convenient wavelengths.

3. Preparation of Samples and Flash Technique. Test solutions were degassed on the vacuum line by freeze–thaw cycles with vigorous agitation[7] and were sealed off under "sticking vacuum" in an

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[1] This work was supported by a grant from the U. S. Atomic Energy Commission to Brandeis University (Grant No. AT(30-1)-2003).

[2] NATO Fellow, 1964–1965 (from Laboratoire de Chimie Physique, Faculté des Sciences, Paris).

[3] H. Linschitz, J. Rennert, and T. M. Korn, *J. Am. Chem. Soc.*, **76**, 5839 (1954).

[4] J. Picard, *Ber.*, **46**, 1853 (1913).

[5] S. E. Church, Ph.D. Thesis, Syracuse University, 1957.

[6] We wish to thank Mr. Wilmon Willen-Bryan for assistance with these experiments.

[7] H. Linschitz, C. Steel, and J. A. Bell, *J. Phys. Chem.*, **66**, 2574 (1962).

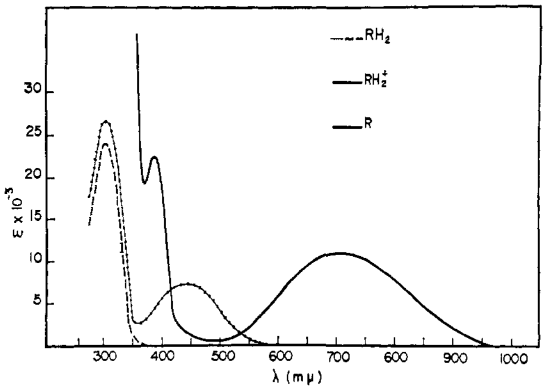

Figure 1. Absorption spectra: diphenyl-*p*-phenylenediamine in ethanol (dashed line); diphenyl-*p*-phenylenediimine in ethanol (dotted line); semiquinone positive ion in 50% EPA-acetic acid (solid line).

ampoule assembly carrying a 5-cm flash irradiation cell (quartz) and a 1-cm cell for absorption spectra measurements (Cary Model 14). The flash apparatus and procedure were essentially those previously described,[7,8] except that the four lamps were made of quartz capillary (5-mm i.d., 5.5 cm between electrodes), terminated with quartz standard-taper joints, and filled with oxygen[9] at about 10 mm pressure. The electrodes were tungsten or stainless steel, mounted in tapered stainless steel plugs, which were waxed into the ground joints. The lamps were mounted accurately at the outer foci of a four-leaved elliptical reflector.[8] The photolysis cell was placed axially at the central focus in a flat-bottomed unsilvered quartz dewar, through which was passed a controlled flow of cold nitrogen, obtained from a heating coil immersed in liquid nitrogen. Temperatures were measured by a thermocouple placed in the dewar close to the photolysis cell and could be held constant to better than ±0.3° over the available range, from room temperature down to −160°. A square holder, mounted around the dewar, permitted light filters to be interposed between the flash lamps and the photolysis cell. Corning 9863 filters were generally used, which greatly diminished scattered light corrections from the flash in the 400–700-mμ region. The monochromator was a Bausch & Lomb 500-mm grating instrument, and the measuring light source was a battery-operated strip filament tungsten lamp.

Table I. Molar Decadic Extinction Coefficients

Substance	λ, mμ	$\epsilon \times 10^{-4}$
DPPD (RH_2)	307	2.40
Diimine (R)	450	0.74
	390	0.46
DPPD$^+$ (RH_2^+)	390	2.20
	450	0.12
	600	0.65
	710	1.10
	750	1.00

4. **Phosphorescence Measurements.** The flash apparatus was converted to measurement of phosphorescence decay simply by closing the measuring lamp shutter and opening the monochromator slits to 5 mm. Even at our working sample-to-monochromator distance of about 100 cm, enough phosphorescence intensity was available at the photocell to provide good decay curves, at sample temperatures (DPPD) below −140° (see Figure 2G below). Use of the identical sample and experimental configuration to measure both transient absorption and emission permits particularly convenient and accurate kinetic comparisons to be made. In absorption measurements, the slits were always so narrow (1 mm) that sample luminescence introduced negligible errors.

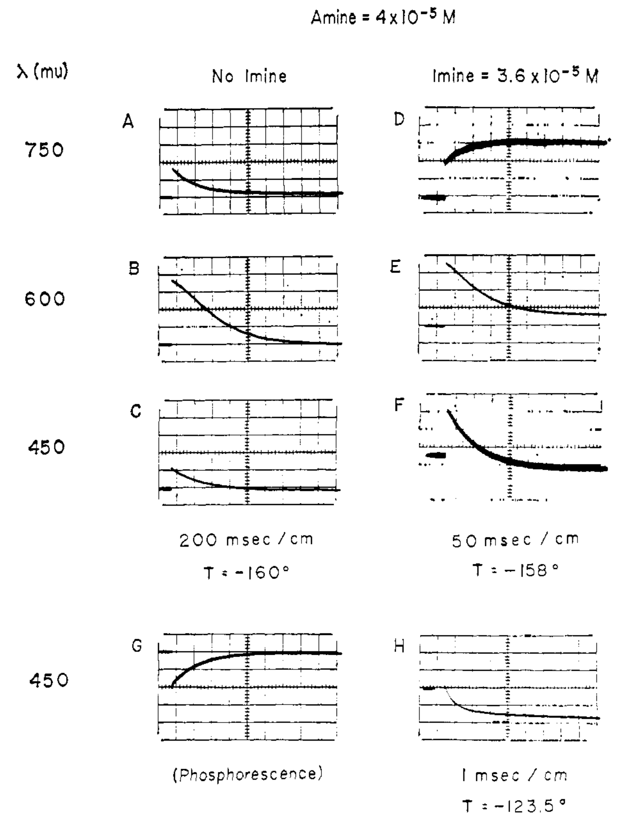

Figure 2. Typical flash oscillograms of solutions of DPPD in EPAG (4 × 10^{-5} *M*) containing no added imine (A–C, G) and with 3.6 × 10^{-5} *M* added imine (D–F, H); absorption changes at 750 (A, D), 600 (B, E), and 450 mμ (C, F, H); phosphorescence at 450 mμ (G); A–C, G: −160°, sweep = 200 msec/cm; D–F: −158°, sweep = 50 msec/cm; H: −123.5°, sweep = 1 msec/cm; gain = 1 v/cm except for H, which is 2 v/cm; V_0 (A, D, F, H) = 6 v; V_0 (B, C, E) = 4 v; cell length = 5 cm.

Results

1. **General Behavior of DPPD Solutions. Formation of Triplets and Radical Ions.** Aerated solutions of the amine in EPA are rather unstable, developing the yellow color of the imine (450-mμ band) after standing for a few hours. Degassed solutions are stable in the dark but are slowly oxidized to the imine upon exposure to ultraviolet light. Addition of small amounts of acid to the EPA prevents this irreversible photoxidation. For example, a 4 × 10^{-5} *M* solution of DPPD in EPA is about 10% converted to imine under our experimental conditions after 40 (~200 joules) flashes, while a similar solution in the acidified solvent, EPAG, shows no measurable imine formation (<1% conversion) after 60 flashes. To avoid accumulation of imine and ensuing complications (see below), flash studies on "pure" DPPD solutions were therefore made in EPAG.

Figure 2A–C shows some typical oscillograms obtained on flashing such amine solutions at −160°. The immediate result of flashing is an increase in absorption throughout the visible, with a transient peak at 610 mμ. Most of this absorption disappears rapidly, leaving a trace of long-lived intermediate (Figure 2A), which then decays much more slowly, back to the original base line. Figure 3 shows typical difference spectra (referred to the original solution) of a DPPD solution, immediately after flashing (A) and at the completion of the fast decay process (B). It is evident that

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[8] H. Linschitz and K. Sarkanen, *J. Am. Chem. Soc.*, **80**, 4826 (1958).

[9] S. Claesson and L. Lindqvist, *Arkiv Kemi*, **11**, 535 (1957).

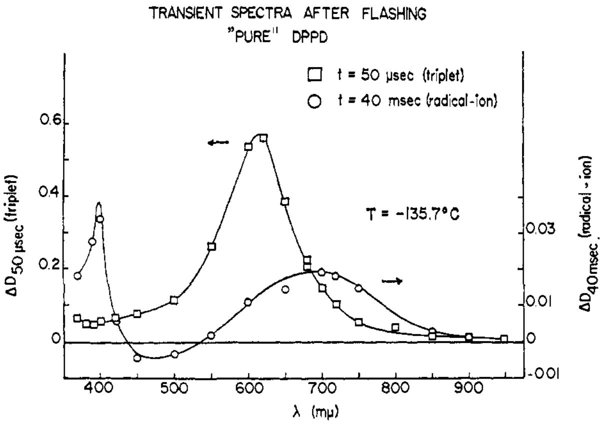

Figure 3. Spectral changes following flash excitation of "pure" DPPD (4×10^{-5} *M*) in EPAG: □, 50 μsec after flash (left-hand scale); ○, 40 msec after flash (right-hand scale); −135.7°; cell length, 5 cm. Note lack of 390-mμ peak in initial flash spectrum and slight bleaching at 450 mμ in long-lived transient.

the two decay periods correspond to two different intermediates.

At temperatures below −140°, DPPD solutions in EPAG emit a blue phosphorescence (maximum near 450 mμ), detectable in the flash apparatus. The decay of this phosphorescence corresponds precisely to the decay of the transient absorption peak at 610 mμ (Figure 2G and 2A–C) at all temperatures studied (Figure 5, below). We therefore assign the main short-lived 610-mμ transient to the triplet state of DPPD.

The second (long-lived) transient, which appears in very much smaller amount, has absorption maxima at 390 and 710 mμ, with peak heights in the ratio 2:1. Comparison of Figure 3B with Figure 1C shows the close similarity of the transient spectrum to that of RH_2^+, as prepared by either chemical or photochemical oxidation of RH_2,[3] and immediately identifies the long-lived intermediate as the semiquinone positive ion.

2. Flash Photolysis of Pure Imine Solutions. At room temperature, flashing degassed solutions of imine in EPAG causes an immediate drop at the 450-mμ band and a stoichiometrically equivalent (1:1) rise at the radical-ion peaks at 390 and 710 mμ. The semiquinone fades by second-order kinetics, but no imine regeneration is observed. The first product of the irreversible photobleaching reaction, or at least a major product, is the amine. This is indicated by the gradual appearance, after a few flashes, of the amine triplet band at 610 mμ, as well as increased yields of RH_2^+ (see below). Moreover, the irreversible absorption drop at 450 mμ is not accompanied by a corresponding decrease at the 307-mμ imine band, suggesting that the development of the overlapping amine band compensates for the disappearance of imine absorption in this region.

As the temperature is lowered, the extent of transient radical formation and equivalent irreversible bleaching of imine in EPAG decrease, so that below −145° no absorbance change on flashing is observed anywhere in the available spectral region. In the absence of acidic solvent components, the yields of irreversible bleaching are extremely small, even at room temperature. Thus, in ether–isopentane, neither transient changes nor irreversible bleaching can be detected in flashed imine solutions in the whole range from room temperature down to −145°.

3. Flash Photolysis of Mixed Amine–Imine Solutions at Low Temperature. Flash excitation of mixed amine–imine solutions in EPAG causes some irreversible bleaching of the imine. This bleaching diminishes as the temperature is lowered and becomes negligible below −110°. Both the extent of imine bleaching and its temperature dependence are similar to that observed in pure imine solutions, and we attribute this, as before, to direct photoreduction of imine, quite independent of any specific amine participation. In this section, we confine our discussion to phenomena observed in the low-temperature range (below −120°) in which complications due to irreversible side reactions play no role.

In mixed amine–imine solutions, flashing produces the same two transients that are observed with "pure" amine, $^3RH_2$ and RH_2^+, but the detailed pattern of the changes is altered. The initial result of flashing is, again, a broad transient absorption, peaking at 610 mμ (Figure 2D–F), and assigned to the triplet. Allowing approximately for inner filter effects due to overlapping amine–imine absorption, the triplet yield is about the same as in solutions containing amine alone. However, the radical-ion band at 390 mμ is now found to develop strongly as the triplet decays. That the enhanced 390-mμ band is indeed due to radical-ion formation is shown by a corresponding rise near 710 mμ, although this is somewhat obscured by the overlapping 610-mμ triplet absorption. However, the far-red growing-in is easily seen at wavelengths beyond 730 mμ, as in Figure 2D. Finally, the absorbance decay at 610 and development at 390 and 750 mμ is accompanied by a bleaching near 450 mμ, the absorption peak of the imine (Figure 2F,H). These data alone do not indicate whether the observed bleaching at 450 mμ, which increases with imine concentration, results from an *initial* bleaching of imine, simultaneous with triplet formation and masked by the overlapping triplet absorption, or is due to imine disappearance *accompanying* the triplet decay. The question is resolved by measurements of the ratio of *initial* absorbance changes at 610 and 450 mμ. The data of Table II show that this ratio, $[\Delta D(610)/\Delta D(450)]_{t=0}$, is 7.0 ± 0.5 in "pure" amine solution and remains constant, independent of the concentration of added imine. Thus, the initial flash difference spectrum is constant, and the bleaching at 450 mμ must result from processes occurring *after* the flash. This conclusion is in agreement with the absence of any observable phototransients in pure imine solutions at low temperatures.

Figure 4 shows typical difference spectra of a mixed amine–imine EPAG solution, immediately after flashing and at a time corresponding to completion of the 610-mμ decay or the 390- or 750-mμ development. Comparison of Figures 1, 3, and 4, together with the remarks above, indicates that we are observing a reaction between amine triplet and imine, to form the semiquinone positive ion

$$^3RH_2 + R + 2H^+ \longrightarrow 2RH_2^+ \qquad \text{(I)}$$

the two protons being contributed by the solvent.[3]

This interpretation is unequivocally established by the kinetics and magnitudes of the observed spectral changes. Table II and Figure 5 show that the (pseudo-first-order, see below) rates of absorbance decay at 600

Table II. Absorbance Changes in Flashed DPPD–Imine Solutions, and Kinetics of Triplet Decay[a]

Imine $\times 10^5$, M	Temp, °C	$\Delta D(^3RH_2)$[b] 600 mμ	$\Delta D(^3RH_2)$[b] 450 mμ	$\Delta D(RH_2^+)$[c] 390 mμ	$\Delta D(RH_2^+)$[c] 600 mμ	Rate constant, k', sec^{-1} 600 mμ	Rate constant, k', sec^{-1} 450 mμ	Rate constant, k', sec^{-1} 390 mμ	Rate constant, k', sec^{-1} Phosphorescence	$\Delta D_{600}/\Delta D_{450}$ ($t = 0$)
<0.1	−135.7	0.537	0.076	0.036	0.009	210	218			7.1
...	−151	1.0	0.133	0.056	0.013	21	27			7.5
...	−159.3	0.854	0.127			2.5	2.8			6.7
...[d,e]	−160	1.15	0.162	0.013[g]	0.005	3.1	3.6	3.6[g]	3.6	7.1
...[d,f]	−133	1.8		0.01	0.007	535				
0.4	−152	0.770			0.022	30				
0.54	−135.5	0.480		0.100	0.027	830	1050			
0.95	−147	0.890	0.130	0.264	0.070	170	205	212		6.8
1.5	−149	0.430		0.178	0.042	110				
1.5	−158	0.377		0.144	0.034	18.4		18.9		
1.9	−156	0.490	0.070	0.229	0.064	33	30	41		7.0
2.56	−111	0.512		0.320	0.094	8000	7600	10,100		
2.8	−155.5					36.7				
2.8	−153.3					65				
2.8	−138.9					1050				
3.6	−158					35.5	34	34.5[g]	34	
5.3	−152	0.210	0.034	0.112	0.029	230		230		6.2
6.3	−153.6	0.270		0.162	0.042	170		170		
6.3	−155	0.280		0.159	0.042	140		160		
6.3	−156.4	0.377		0.222	0.057	96		125		
6.3	−149	0.376			0.065	530				
6.3	−143.2	0.342		0.200	0.059	1540				
6.3	−138.5	0.376			0.065	3450				

[a] Path length, 5 cm; DPPD = 4×10^{-5} M. [b] Measured at $t = 0$; variation is due mainly to different flash energies (200–800 joules). [c] Measured at completion of initial fast decay (600 mμ). [d] Freshly distilled EPA. [e] DPPD freshly recrystallized six times from ethanol. [f] DPPD = 7×10^{-5} M, flash energy = 800 joules. [g] Measured at 750 mμ.

mμ (disappearance of $^3RH_2$), phosphorescence decay at 450 mμ ($^3RH_2$), bleaching at 450 mμ (disappearance of R), and growing-in at 390 and 750 mμ (formation of RH_2^+) are all precisely the same, and vary with imine concentration in the same way. The stoichiometric ratio of imine bleaching to radical formation may also be obtained from the flash data, using the extinction coefficients of Table I. In Table III, which summarizes some typical results, the ΔD's refer to absorbance changes measured at the completion of the triplet decay or development of the radical-ion bands. Since the lifetime of the radical is very much longer than that of the triplet at these temperatures (seconds compared with milliseconds), the ΔD's may be experimentally determined with good precision. However, the values of the concentration ratios, $\Delta[RH_2^+]/\Delta[R]$, will reflect errors in the extinction coefficients as well as variations in the intensity of successive flashes required to obtain the ΔD's at different wavelengths. The data of Table III thus demonstrate with acceptable accuracy that two radical ions are formed per imine reacted, in accord with reaction I.

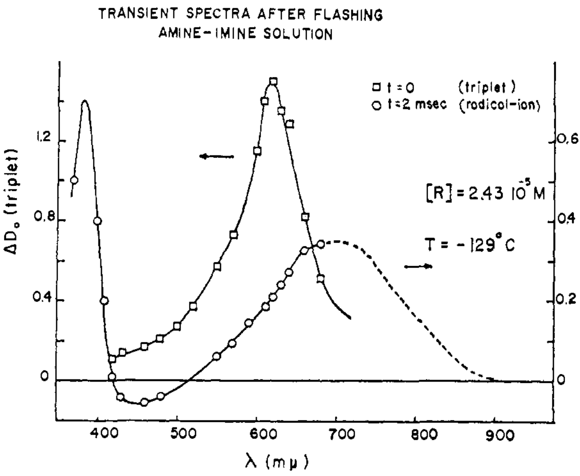

Figure 4. Spectral changes following flash excitation of DPPD (4×10^{-5} M) with added imine (2.4×10^{-5} M) in EPAG solution: □, immediately after flash (left-hand scale); ○, 2 msec after flash (right-hand scale); −129°; 5-cm cell.

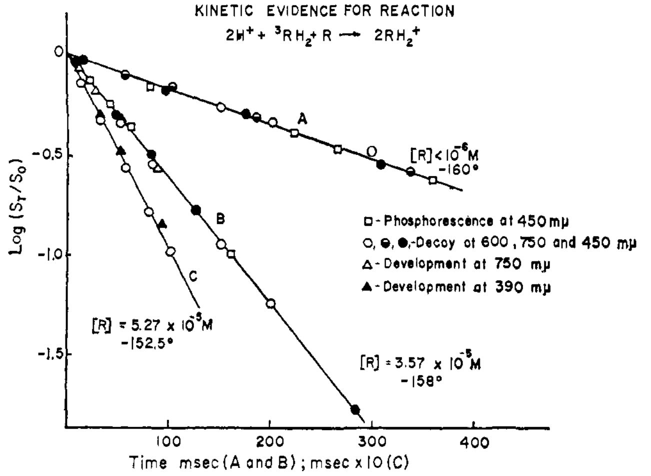

Figure 5. Kinetics of processes following flashing DPPD (4×10^{-5} M) in EPAG solution; upper line (A) no added imine, −160°; middle line (B), imine = 3.57×10^{-5} M, −158°; lower line (C), imine = 5.27×10^{-5} M, −152.5°. Absorbance decay at 600 (○), 750 (⊖), and 450 mμ (●); absorbance development at 750 (△) and 390 mμ (▲); □, phosphorescence at 450 mμ; S_0 = reading immediately after flash; S_t = reading at time t after flash.

The possibility that excited imine is involved in the oxidation of $^3RH_2$ may be ruled out for two reasons. First, the lack of *any* visible absorbance change on flashing pure imine solutions at low temperatures in-

Table III. Long-Lived Flash Transient Absorbance Changes and Stoichiometry of Amine–Imine Reaction[a]

Temp, °C	Imine, R × 10^5 *M*	ΔD_{390}	ΔD_{600}	ΔD_{710}	$-\Delta D_{450}$	$\Delta[RH_2^+]/\Delta[R]$ at λ[b] 390 mμ	600 mμ	710 mμ
−154	1.89	0.244	0.064		0.032	1.96	1.67	
−129	2.43	0.520	0.155		0.060	2.12	1.99	
−111	2.56	0.320	0.094		0.036	2.15	2.01	
−158	3.65		0.118		0.046		1.98	
−99	3.92			1.18	0.292			1.88
−99	6.75			0.85	0.214			1.86
−105	6.75			1.30	0.260			2.18
−116	6.75			1.40	0.323			1.98
−122	6.75			1.40	0.323			1.98

[a] DPPD concentration = 4 × 10^{-5} *M*. [b] To correct for overlapping R and RH_2^+ absorption at 450 and 390 mμ; this is calculated from the formula $\Delta D_\lambda/\Delta D_{450} = [x\epsilon(RH_2^+)_\lambda - \epsilon(R)_\lambda]/[x\epsilon(RH_2^+)_{450} - \epsilon(R)_{450}]$, where $x = \Delta[RH_2^+]/\Delta[R]$ and the ε's are given in Table I (note: ΔD_{450} is negative).

dicates that the deactivation of excited imine is very rapid, compared to the time required for radical-ion formation. Second, the data of Figure 5 and Table III refer to observations on the 450-mμ absorption band of *ground*-state imine, whose reaction is thus directly observed.

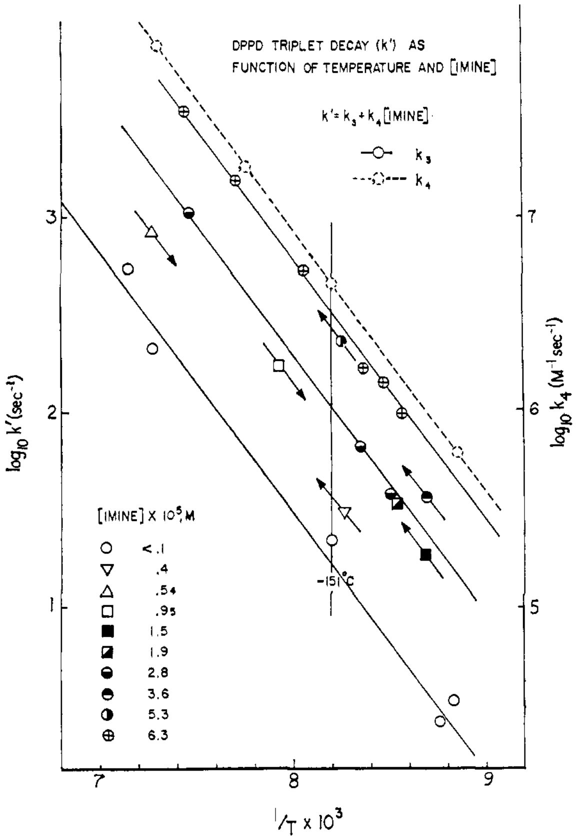

Figure 6. DPPD triplet decay (measured at 600 mμ) as a function of temperature and imine concentration: solid lines, log *k'* (left-hand scale); dotted line, log k_4 (right-hand scale); [R] as indicated.

4. Kinetics and Evaluation of Rate Constants for Triplet Amine–Imine Reaction. We write the following sequence, representing the steps in the photochemical amine–imine reaction at low temperature (−100 to 160°) in weakly acidic media

$$RH_2 \underset{k_1}{\overset{h\nu}{\rightleftarrows}} {}^1RH_2^* \tag{1}$$

$$^1RH_2^* \xrightarrow{k_2} {}^3RH_2^* \tag{2}$$

$$^3RH_2 \xrightarrow{k_3} RH_2 \tag{3}$$

$$2H^+ + {}^3RH_2 + R \xrightarrow{k_4} 2RH_2^+ \tag{4}$$

$$2RH_2^+ \xrightarrow{k_5} R + RH_2 + 2H^+ \tag{5}$$

$$2RH_2^+ \xrightarrow{k_6} \text{products} \tag{6}$$

The triplet–imine redox reaction (k_4) is slow compared to the competing triplet decay (k_3), and relatively high concentrations of imine must be used to obtain good conversion of $^3RH_2$ to RH_2^+. The fractional conversion of imine to radical ion is correspondingly small. For example, the data of Table II show that at the flash energies and DPPD concentrations used here, and at imine concentrations of 1 × 10^{-5} *M*, only about 15% of the imine reacts to form the semiquinone ion. At higher imine concentrations, the fraction converted is even less. Under these circumstances, the decay of $^3RH_2$ and formation of RH_2^+ becomes pseudo first order, as shown in Figure 5, with an effective rate constant $k' = k_3 + k_4[R]$. The constant, k_4, is most simply and directly determined from the variation of *k'* with imine concentration.

A large number of experiments are summarized in Figure 6, which plots log *k'* (Figure 5) *vs.* T^{-1} for various imine concentrations. Figure 6 shows that within experimental error the temperature coefficient of *k'* is independent of imine concentration over the entire range of triplet decay, from practically complete transition to the amine ground state to almost complete scavenging by the imine and conversion to the radical ion. This striking result requires that k_3 and k_4 have the same activation energy, which is found from Figure 6 to be 6200 ± 200 cal/mole. Since it is experimentally very inconvenient, with our cooling technique, to adjust the temperature precisely to a given setting for a large number of determinations, these results were used to correct the experimental *k'* values at measured temperatures to nearby standard temperatures, at which the effect of varying the imine concentration could then be isolated. The resulting plots of *k'* (corrected) *vs.* [R] are reasonably linear, as indicated by Figure 7, which gives a value of k_4 = 4.5 × 10^6 M^{-1} sec^{-1} at −151°. From the slopes of such lines we obtain the values of

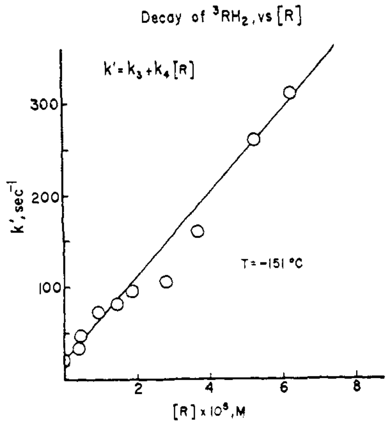

Figure 7. Effective first-order rate constant, k', as function of imine concentration, [R]; data from Figure 6, corrected to −151°.

k_4 shown by the upper (dotted) line of Figure 6 (right-hand scale). In the interval from −100 to −160°, k_3 and k_4 are given by

$$k_3 = 1.35 \times 10^{12} \exp(-6200/RT) \text{ sec}^{-1}$$

$$k_4 = 4.5 \times 10^{17} \exp(-6200/RT)\ M^{-1} \text{ sec}^{-1}$$

In addition to the kinetic determinations of the rate constants k_3 and k_4, as summarized in Figures 6 and 7, the ratio k_3/k_4 and the triplet extinction coefficient may be obtained from measurements of the relative triplet and semiquinone yields, as function of imine concentration. According to the above reaction scheme, the quantum yield of semiquinone, $\varphi(RH_2^+)$ is

$$\varphi(RH_2^+) = 2\varphi(^3RH_2)\left(\frac{k_4[^3RH_2][R]}{k_3[^3RH_2] + k_4[^3RH_2][R]}\right) \quad (7)$$

or

$$\frac{\varphi(^3RH_2)}{\varphi(RH_2^+)} = \frac{1}{2}\left(1 + \frac{k_3}{k_4[R]}\right) \quad (8)$$

Since the triplet and semiquinone are *both* formed as a result of the *same* light flash, the ratio of φ's is also the ratio of the corresponding chemical yields. At wavelengths where only the imine has overlapping absorption, eq 8 may then be written, in terms of the directly observed absorbance changes, as

$$\frac{\Delta D_{\lambda(t=0)}}{\Delta D_{\lambda'(\max)}} = \frac{\epsilon(^3RH_2)_\lambda}{[2\epsilon(RH_2^+) - \epsilon(R)]_{\lambda'}}\left(1 + \frac{k_3}{k_4[R]}\right) \quad (9)$$

in which $\Delta D_{t=0}$ is measured immediately after the flash and $\Delta D_{\max}$ is the long-lived absorption at the completion of triplet decay.

In Figure 8, we plot the absorbance ratios against imine concentration, using measurements at 600 mμ for both $\Delta D_{t=0}$ and $\Delta D_{\max}$ and 390 mμ for $\Delta D_{\max}$ (Table II). Data at all temperatures are included, since k_3/k_4 has been shown to be temperature independent. The limiting value of the absorbance ratio with increasing [R] corresponds to complete trapping and conversion of $^3RH_2$ to RH_2^+. From this limiting ratio (~0.60) and the data of Table I, we obtain for the molar decadic extinction coefficient of the amine triplet at 600 mμ the value $\epsilon = (6.7 \pm 1.5) \times 10^4$.

The application of eq 9 to our results is shown in Figure 9. The solid line in Figure 9 is calculated from the kinetic measurements at −151° (Figures 6 and 7), taking $k_3 = 16.5$ sec^{-1}, $k_4 = 4.5 \times 10^6\ M^{-1}$ sec^{-1}, and $\epsilon_{600}(^3RH_2) = 6.7 \times 10^4$, while the dotted line is drawn to fit the yield data. The agreement is certainly within the experimental spread, for the points at high imine concentration. At very low [R], there appears to be a tendency for the experimental points to deviate upward from the calculated line.

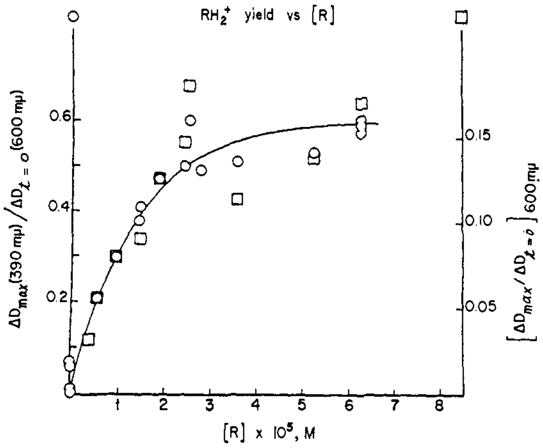

Figure 8. (Radical–ion/triplet amine) ratio, as function of imine concentration: ○, [ΔD(390, long-lived)/ΔD(600, t = 0)], left-hand scale; □, [ΔD(600, long-lived)/ΔD(600, t = 0)], right-hand scale; points at all temperatures (−110 to −160°).

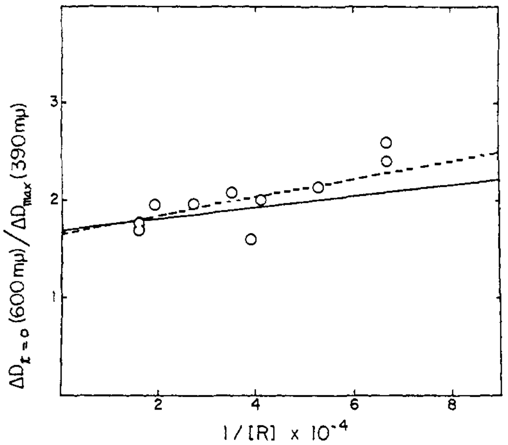

Figure 9. [ΔD(600 mμ, t = 0)/ΔD(390 mμ, long-lived)] *vs.* $[R]^{-1} \times 10^{-4}$; data of Figure 8: solid line, calculated from eq 9, using k_3 and k_4 from rate measurements (Figures 5–7) and extinction coefficients from Table I and Figure 8; dotted line, from yield data.

5. Kinetics of Semiquinone Decay. The final process observed following flashing of DPPD–imine solutions is the decay of the long-lived transient bands at 390 and 710 mμ and, at a corresponding rate, recovery of absorption at 450 mμ. Since the degree of irreversibility per flash is small, and the ratio of imine reacted to radical ion formed has been shown to be 1:2 (Table III), the final recovery process must be the dismutative back-reaction (step 5, above)

$$2RH_2^+ \xrightarrow{k_5} R + RH_2 + 2H^+$$

Direct confirmatory measurements of the extent of recovery of amine are difficult, because of the overlapping R, RH_2, and RH_2^+ spectra.

The kinetics of the recovery process are second order, as shown by linear plots of $(\Delta D_\lambda)^{-1}$ *vs.* time, for mea-

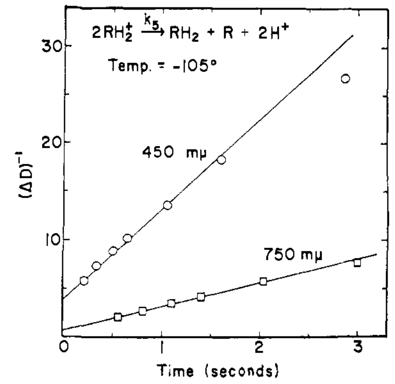

Figure 10. Second-order kinetics (k_5) of radical-ion decay, ΔD^{-1} *vs.* time: ○, 450 mμ; □, 750 mμ; $-105°$.

surements at both 450 and 710 mμ (Figure 10). Defining the rate constant by

$$-\frac{d[RH_2^+]}{dt} = k_5[RH_2^+]^2 = 2\frac{d[R]}{dt}$$

k_5 is obtained from the slope, m, of the $(\Delta D_{750})^{-1}$ *vs.* time plot as $k_5 = m/\epsilon_{750}(RH_2^+)$, where l is the cell path length (5 cm). At 450 mμ, again taking account of the stoichiometry and overlapping radical and imine absorption, we have $k_5 = ml[\epsilon(RH_2^+) - {}^1/_2\epsilon(R)]_{450}$.

The kinetic results are summarized in Table IV. The recovery rate constants measured at 710 or 750 mμ are in good agreement with those obtained at 450 mμ, particularly in view of the sensitivity of the latter values to errors in the extinction coefficients. In the temperature range -90 to $-135°$, $k_5 = 3.6 \times 10^{10} \exp(-4200/RT)$ M^{-1} sec^{-1} (Figure 11). The rate of radical-ion decay appears to be sensitive to catalytic impurities. In early experiments, using less carefully purified materials, several-fold higher rates were observed, with somewhat higher activation energies as well.

Table IV. Kinetics of Radical-Ion Decay and Imine Recovery

Temp, °C	Imine $\times 10^5$, M	$k_5 \times 10^{-5}$ M^{-1} sec^{-1} 710 mμ	450 mμ
−99	3.9		2.2
−99	6.75	1.80[a]	1.93
−105	6.75	1.21[a]	1.23
−115.5	3.9	0.70	0.75
−116	6.75	0.61	0.81
−121	6.75	0.44	0.64
−123	3.9	0.29	0.28
−130	6.75	0.15	0.15
−131	3.9	0.12	

[a] At 750 mμ.

Discussion

1. Evidence for Complex Mechanism in Triplet Amine–Imine Reaction. While the stoichiometry and formal kinetic scheme of the triplet amine–imine reaction seem to be well established by the results reported here, the experimental bimolecular rate constant, $k_4 = 4.5 \times 10^{17} \exp(-6200/RT)$ M^{-1} sec^{-1}, evidently demands further discussion. Allowing even several times the maximum error in the activation energy of Figure 6, and computing the corresponding smallest possible value of the preexponential factor of k_4, one still obtains a result which is orders of magnitude greater than any reasonable encounter number. Consideration must also be given to the proton transfers involved in the reaction. Thus, a complex mechanism is indicated.

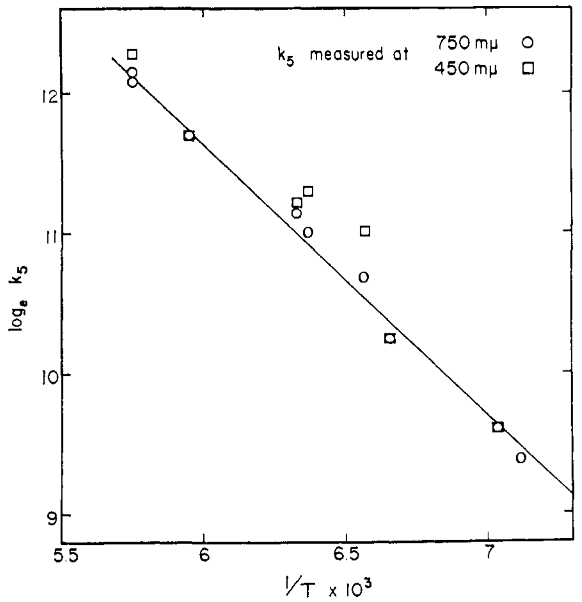

Figure 11. Ln k_5 *vs.* $T^{-1} \times 10^3$: ○, measured at 710 and 750 mμ; □, measured at 450 mμ. The line favors results which we believe to be most reliable.

A simple possibility is the formation of an equilibrated reaction intermediate between $^3RH_2$ and R, which could then decompose to $2RH_2^+$. Protonation might occur either in the formation or decomposition of the complex. Assuming the latter, we have

$$^3RH_2 + R \underset{k_B}{\overset{k_A}{\rightleftharpoons}} (^3RH_2 \cdot R)$$

$$(^3RH_2 \cdot R) \xrightarrow[k_C]{H^+} 2RH_2^+$$

The rate constant k_4 then becomes $k_4 = k_Ak_C/k_B$ and $E_4 = E_C + E_A - E_B$. This formulation is attractive since the electron transfer within the complex might be promoted by the very charge-resonance or transfer interactions which contribute to the excimer binding.[10–12] Such charge-transfer complexes have been proposed earlier on the basis of other arguments, in connection with the quenching of excited states,[13,14] and have been conclusively identified by their luminescence.[15,16] It is relevant also to note the possible direct demonstration of excimer formation by recombination of aromatic hydrocarbon cations and anions,[17] a process that is the reverse of the electron transfer *following* excimer formation which is postulated here.

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To account for the pseudo-first-order kinetics (Figures 5 and 7) and the absence of any transient absorption which might correspond to the complex, we need $[^3RH_2 \cdot R] \ll [^3RH_2]$. If we assume this ratio to be less than 10^{-2} for $[R] \sim 10^{-4}\ M$, then k_A/k_B must be less than $10^2\ M^{-1}$. With these limiting values, and taking $k_4 \cong 10^7\ M^{-1}\ sec^{-1}$ at $-151°$, k_C must then be about $10^5\ sec^{-1}$. Assuming further that k_B/k_C is at least 10 requires that k_A be at least $10^8\ M^{-1}\ sec^{-1}$. Rough data[18] on the viscosity of EPA in the temperature range of our experiments indicate that this value of k_A is not unreasonable.

Other mechanisms may, of course, be written which do not assume equilibration of the complex. An intuitively satisfying possibility allows the complex either to decompose to the ground state (k_B) or to react with the protonating agent to give the radical ion (k_C). With the assumption that $k_B \gg k_C$, this leads to the same formal relationships as before. The observed, rather remarkable, similarity in the temperature dependence of k_3 and k_4 is in agreement with the sense of this mechanism since the main processes controlling triplet decay in fluid solvents appear to be pseudo-first-order quenching reactions.[7,19] Thus, k_3 and k_4 would be expected to have similar properties. This implies, however, that the entire observed activation energy, 6200 cal/mole, should be ascribed to E_A, or that $E_B = E_C$. Under these conditions, the rate of formation of complex becomes much to slow to account for k_4. In addition, this mechanism limits the maximum yield of radical ion at high imine concentrations to $\varphi_{max}(RH_2^+) = 2\varphi(^3RH)_2 k_C/(k_C + k_B)$. The triplet extinction coefficient thus may be in error by the indicated rate factor, if appreciable quenching by the imine occurs. Taking $k_B/k_C \sim 10$ leads to a molar extinction coefficient tenfold greater than the already quite high value given above. This must be taken as evidence against a competitive imine quenching reaction, despite the parallelism of the k_3 and k_4 Arrhenius plots. Conversely, an independent determination of the triplet extinction coefficient would help clarify the situation. Further speculation on mechanism does not appear to be fruitful, pending the completion of new experiments on this system, particularly on the effect of varying solvent acidity.

2. **Relation of Photochemical Amine–Imine Reaction to Ground-State Equilibrium.** Solutions of DPPD and the imine in 3% acetic acid–EPA show no semiquinone absorption bands. Much stronger acid is needed to develop the radical.[3] The photochemical reaction may thus be regarded as resulting from a shift in the redox potential of the amine–imine couple upon excitation. Since the absorption spectrum of the radical ion lies at much lower energies than that of the amine phosphorescence, such a shift is in the expected direction, even if the semiquinone is formed initially in its excited state. For the triplet amine–imine reaction, the question must remain open at this time regarding the excitation state of the immediate products of the presumed excimer decomposition. However, the observed back-reaction (k_5) evidently deals with the same species that occur in the ground-state reaction. Thus, flash measurements of the rate of the back-reaction (k_5) afford the possibility of isolating some of the kinetic factors involved in the *ground*-state equilibrium.

3. **Does "Direct" Photoxidation of DPPD Occur?** We have noted that in flashed EPAG solutions of DPPD containing no *added* imine, the yield of radical ion is extremely low, relative to the triplet (Table II, Figure 3). In other solvents, such as neutral EPA, EP (8:3), ethanol, or tetrahydrofuran, we observe the same general pattern of triplet and traces of radical-ion formation, although the semiquinone/triplet ratio is even smaller than in EPAG, and becomes rather irreproducible. These effects, at least in part, are certainly caused by varying amounts of imine contamination, arising from irreversible photochemical or dark oxidation of the original DPPD solutions. However, the question now arises whether any part at all of the RH_2^+ formed by flashing DPPD in EPAG arises from an *intrinsic* photoionization of the pure amine, producing some RH_2^+ already at $t = 0$, or whether radical formation is entirely and solely due to oxidation of the triplet by unavoidable traces of imine or other oxidizing impurity. This question is of great importance, in view of the many studies which have been made on the mechanism of photoionization in condensed phase,[20] using test substances which are easily oxidized chemically. The fact that no growing-in of radical ion can be seen in flashed "pure" DPPD solutions does not immediately dispose of the matter, since the small amount of radical absorption is overlapped everywhere by the relatively much larger triplet bands, and any radical development would be completely masked by triplet decay.

Using the results of Figure 8, and taking the curve for *pure* amine solutions to pass through the origin, one can estimate that the amount of imine impurity required to produce a semiquinone absorbance of, say, 0.01 in a 5-cm cell would be practically undetectable by standard spectrophotometric means. More sensitive tests are to look for *residual* bleaching effects at 450 mμ, or traces of a 390-mμ peak in the *initial* difference spectrum of flashed "pure" amine solutions. Slight residual bleachings at 450 mμ were indeed found, corresponding closely to the residual radical-ion formation (Figure 2C) while the difference spectrum immediately after the flash showed no trace of a peak at 390 mμ (Figure 3). These results, together with the steady trend of decreasing semiquinone yield with increasingly painstaking amine and solvent purification, lead us to conclude that direct photoejection of electrons from DPPD (either by one or two-photon processes) does not occur in these flash experiments.

This result is to be contrasted with our earlier observations in rigid solvents.[3] The steady irradiation experiments can, of course, detect processes with very low quantum yields. In addition, the flash and rigid solvent experiments have used different excitation sources and further comparisons require information on the wavelength and intensity dependence of photoionization yield. In any event, there can be no doubt that bimolecular oxidation of triplets by suitable reagents affords a simple pathway to form radical ions at low excitation energies. The possibility of this process must be kept in mind in photoionization studies.

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