Here the dissociation of the daughter $C_3H_5T^+$ ions is largely prevented. When the dissociation takes place, it is limited to its first step involving the formation of $C_3H_4T^+$ ions, which react with inactive propane to give C_3H_5T, the major product observed.

Acknowledgments. The authors are indebted to G. Giacomello for his continued interest in this work, and to G. G. Volpi and S. Wexler for their stimulating discussions and encouragement. M. C. acknowledges a fellowship from the National Research Council (CNR).

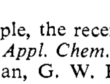
Flash Photolysis Studies of 1,3,5-Cyclooctatriene. A Reversible Ring Opening[1a,b]

Theodore D. Goldfarb[2] and Lars Lindqvist

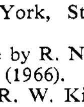
Contribution from the Laboratoire de Chimie Physique,
Faculte des Sciences, Orsay, France. *Received March 31, 1967*

Abstract: Studies of 1,3,5-cyclooctatriene in cyclohexane and *n*-hexane by flash photolysis have resulted in the detection of two transient species, both of which decay by first-order processes with lifetimes (at 25° in *n*-hexane) of 91 msec and 23 sec. Both transients are formed during the flash. A fivefold increase in the concentration of the long-lived species occurs simultaneously with the disappearance of the short-lived species. From spectroscopic and kinetic evidence the long-lived species is identified as *cis,cis*-1,3,5,7-octatetraene, the instability of which results from a low activation energy (17 kcal/mole) for recyclization to 1,3,5-cyclooctatriene. Arguments are presented for the identification of the short-lived transient as a strained, cyclic stereoisomer of 1,3,5-cyclooctatriene. The opening of this cyclic transient to form octatetraene has an Arrhenius activation energy of 16 kcal/mole. The formation of stable 1,3,5,7-octatetraene (*cis,trans* and/or *trans,trans*) has been observed and has been found to occur *via* the photoisomerization of the unstable *cis,cis* stereoisomer, thus providing an example of a biphotonic process.

There has been much recent interest in the photochemistry of cyclic polyenes. Numerous rearrangement reactions have been investigated yielding results of considerable importance from a mechanistic point of view.[3] Although one would expect that transient as well as stable photoisomers might be involved in the photochemical rearrangements of these molecules, previous work has been directed almost exclusively toward observing the stable products. In an attempt to detect and characterize transient species, we have applied the flash photolysis technique to the study of a representative compound, 1,3,5-cyclooctatriene (I). Previous photochemical studies[4-6] have shown that prolonged photolysis of I in a variety of solvents produces a bicyclic isomer (II) as well as a tricyclic isomer (III). These results differ markedly from those reported for 1,3-cyclohexadiene for which the primary photochemical process in solution[7a] is ring opening to 1,3,5-hexatriene. As suggested by Barton,[7b] a ring with $2n$ members containing $n - 1$ conjugated double bonds should undergo facile photochemical conversion to an open chain compound with n conjugated double bonds. The failure of previous workers[4-6] to isolate 1,3,5,7-octatetraene as a major photolysis product of I is shown by the present results to be due to the unexpected rapidity with which the *cis,cis* isomer of this conjugated polyene recyclizes to I. Evidence will also be presented for the identification of a second important transient as a photochemically produced stereoisomer of I.



II



III

Experimental Section

The flash photolysis apparatus consists of six oxygen-filled quartz discharge tubes, each 20 cm long, capable of producing flashes with a total discharge energy of 3750 joules and a duration of 4 μsec.[8] Solutions to be studied were contained in a jacketed 20-cm quartz cell. The filter jacket was filled with distilled water during all runs except for one experiment using a glacial acetic acid filter as described below.

Transient changes in optical density following a flash were followed by employing a d.c. xenon lamp (Osram XBO 150 W/1), a grating monochromator (Bausch and Lomb f/4.4 0.5M) adjusted for 1-mμ band width, a photomultiplier tube (EMI 955 8 BQ), and an oscilloscope (Tektronix 535) fitted with a Polaroid camera in the standard manner.

I was synthesized, purified, and separated from its thermal bicyclic isomer according to the procedure described by Cope, *et al.*[9]

Transient optical density changes were measured over the 250–500-mμ wavelength range at intervals of 20 mμ after flashing solutions of I in Spectrograde cyclohexane ($1\text{–}30 \times 10^{-6}$ *M*). The region where a positive result was obtained was reinvestigated at intervals of 2–3 mμ.

---

[1] (a) This work was supported in part by the AFOSR (SRC)-OAR USAF under grant No. 837-65; (b) presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] To whom inquiries should be addressed at the Department of Chemistry, State University of New York, Stony Brook, N. Y. 11790.

[3] See, for example, the recent article by R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966).

[4] O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Am. Chem. Soc.*, **86**, 2660 (1964).

[5] J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).

[6] W. R. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964).

[7] (a) The results of these studies are summarized in the recent review article by R. Srinivasan, *Advan. Photochem.*, **4**, 128 (1966); (b) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

[8] A detailed description of this apparatus is presently being prepared for publication by L. L.

[9] A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbal, *J. Am. Chem. Soc.*, **74**, 4867 (1952).

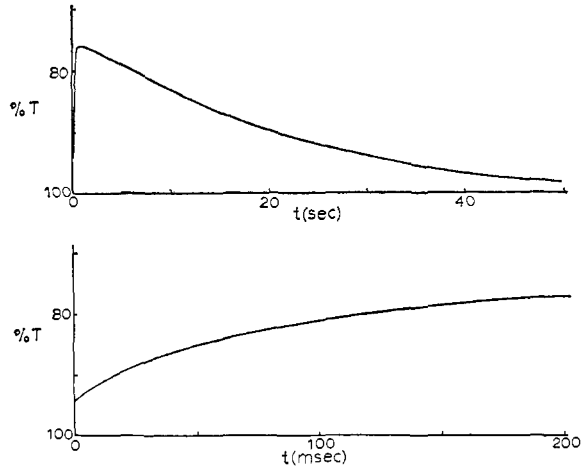


Figure 1. Enlarged oscilloscope traces of the change in transmittance, *T*, as a function of time, *t*, at slow (upper curve) and fast (lower curve) sweep rates.

Data for Arrhenius plots were obtained with solutions maintained at fixed temperatures (to ±0.1°) over the range 9.9–50.0° by flowing water from a thermostatically controlled bath through the filter jacket of the cell. Spectrograde *n*-hexane was used as the solvent in these measurements.

Results

At low flash intensities (less than 500 joules discharge energy) a reversible change in optical density was observed at all wavelengths from 248 to 320 mμ for solutions of I (absorption maximum at 254 mμ) in cyclohexane or *n*-hexane. At higher light outputs the transmittance change was not completely reversible. Experiments in which glacial acetic acid (which cuts off the shorter wavelength half of the absorption band of I) was used as a filter gave qualitatively identical results with those obtained with a water filter. The same results were obtained using either thoroughly degassed or air-saturated solutions. The kinetics of the optical density changes observed were independent of concentration over the range studied (1×10^{-6}–3×10^{-5} *M*).

Figure 1 presents two typical oscillograms taken with the monochromator set at 295 mμ at sweep rates of 5 (upper curve) and 0.02 sec/cm (lower curve) following the low-intensity flashing of a 1.4×10^{-5} *M* solution of I in cyclohexane at 25°. The light transmitted by the solution before the flash is indicated as 100% on the ordinate scale. Immediately following the flash (the time resolution was about 20 μsec) a 6% drop in transmittance was observed, followed by an additional 18% decrease occurring over a period of about 0.2 sec. The transmittance then increased slowly approaching the original level. After 120 sec no additional changes were detected. Results of this general character were observed over the 250–320-mμ wavelength interval, clearly revealing the formation of two intermediate products, one with a short lifetime (X) and one with a longer lifetime (Y). Under the conditions of this experiment the permanent decomposition of I in a single flash was about 1% as measured both from spectra of the solution taken before and after a series of flash exposures as well as from the gradual decrease in the transient optical density changes following repetitive flashing. The products of this slight decomposition produced no detectable new absorption at wavelengths greater than 220 mμ. At higher flash energies a considerable increase in the transient effect was achieved but only at the expense of a larger decomposition of I accompanied by the appearance of a permanent absorption which was readily identified from its published spectrum[10,11] as being due to the formation of 1,3,5,7-octatetraene. The production of octatetraene went up very rapidly with increasing flash intensity, indicating that a biphotonic process was responsible for its formation. Because of the rapid onset of this two-photon side reaction it was necessary to measure the spectra of the transient species and to determine the effect of temperature on the decay rates at flash energies that were much below those required to achieve light saturation.

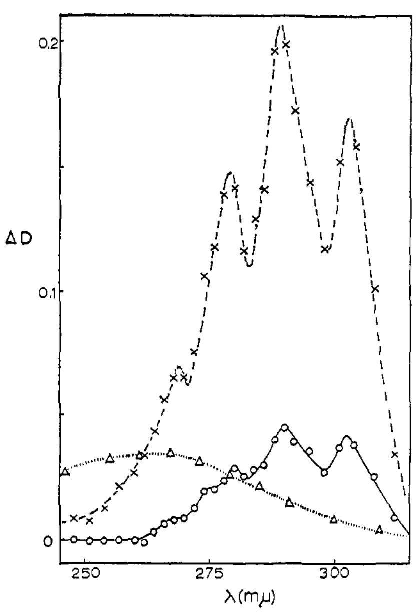


Figure 2. Difference spectra: ΔD_m, ○; ΔD_M, ×. Spectrum of 1,3,5-cyclooctatriene, △.

The spectral curves (difference spectra) shown in Figure 2 were constructed from the transient absorption changes for 1.1×10^{-5} *M* solutions of I in cyclohexane. The solid curve represents the observed changes in optical density (ΔD_m) immediately following the flash. The dashed curve is a plot of the decrease in optical density (ΔD_M) reached after the decay of X was virtually complete which corresponds to the difference between 100% and the minimum transmittance value on the oscillogram shown in Figure 1.

The ΔD_M values result from the increase in optical density due to the absorption of transient species Y modified by the decrease in optical density due to the decomposition (temporary and/or germanent) of I. The maxima in the dashed curve agree within experimental error (±1 mμ) with both the published λ_{max} values of the stable stereoisomers of 1,3,5,7-octatetraene[10,11] and those observed for the permanent product produced by flashing at high light intensities. Assuming that the maximum extinction coefficient of Y is approximately the same as that of stable *cis,trans*-1,3,5,7-octatetraene[11] (see Discussion section for a justification of this assumption), it is estimated that about 4% of I was converted to Y under the conditions used in these runs. The absorption spectrum of a 20-

---

(10) G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, 71, 1396 (1949).

(11) W. Ziegenbein, *Chem. Ber.*, 98, 1427 (1965).

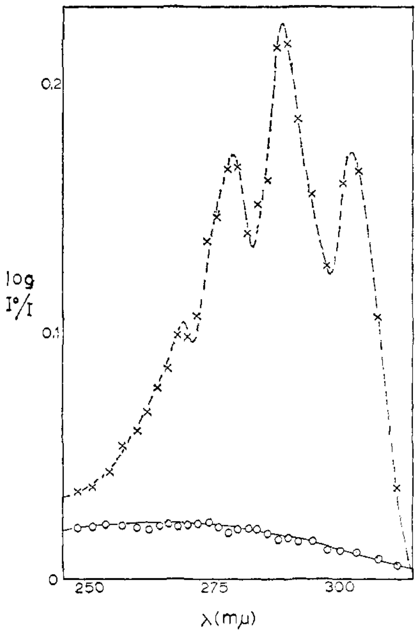


Figure 3. Calculated spectra: species X, ○; species Y, ×.

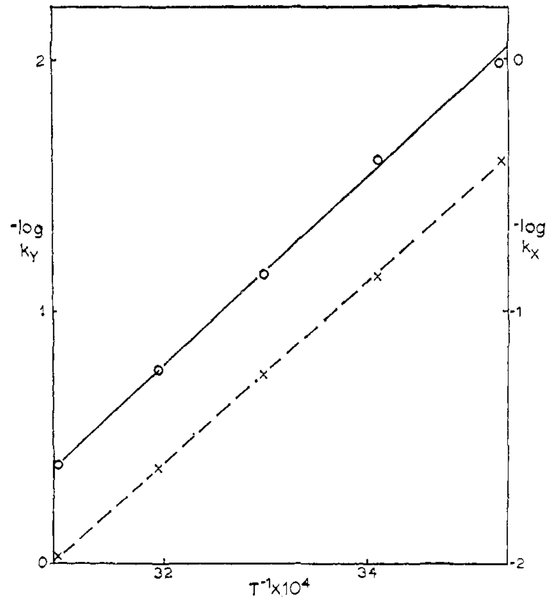


Figure 4. Plots of lifetime ($-\log k$) *vs.* T^{-1} for species X, ×, and for species Y, ○.

cm path length of a 4.4×10^{-7} *M* solution of I (4% of the original concentration) is shown by the dotted curve in Figure 2. Adding the dashed and dotted curves of Figure 2 should yield the undistorted spectrum of Y which is shown by the dashed curve in Figure 3.

The absorption peaks in the ΔD_m difference spectrum (solid curve in Figure 2) are seen to coincide in wavelength and relative intensity with those of Y, and it must therefore be assumed that some Y (about 20% of the total Y produced) has been formed during the flash, the remainder being formed from the short-lived transient, X. If it is assumed that all of the X formed is converted to Y, it is possible to construct an approximate spectrum of X by subtracting 20% of the dashed curve in Figure 3 from the solid curve in Figure 2, thus cancelling the effect of Y produced during the flash, and adding to this the dotted curve in Figure 2 in order to correct for the 4% decrease in the concentration of I. The result of this procedure is the solid curve in Figure 3. If some X reverts directly to I (the only other alternative consistent with the reversible nature of the photolytic process), the spectrum of X calculated by the above procedure should be modified by adding to it an additional fraction of the spectrum of I. In any event, species X is found to have a broad unstructured near-ultraviolet absorption band comparable in intensity to that of I but shifted to somewhat longer wavelengths. This latter point was verified by an experiment performed on a more concentrated sample (3×10^{-5} *M*) in which it was possible to observe transient changes at wavelengths as long as 324 mμ. Above about 318 mμ the increase in optical density immediately following the flash was followed by a *decrease* in absorbance with kinetics appropriate to the X → Y conversion process. This means that in this region X, although absorbing only weakly, has a higher extinction coefficient than either I or Y.

The difference in lifetime of species X and Y is large enough so that good kinetic data could easily be obtained from both the conversion of X to Y and for the disappearance of Y. A first-order decay was found for both processes at all concentrations, wavelengths, and temperatures studied. Arrhenius plots based on data taken at 10° intervals from 10 to 50° are shown in Figure 4. The values of the Arrhenius parameters for the decay of species X and Y are $A = 9.0 \times 10^{12}$ and 1.1×10^{11} sec^{-1} and $E_a = 16.3$ and 17.0 kcal/mole, respectively.

A few experiments were performed to investigate the nature of the biphotonic process which resulted in the irreversible conversion of I to 1,3,5,7-octatetraene. It seemed probable that photolysis of one or both of the transients was involved. To study the photolysis of Y, a solution of I in *n*-hexane (1.5×10^{-5} *M*), cooled to −10°, was exposed to two low-energy flashes spaced 15 sec apart. Only a very small fraction of the Y produced by the first flash had decayed prior to the second flash due to its long lifetime at this temperature. A very pronounced permanent production of 1,3,5,7-octatetraene was produced in this manner, whereas none of this product was produced when the time interval between flashes was long enough to permit virtually all of the Y to disappear prior to the second flash. This is conclusive evidence that stable octatetraene can be produced by the photolysis of Y. Photolysis of X may also contribute to the biphotonic production of octatetraene, but the lifetime of X is too short to permit an analogous study of this transient with the apparatus used in this investigation.

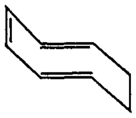
Discussion

The results definitely establish the formation of two short-lived products in the photolysis of I. These species apparently are not of radical or triplet nature, since the decay is strictly first order at all concentrations and is not influenced by oxygen, and since no important permanent decomposition was observed. Triplets would be expected to be at least partially quenched by second-order triplet–triplet reactions and also to be very sensitive to oxygen, whereas radicals would be expected to give rise to permanent photochemical change by reactions with the solvent. One may therefore assume that the transient species are isomers of the starting compound, I.

The long-lived transient, Y, has a characteristic absorption spectrum which is almost identical with that of stable 1,3,5,7-octatetraene. The synthesis of this latter compound described by Woods and Schwartzman[10] has been shown to produce exclusively the *trans,-trans* isomer.[12] Recently the *cis,trans* isomer has been synthesized[11] and found to have an ultraviolet absorption spectrum virtually indistinguishable from that of the *trans,trans* isomer save for small changes in the $\lambda_{\max}$ extinction coefficients. A synthetic approach that would ordinarily be expected to produce the *cis,cis* isomer was surprisingly found[11] to yield I instead. Since about 4% of transient Y was produced in a flash that resulted in no more than 1% permanent decomposition of I, it is evident that I is regenerated from Y. These facts clearly lead to the conclusion that Y is *cis,cis*-1,3,5,7-octatetraene which rapidly recyclizes at room temperature to I. The analogous ring closing of 1,3,5-hexatriene has been studied by Lewis and Steinen.[13] The *cis* and *trans* isomers of this molecule, which have nearly identical ultraviolet spectra, are both stable at room temperature. At elevated temperatures the *cis* isomer cyclizes to 1,3-cyclohexadiene by means of a first-order process. An extrapolation of the published data[13] indicates that *cis*-1,3,5-hexatriene would have a lifetime of a few seconds at about 200°, comparable to that observed for *cis,cis*-1,3,5,7-octatetraene at 25°. The greater stability of the hexatriene isomer is found to result from the higher (29 kcal/mole) activation energy for cyclization[13] as compared to the value (17 kcal/mole) observed for octatetraene in the present work. The lower barrier for closing the eight-membered ring can be easily rationalized if one considers the steric problem of rotating the conjugated triene and tetraene into a configuration such that the p orbitals on the end carbon atoms can overlap and begin to form a σ bond as the transition state is approached. Hexatrienes have been shown to cyclize thermally by a disrotatory process.[14] If a Dreiding model of *cis*-1,3,5-hexatriene is rotated about its single C–C bonds in a disrotatory manner it is observed that considerable "strain" would be required to bring the end atoms into position for appreciable p-orbital overlap. On the other hand, *cis,cis*-1,3,5,7-octatetraene can be rotated in either the conrotatory (as Woodward and Hoffmann's rules dictate[14]) or the disrotatory manner into configurations that would allow p-orbital overlap at about the normal C–C single bond distance with little or no strain or steric interference. The greater stability of the six- as compared to the eight-membered ring has, of course, no bearing on the kinetics of the cyclization processes.

The flash study showed that Y is formed predominantly from the short-lived component X. This compound was seen to have an absorption spectrum very similar to that of the initial compound, I, except for a shift to longer wavelengths. The strong, long wavelength absorption eliminates isomers without conjugated double bonds. The only isomer of I that has conjugated double bonds and might conceivably open rapidly to give 1,3,5,7-octatetraene is known to be a stable thermal isomer of I. The only possibility that comprises all the required characteristics seems to be that X is an unstable cyclic stereoisomer of I. Stable I is the *cis,cis,cis* isomer which has a "tub" configuration (IV). Although this is the only reasonably strain-free configuration it is likely that other local minima in the potential surface for this system exist at configurations such as the *trans,cis,trans* "chair" isomer (V), the *cis,cis, trans* isomer, or the *cis,trans,cis* isomer, all of which would require only moderate twisting about the double bonds. If one of these isomers results from an electronically excited state of I, the conversion to IV in the ground state may involve a sufficiently high potential barrier to cause the observed ring opening to be the preferred process. The spectrum of one of the stable stereoisomers of I would probably be similar to that of IV with a shift to longer wavelengths reflecting the elevated position of its potential energy minimum. The recently reported[15] photosensitized conversion of *cis,cis*- to *cis,trans*-1,3-cyclooctadiene lends further support to the proposed identification of X as a photochemically produced stereoisomer of IV.

IV



V

The stable product of the biphotonic process occurring at high light intensities is undoubtedly one of the stable stereoisomers of 1,3,5,7-octatetraene resulting from photolysis of the unstable *cis,cis* molecule. Whether it is the *cis,trans* isomer, the *trans,trans* isomer, or both, has not been ascertained.

A comparison of the results of this investigation with those reported for previous photochemical studies of I[4–6] reveals an apparent discrepancy in that none of the products appearing in the flash photolysis is observed in the low-intensity studies, and *vice versa*. In the previous studies only the stable photoproducts were analyzed, and the transient compounds X and Y would obviously not be observed. At low light intensities one would not expect the photoisomerization of Y to occur to any appreciable extent. The formation of II and III was observed after prolonged low-intensity photolysis of I,[4–6] and the quantum yields for their formation may be very low. These photoproducts do not absorb in a region easily accessible to study by the flash technique. It is possible that the 1% decrease in concentration of I observed in this study on flashing at low intensity is due in fact to formation of these products.

In summary we find that photoexcitation of I results in the following transformations

$$\begin{tikzcd}
\text{1,3,5-cyclooctatriene} \arrow[r, "h\nu"] & \text{excited state} \arrow[dl] \arrow[d] \\
\text{\textit{cis,cis}-1,3,5,7-octatetraene} \arrow[u, "kT"'] \arrow[d, "h\nu"] & \text{unstable stereoisomer of 1,3,5-cyclooctatriene} \arrow[l, "kT"'] \\
\text{\textit{cis,trans}- and/or \textit{trans,trans}-1,3,5,7-octatetraene} &
\end{tikzcd}$$

---

[12] E. R. Lippincott, W. R. Feairheller, and C. F. White, *J. Am. Chem. Soc.*, **81**, 1316 (1959).

[13] K. E. Lewis and H. Steinen, *J. Chem. Soc.*, 3080 (1964).

[14] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

[15] S. H. Liu, *ibid.*, **89**, 112 (1967).

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]

Henry Linschitz, Michael Ottolenghi, and Rene Bensasson[2]

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

---

(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).