Electron Spin Resonance Study of Charge-Transfer Complexes of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone with N-Substituted *p*-Phenylenediamines[1a,b]

Nancy H. Kolodny*[2] and Kerry W. Bowers

Contribution from the Department of Chemistry and
Research Laboratory of Electronics, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139, and Department of Chemistry,
Wellesley College, Wellesley, Massachusetts 02181. *Received May 3, 1971*

Abstract: The interaction between the donor and acceptor molecules comprising charge-transfer complexes in solution has been studied by means of electron spin resonance spectroscopy. Solutions of strong donors and acceptors in solvents of widely differing polarity were mixed in an oxygen-free flow system. This flow system allowed electron spin resonance spectra to be recorded of any paramagnetic species with a lifetime longer than 0.04 sec. Charge-transfer systems were observed for periods ranging from 30 min to 6 hr. It was found that the complexes composed of *p*-phenylenediamine (PPD) or *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (in solvents such as 1,2-dimethoxyethane (DME, ϵ 7.2) and acetonitrile (CH_3CN, ϵ 37)) dissociated for the most part into the radical cation and anion. However, in the system PPD–DDQ in CH_3CN, a third paramagnetic species was observed which has been identified as either $(PPD\text{–}DDQ)\cdot^-$ or $(PPD\text{–}(DDQ)_2)\cdot^-$.

It is the purpose of this study to demonstrate, by means of electron spin resonance (esr) spectroscopy, how the partners in a donor–acceptor (DA) or charge-transfer (CT) complex in solution interact and what effect such variables as solvent polarity, donor and acceptor strength, and time have upon this interaction. Model systems have been chosen consisting of D and A molecules which interact to give relatively "strong" complexes. Such complexes dissociate so that a sufficient concentration of radical ions is present in solution for detection. In addition, D and A were chosen which may be independently oxidized or reduced to radical ions with interpretable esr spectra. Apparatus has been developed during the course of this work whereby solutions and D and A molecules are made to flow together directly above the microwave cavity of an esr spectrometer, and the esr spectrum of the complex is recorded immediately upon complex formation (flowing) or throughout any time period after formation (not flowing).

The basic theoretical work on charge-transfer or donor–acceptor complexes was published by Mulliken in a series of papers appearing from 1950 to 1969 and compiled in a recent book.[3] Since Mulliken's work appeared, theoretical treatments of DA complexes challenging or modifying those of Mulliken have been proposed.[4–7] Generally, however, most experimental results have been treated with reference to Mulliken's theory.[8]

Mulliken postulated that in nonpolar solvents, the ground state of a "tight" or "strong" complex is comprised of approximately equal amounts of $\psi_0(D,A)$ and $\psi_1(D^+A^-)$, where $\psi_0(D,A)$ is a "no-bond" wave function and $\psi_1(D^+A^-)$ is a dative wave function corresponding to the transfer of an electron from D to A.[3] He suggested that in polar solvents dissociation of the complex into ions is governed by a slow, stabilizing solvation process rather than the increased stability due to the inequality $\langle\psi_1(D^+A^-)/H/\psi_1(D^+A^-)\rangle < \langle\psi_0(DA)/H/\psi_0(DA)\rangle$ for the undissociated complex. Information about the relative orientation of D and A in 1:1 complexes has generally been obtained from studies of solid complexes. It has been assumed by most investigators that the same geometry exists in solution.[8] Both the role of the solvent and the assumption of constant geometry are discussed below for the model systems under consideration.

CT complexes in solution have been studied by esr spectroscopy, but information about the nature of the interaction between the D and A species was never obtained. In each case, the spectrum of only one radical ion, usually $A\cdot^-$, appeared. In fact, the earlier esr experiments often lacked the spectral resolution necessary to assign the spectra to any particular species. Miller and Wynne-Jones,[9] for example, studied complexes of the acceptor *s*-trinitrobenzene (1,3,5-trinitrobenzene, $C_6H_3(NO_2)_3$) with aliphatic and aromatic amines, pyridine, and hydrocarbons, either in solution in the amines or in acetone. They obtained an unresolved spectrum which they attributed to $C_6H_3(NO_2)_3\cdot^-$, the acceptor portion of the complexes formed, because its *g* value and line width corresponded to that for $C_6H_3(NO_2)_3$ dissolved with Na in 1,2-dimethoxyethane.

---

(1) This research was supported in part by (a) U. S. Army Electronics Command Contract DA 28-043 AMC-02536(E); (b) Faculty Research Award to Nancy H. Kolodny, Wellesley College.

(2) National Institutes of Health Predoctoral Fellow, Massachusetts Institute of Technology, 1966–1969; Wellesley College.

(3) R. S. Mulliken and W. B. Person, "Molecular Complexes: A Lecture and Reprint Volume," Wiley, New York, N. Y., 1969.

(4) M. W. Hanna, *J. Amer. Chem. Soc.*, **90**, 285 (1968).

(5) M. W. Hanna and D. E. Williams, *ibid.*, **90**, 5358 (1968).

(6) J.-P. Malrieu and P. Claverie, *J. Chim. Phys.*, **65**, 736 (1968).

(7) M.-J. Mantione, "Molecular Association in Biology," B. Pullman, Ed., Academic Press, New York, N. Y., 1968, p 411.

(8) Some reviews are (a) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; (b) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964; (c) E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965); (d) A. Pullman and B. Pullman, *Quantum Theory At., Mol., Solid State*, 345 (1966); (e) S. Yomosa, *Progr. Theor. Phys., Suppl.*, **40**, 249 (1967); (f) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, London, 1969.

(9) R. E. Miller and W. F. K. Wynne-Jones, *Nature (London)*, **186**, 149 (1960).

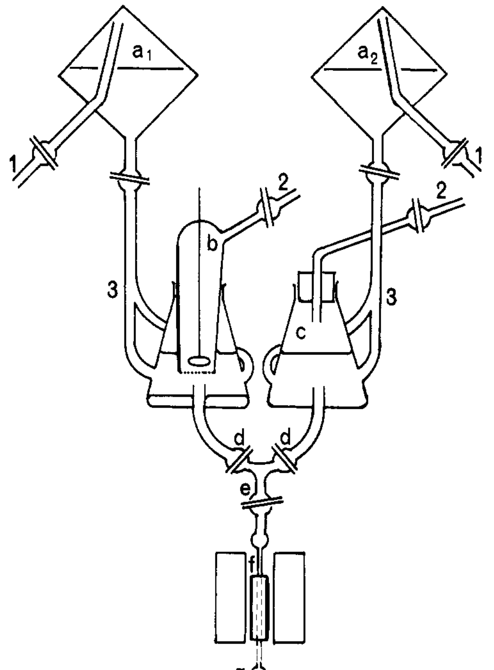

Figure 1. Flow system: (a_1, a_2) stainless steel tanks for degassing and storage of solutions; (b, c) electrolytic cells; (d, e) Teflon stopcocks; (f) 3-mm o.d. Spectrosil quartz tube passing through cavity of Varian E-3 esr spectrometer; (g) Teflon needle valve; (1, 2, 3) gum rubber tubing.

In somewhat later work, Lagercrantz and Yhland[10] found that *s*-trinitrobenzene, when photolyzed in donor solvents such as tetrahydrofuran (THF), *p*-dioxane, benzaldehyde, xylene, and mesitylene, has a spectrum with hyperfine structure again due only to the acceptor part of the DA complex. Similarly, *p*-chloranil in donor solvents, when photolyzed, gave the single, narrow-line spectrum of the *p*-chloranil anion radical. Before photolysis no signals were observed, leading these authors[10] to postulate that the absorption of radiation caused a charge transfer which resulted in the unpairing of electrons. The subsequent reactions of the paramagnetic complex were assumed to be either the return of the excited complex to its initial state without dissociation into radical ions (*p*-chloranil complexes) or dissociation of the complex (*s*-trinitrobenzene complexes). However, no evidence was found for the existence of positive radical ions in solution individually or interacting with the negative radical ions. To explain this they suggested that the lifetime of the positive radical ions might be so short that the ions decayed before an esr spectrum could be obtained. It has since been suggested that this short lifetime is due to dimerization or disproportionation of the radical ions.

As in all earlier studies of CT complexes in solution, the esr spectrum of only one paramagnetic species was observed by Stewart and Eisner.[11,12] They studied four complexes of tetracyanoethylene with n-donor solvents (dimethyl sulfoxide, DMSO; *N,N*-dimethylacetamide, DMA; acetone; and THF). Since the donors in these experiments are solvents, and since $D\cdot^+$ and $A\cdot^-$ are presumably produced in equal concentration, the ratio between $[D\cdot^+]$ and [D] was probably on the order of 10^{-5}; Stewart and Eisner concluded that if there is a reasonable probability of a spin flip during a collision of D and $D\cdot^+$, the lifetime of a D ion spin state is of the order of the Larmor period and the esr spectrum of $D\cdot^+$ will be broadened beyond the limits of detectability.

In the work presented here, the spectra of both the donor and acceptor radical ions are observed. The longer lifetime of one radical ion with respect to the other is demonstrated by the observation of the esr spectrum of the DA complex in solution over a period of time immediately following complex formation.

Experimental Section

Donors. *p*-Phenylenediamine (PPD) (crude, Eastman Organic Chemicals, Rochester, N. Y.) was recrystallized three times from benzene and sublimed *in vacuo* at 150°. During the first recrystallization, decolorizing charcoal was added. Colorless crystals resulted.[13]

N,N,N′,N′-Tetradeuterio-*p*-phenylenediamine (d-PPD) was prepared by dissolving PPD in a solvent containing 4% (v/v) D_2O. The amino protons exchanged with the excess deuterons yielding the deuterated species.[14]

N,N,N′,N′-Tetramethyl-*p*-phenylenediamine (TMPD) was obtained upon addition of dilute ammonia to an aqueous solution of crude TMPD·2HCl (Eastman Organic Chemicals, Rochester, N. Y.). The white precipitate was sublimed at 150° under high vacuum and stored under high vacuum.

Tetracene (K & K Laboratories, Plainview, N. Y.) was recrystallized three times from xylene. Orange crystals resulted.

Acceptors. Tetracyanoethylene (TCNE) (crude, Eastman Organic Chemicals) was recrystallized three times from chlorobenzene and sublimed *in vacuo* at 140°. Colorless crystals were obtained.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Aldrich Chemical Co., Milwaukee, Wis.), an orange-yellow powder, was used without further purification.

p-Chloranil (synthesized by Dr. Kerry W. Bowers, MIT) was recrystallized three times from toluene.

Pyromellitic dianhydride (PMDA) (K & K Laboratories) was used without further purification.

Solvents. Acetonitrile (CH_3CN) (Mallinkrodt "Nanograde," St. Louis, Mo.) was refluxed over phosphorus pentoxide, P_2O_5, for 24 hr and distilled through a helix-packed column. Middle fractions were collected and stored in glass-stoppered flasks.

1,2-Dimethoxyethane (DME, ethylene glycol dimethyl ether; glyme) (Ansul Ether 121, Marinette, Wis.) was refluxed over sodium–potassium alloy and distilled and stored in the same manner as CH_3CN.

N,N-Dimethylformamide (DMF) ("Baker Analyzed" Reagent, J. T. Baker Chemical Co., Phillipsburg, N. J.) was distilled through a helix-packed column. The middle fractions were collected and stored as in the case of CH_3CN.

Deuterium oxide (D_2O) (99.5%, Columbia Organic Chemicals, Columbia, S. C.) was used without further purification.

Electrolyte. Tetra-*n*-butylammonium perchlorate (n-Bu_4NClO_4) was prepared from tetra-*n*-butylammonium hydroxide titrant (25% in methanol, Eastman Organic or 1 *M* in water, Columbia Organic) by titrating an aqueous solution of the hydroxide with perchloric acid (71.3%, J. T. Baker) to pH 7.0 and washing the resulting white precipitate with water. The salt was then recrystallized from acetone, filtered, and dried under high vacuum.

Solutions. Solutions for flow studies were prepared which were 3.0×10^{-3} *M* in donor or acceptor and 5.0×10^{-2} *M* in n-Bu_4NClO_4 by dissolving weighed amounts of D or A and electrolyte in 500 ml of solvent in a 500-ml volumetric flask. Each solution was immediately transferred to a stainless steel degassing task and degassed on a high vacuum line by repeated freeze–pump–thaw cycles. It was found that after three cycles little or no dissolved gas remained.[15]

---

(10) C. Lagercrantz and M. Yhland, *Acta Chem. Scand.*, **16**, 1043 (1962).

(11) F. E. Stewart, M. Eisner, and W. R. Carper, *J. Chem. Phys.*, **44**, 2866 (1966).

(12) F. E. Stewart and M. Eisner, *Mol. Phys.*, **12**, 173 (1967).

(13) The purity of all materials was attested to either by melting point determination or by lack of foreign species in esr spectra.

(14) M. T. Melchior and A. H. Maki, *J. Chem. Phys.*, **34**, 471 (1961).

Table I. Results of Flow Experiments

Radical ion	Solvent	Method of production	Hyperfine splitting constants and line widths (G)	[Radical ion]$_t$/[radical ion]$_0$
1. PPD	CH_3CN	Electrolytic, +0.55 V	$a_N = 5.11$, $a_{H(amine)} = 5.72$, $a_{H(ring)} = 2.07$, LW = 0.190	<0.15, t = 10 min
2. PPD	CH_3CN	CT complex with DDQ	Same as radical ion 1	<0.10, t = 30 min
3. PPD	CH_3CN (+4% H_2O)	CT complex with DDQ	Same as radical ion 1	0.33, t = 22 min
4. DDQ	CH_3CN	Electrolytic, −1.0 V	$a_N = 0.50$, LW = 0.40	
5. DDQ	CH_3CN	CT complex with PPD	$a_N = 0.58$, LW = 0.11	~1.0, t = 34 min
6. DDQ	CH_3CN (+4% H_2O)	CT complex with PPD	$a_N = 0.54$, LW = 0.25	~1.0, t = 22 min
7. New species	CH_3CN	CT complex, PPD–DDQ	Undetermined	~0.80, t = 24 min
8. d-PPD	CH_3CN	Electrolytic, +0.55 V	$a_N = 5.00$, $a_{D(amine)} = 0.875$, $a_{H(ring)} = 2.10$, LW = 0.15	
9. d-PPD	CH_3CN	CT complex with DDQ	Same as radical ion 8	>0.50, t = 90 min
10. DDQ	CH_3CN	CT complex with d-PPD	$a_N = 0.56$, LW = 0.16	~1.0, t = 90 min
11. PPD	DME	Electrolytic, +0.55 V	$a_N = 5.11$, $a_{H(amine)} = 5.72$, $a_{H(ring)} = 2.07$, LW = 0.185	<0.15, t = 10 min
12. PPD	DME	CT complex with DDQ	Same as radical ion 11	<0.10, t = 30 min
13. PPD	DME (+4% H_2O)	CT complex with DDQ	Same as radical ion 11	>0.50, t = 90 min
14. DDQ	DME	Electrolytic, −1.0 V	$a_N = 0.55$, LW = 0.20	
15. DDQ	DME	CT complex with PPD	$a_H = 0.56$, LW = 0.30	<0.50, t = 34 min
16. DDQ	DME (+4% H_2O)	CT complex with PPD	Same as radical ion 15	~1.0, t = 90 min
17. d-PPD	DME	Electrolytic, +0.55 V	$a_H = 5.00$, $a_{D(amine)} = 0.914$, $a_{H(ring)} = 2.08$, LW = 0.185	
18. d-PPD	DME	CT complex with DDQ	Same as radical ion 17	<0.10, t = 30 min
19. DDQ	DME	CT complex with d-PPD	$a_N = 0.56$, LW = 0.40	~1.0, t = 90 min
20. TMPD	CH_3CN	Electrolytic, +0.24 V	$a_{CH_3} = 6.80$, $a_H = 2.01$, a_N = unresolved, LW = 0.32	
21. TMPD	CH_3CN	CT complex with DDQ	Same as radical ion 20	~1.0, t = 30 min
22. DDQ	CH_3CN	CT complex with TMPD	Unresolved	<0.10, t = 12 min
23. TMPD	DME	Electrolytic, +0.24 V	Same as radical ion 20	
24. TMPD	DME	CT complex with DDQ	Same as radical ion 20	<0.10, t = 34 min
25. DDQ	DME	CT complex with TMPD	$a_N = 0.58$, LW = 0.32	<0.10, t = 56 min

Samples for individual electrolysis were prepared by dissolving a weighed amount of D or A and electrolyte in 10 ml of solvent in a dry 10-ml graduated cylinder, affording solutions 3.0×10^{-3} M in D or A and 5.0×10^{-2} M in n-Bu_4NClO_4. Solutions were then poured into the bulb of the electrolytic cell and degassed in the same manner as solutions for flow studies.

A flow system is employed whereby degassed solutions of donor and acceptor molecules are flowed separately under positive pressure of nitrogen, through electrolytic chambers, to a point at which they are mixed, through the cavity of a Varian E-3 esr spectrometer, and finally into a waste reservoir (Figure 1).[16] The systems PPD–DDQ in CH_3CN, TMPD–DDQ in CH_3CN, and TMPD-DDQ in DME were each run with three sets of solutions; d-PPD–DDQ in CH_3CN and PPD–DDQ in DME with two sets; d-PPD–DDQ in DME, PPD–DDQ in (CH_3CN + 4% H_2O), PPD–DDQ in (DME + 4% H_2O), each with one set. With each set of solutions, anywhere from two to six runs were carried out, each run consisting of the flowing together of either neutral or electrolyzed solutions, recording an esr spectrum during the flow, discontinuing the flow, and recording a series of spectra during the decay of the paramagnetic species.

The electrolytic cell used in these experiments has been described by Nolfi.[17] Controlled potential oxidation or reduction occurred at a mercury cathode placed in the microwave cavity of the E-3. A Heath-built transistorized power supply (Model EUW-17) supplied the required potential (+2.0 to −2.0 V) at a few microamperes of current. The potential output of the power supply was monitored by a Heathkit VTVM (Model IM-13). This cell was used to obtain $D\cdot^+$ and $A\cdot^-$ spectra to compare with those obtained during flow experiments. There is no reason to expect spectra thus obtained to differ from those of radicals produced outside the cavity (by charge transfer) and flowed past the point of spectral measurement.

Since organic free radicals such as $D\cdot^+$ and $A\cdot^-$ have g values approximately equal to that of the free electron (2.0023), spectra were recorded at 9.5 gHz in the neighborhood of 3400 G. Microwave power levels were adjusted to provide a strong esr signal but to avoid saturation of the signal. All other instrumental settings were made to maximize signal resolution. Line widths as narrow as 0.140 G were obtained during flow experiments.

Spectra were simulated by inserting trial values of line widths, line shapes, splitting constants, and numbers of nuclei of each spin, I, into a computer program, WESRP;[18] the program synthesized the spectrum and plotted it to scale, so that visual comparison of simulated and experimental spectra was possible. This was important because, particularly in the case of $DDQ\cdot^-$, spectral resolution (a_N/LW < 2) was not possible instrumentally, and splitting constants could not be read directly from spectra. The accuracy of measurements of hyperfine splitting constants and line widths for these experiments ranged from ±0.01 G for spectra with total widths of 10 G to ±0.02 G for spectra with total widths of 20 or 50 G. Computer calculations were done on an IBM system 360/65/40 at the MIT Computation Center.

Results and Discussion

The charge-transfer complexes investigated here are composed of well-known strong donors and acceptor.[8,19–22] The donor molecule, p-phenylenediamine,

---

[15] Exclusion of paramagnetic gases such as oxygen from solutions of paramagnetic materials, or solutions to be electrolyzed to produce paramagnetic materials, is one of the most important considerations in the design of an esr flow experiment. Dissolved oxygen can have an effect on the relaxation times of spin systems thus shortening T_1 and broadening esr lines. In addition, dissolved oxygen may react with radical ions to produce undesired paramagnetic by-products.

[16] Further details of this flow system are available in the Ph.D. Dissertation of Nancy H. Kolodny, Massachusetts Institute of Technology, Cambridge, Mass., June 1969.

[17] G. J. Nolfi, Jr., Ph.D. Thesis, MIT, 1965; also in C. P. Poole, Jr., "Electron Spin Resonance," Interscience, New York, N. Y., 1967, pp 626–628.

[18] F. J. Wiegert, B.S. Thesis, MIT, 1965; modified to produce a Calcomp plot of output.

[19] M. E. Browne, A. Ottenberg, and R. L. Brandon, *J. Chem. Phys.*, **41**, 3265 (1964).

[20] B. G. Anex and E. B. Hill, Jr., *J. Amer. Chem. Soc.*, **88**, 3648 (1966).

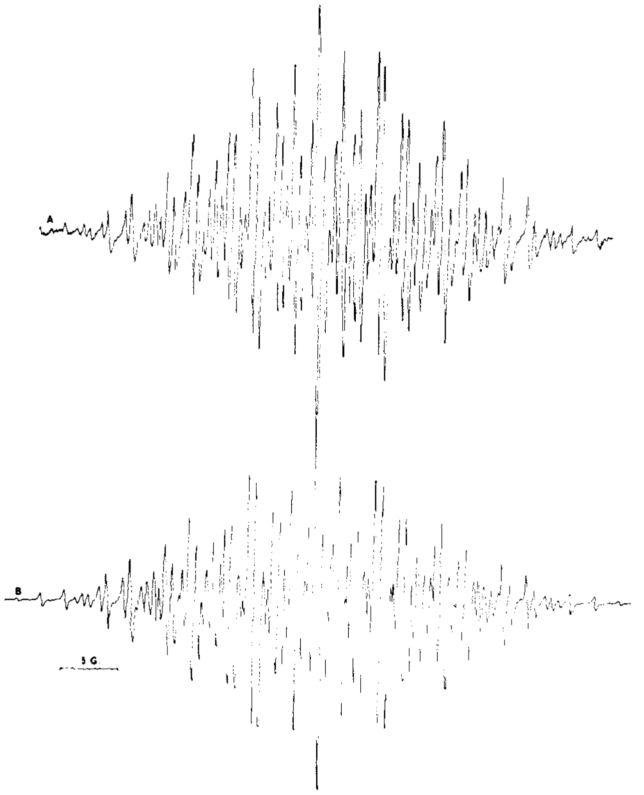

Figure 2. PPD in CH_3CN: (A) electrolytic generation of cation, +0.55 V; (B) computer simulation of spectrum. a_N = 5.11 G, a_H(amine) = 5.72 G, a_H(ring) = 2.07 G, line width = 0.190 G.

has been studied as the monopositive ion by Melchior and Maki,[14] who generated the free-radical cation in acetonitrile. Several studies have also been conducted to determine the hyperfine splitting constants of the TMPD cation radical.[23-25] The acceptor molecule, DDQ, forms a "radical-ion salt" with 1,6-diaminopyrene which is 95% ionic.[22]

The results obtained for all systems in this investigation are presented in Table I; representative spectra are shown in Figures 2-6. These results (for the complexes PPD-DDQ, d-PPD-DDQ, and TMPD-DDQ) indicate that free-radical formation occurs to a significant extent in two solvents which differ greatly in polarity (ϵ_{CH_3CN} 37, ϵ_{DME} 7.2). In both solvents spectra of $D\cdot^+$ and $A\cdot^-$, identical with those obtained from D and A electrolyzed separately, were observed when neutral solutions of D and A were mixed together in the flow system. No direct evidence for the existence of the complex, D^+A^-, was found. However, the presence of $D\cdot^+$ and $A\cdot^-$ resulting from the mixing of solutions of D and A implies the following equilibrium situation

$$D + A \rightleftarrows D^+A^- \rightleftarrows D\cdot^+ + A\cdot^-$$

The data in Table I (hyperfine splitting constants, *a*, and line widths, LW) were obtained from recorded spectra by manual measurements of distances between the first derivatives of Lorentzian absorption lines for each set of equivalent nuclei. Line widths were computed from the distance between the upper and lower turning points of each line. When necessary for the assignment of a group of lines to a given set of nuclei, intensities were computed according to the formula $I \propto (LW)^2h$, where *h* is the amplitude of the first derivative of the absorption. Hyperfine splitting constants, line widths, and general spectral interpretations were verified by computer simulation of spectra. The ratio [radical ion]$_t$/[radical ion]$_0$ was obtained by determining the concentration of a radical ion at a given time, *t*, relative to its concentration immediately following electrolysis or mixing of D and A solutions *via* flow.

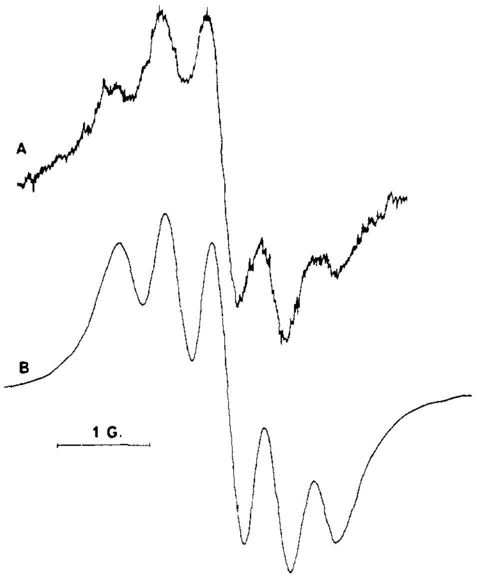

Figure 3. DDQ in CH_3CN: (A) electrolytic generation of anion, −1.0 V; (B) computer simulation of spectrum. a_N = 0.50 G, line width = 0.40 G.

The spectra in Figures 2 and 3 were produced by the electrolytic generation of the PPD cation radical and DDQ anion radical, respectively. Figure 2A shows 77 of the expected 125 lines, and Figure 2B is a computer simulation of this spectrum which is visually identical with it. Figure 3A shows a less well-resolved spectrum which is simulated in 3B. The difficulty encountered in obtaining a well-resolved esr spectrum of the electrolytically generated anion of DDQ is consistent with the observation of Kronick, Scott, and Labes.[22] They found that the DDQ semiquinone anion radical was unstable in solution, as evidenced by a change in color. However, when $DDQ\cdot^-$ was produced as the result of CT complex formation in the present work, it was found to be very stable. (See Table I and Figures 4-6.)

Figures 4, 5, and 6 show representative spectra from a flow experiment. The maximum rate of flow for this system was about 40 cm/sec; a CT complex thus reached the point of spectral measurement within 0.04 sec after it was formed by the mixing of D and A solutions. Any paramagnetic species with a lifetime longer than 0.04 sec was potentially observable during the flow portion of the experiment. After the flow was stopped, the solution containing $D\cdot^+$, $A\cdot^-$, D^+A^-, and any other possible species was allowed to remain at the point of spectral measurement until all but one species had decayed. A superposition of three spectra appears in Figures 4A-C. Two of these may be assigned to $PPD\cdot^+$ and $DDQ\cdot^-$. Figure 6 includes the same total

---

(21) R. L. Hansen, *J. Org. Chem.*, 33, 3968 (1968).

(22) P. L. Kronick, H. Scott, and M. M. Labes, *J. Chem. Phys.*, 40, 890 (1964).

(23) S. I. Weissman, *ibid.*, 22, 1135 (1954).

(24) J. R. Boulton, A. Carrington, and J. dos Santos-Veiga, *Mol. Phys.*, 5, 615 (1962).

(25) H. K. Hausser, *ibid.*, 7, 195 (1963-1964).

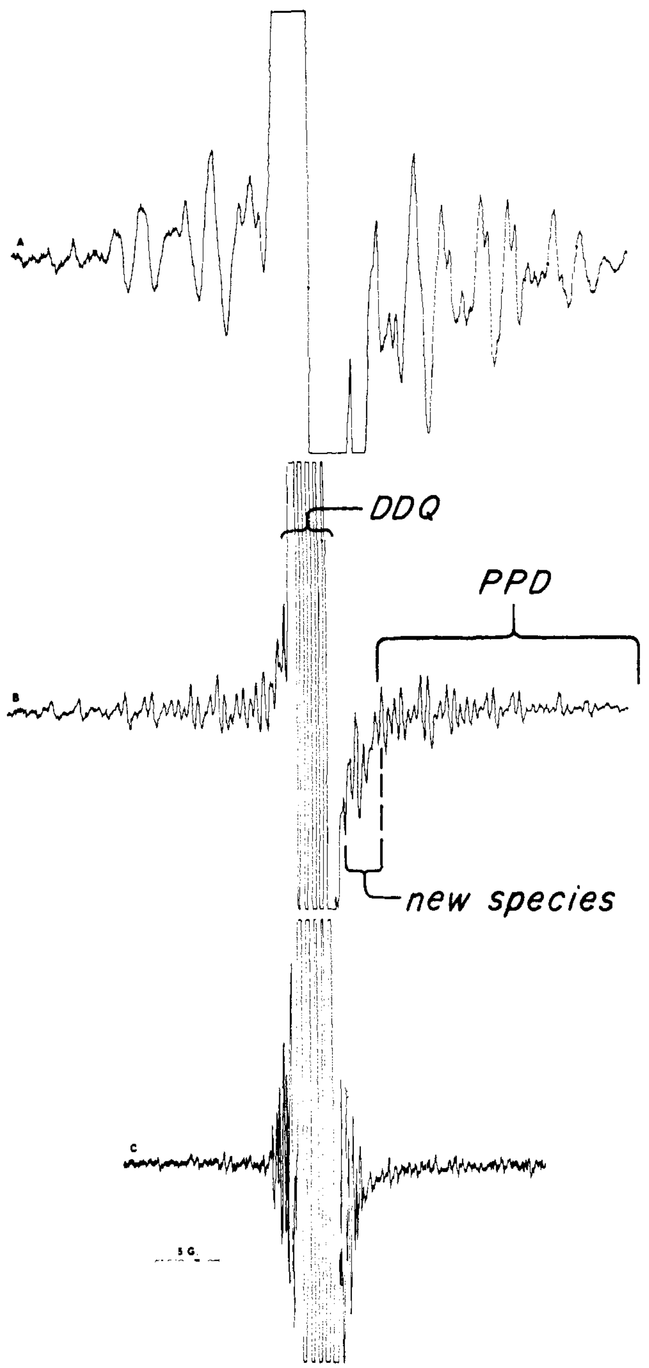

Figure 4. PPD–DDQ in CH_3CN: (A) flowing; (B) $PPD\cdot^+$ decaying; (C) $PPD\cdot^+$ decayed.

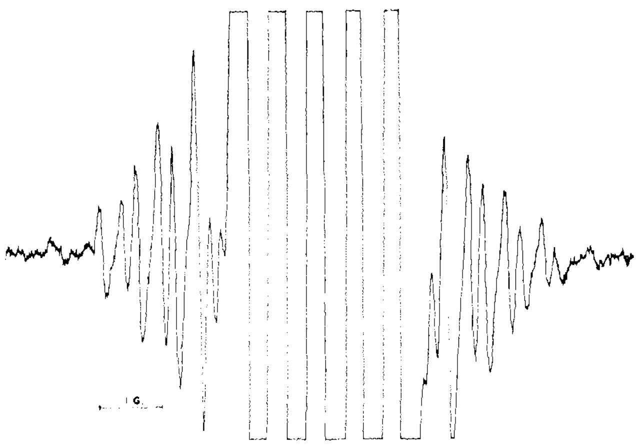

Figure 5. PPD–DDQ in CH_3CN after decay of $PPD\cdot^+$.

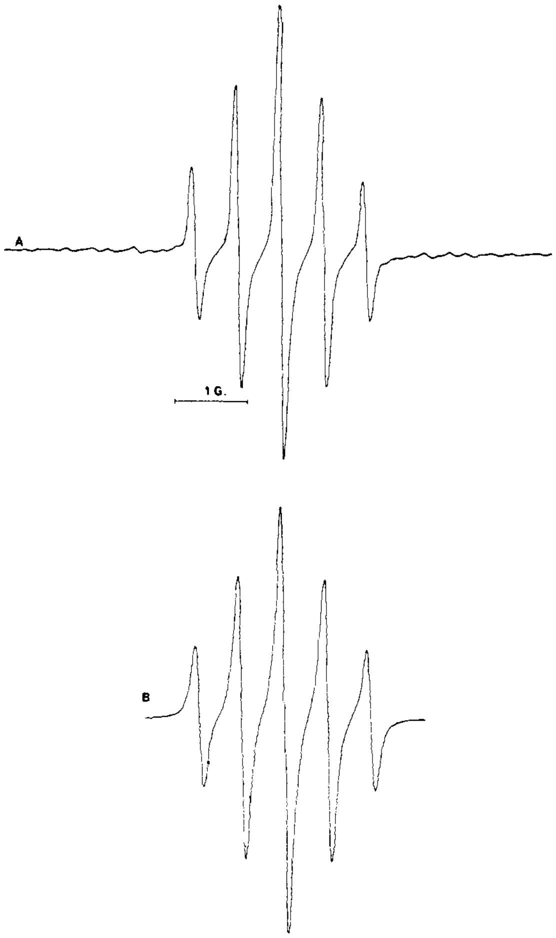

Figure 6. PPD–DDQ in CH_3CN: (A) after decay of $PPD\cdot^+$; (B) computer simulation of spectrum. a_N = 0.58 G, line width = 0.11 G.

spectral width as Figure 5, but the spectrometer gain was decreased in order to display the entire height of the $DDQ\cdot^-$ spectrum. The third species is still visible above the baseline.

Color changes which were noted when D and A solutions were mixed were taken as an indication of charge transfer; *e.g.*, a colorless solution of PPD and a light yellow solution of DDQ produced a dark red-brown solution immediately upon being mixed. The same color was observed when a blue solution of $PPD\cdot^+$ and a deep yellow solution of $DDQ\cdot^-$ were mixed. In addition, the complex PPD–DDQ left a brown residue on the walls of the esr sample tube after the solution had remained stationary during decay. When allowed to come into contact with the air, at the end of the flow system, the solution turned dark green. When d-PPD and DDQ were mixed, a red-brown solution again resulted. A deep purple color was observed when solutions in both CH_3CN and DME of TMPD and DDQ were mixed.

In the past, in general, considerations of solvent effects on charge-transfer complexes have been presented for systems in which charge transfer occurs upon photolysis, *i.e.*, in an excited state.[26,27] Solvent effects on the CT complexes PPD–DDQ, d-PPD–DDQ, and TMPD–DDQ may be studied by observing two sets of

(26) H. M. Rosenberg and D. Hale, *J. Phys. Chem.*, **69**, 2490 (1965).
(27) K. M. C. Davis and M. C. R. Symons, *J. Chem. Soc.*, 2079 (1965).

parameters: effects on hyperfine splitting constants and line widths, and effects on decay rates of radical ions.

From Table I, entries 1 and 11, 20 and 23, it can be seen that the hyperfine splitting constants for $PPD\cdot^+$ and $TMPD\cdot^+$ do not vary from CH_3CN to DME. Small variations in a_D/a_H for d-PPD from solvent to solvent (Table I, entries 8 and 17) are consistent with results obtained by Lawler, Bolton, Karplus, and Fraenkel.[28,29] The change in the nitrogen splitting constant from $PPD\cdot^+$ to d-$PPD\cdot^+$ in both solvents is of the same order of magnitude as that found by Das and Fraenkel for dihydropyrazine and dihydrotetramethylpyrazine cation,[30] and by Cole for NH_3^+ and ND_3^+.[31] The cause for this change has been ascribed to a vibrational mechanism. An alternative interpretation has been suggested which regards deuterium as a weakly electron-donating substituent, with respect to hydrogen.[32]

As discussed above, free-radical formation occurs in both solvents. However, the rate of decay (caused by dimerization, disproportionation, or formation of a diamagnetic CT complex) of some radical ions does vary from solvent to solvent (see Table I). Whereas $[PPD\cdot^+]$ decays at the same rate in CH_3CN or DME when produced by complex formation with DDQ, $[DDQ\cdot^-]$ decays far more rapidly in DME. The longer lifetime of $DDQ\cdot^-$ in CH_3CN may be related to the presence of the new species. When produced by CT with TMPD, $DDQ\cdot^-$ decays more slowly in DME than CH_3CN, while $TMPD\cdot^+$ decays more rapidly.

When D_2O or H_2O is added to either CH_3CN or DME, decay rates of $[PPD\cdot^+]$ or [d-$PPD\cdot^+$] and $[DDQ\cdot^-]$ are different from the rates in the absence of water. In the case of d-PPD–DDQ this is unfortunate in that [d-$PPD\cdot^+$] does not decay enough in relation to $[DDQ\cdot^-]$ during the course of an experiment to allow the positive identification of a third species or even positive confirmation of its existence. The third species in the d-PPD–DDQ system was to have aided in the identification of the third species in the PPD–DDQ in CH_3CN system. If the PPD were involved in the third species, replacing the amino protons with deuterons would change the spectrum of this species and thus allow assignment of splitting to these nuclei.

Since no new species is seen at all in DME, this is less critical but is an indication of a variation in properties caused by differences in solvent polarity. The same behavior as in $CH_3CN + 4\%\ H_2O$ was found for $PPD\cdot^+$ and $DDQ\cdot^-$ in DME to which 4% H_2O had been added, confirming that the addition of water must be affecting the DA complex or the separate ions.

The meaning of these varying decay rates in different solvents is difficult to pinpoint. The addition of H_2O or D_2O to DME represents a more drastic perturbation to the system (in terms of its polarity) than does the addition of H_2O or D_2O to CH_3CN. However, it is not clear whether the solvent polarity is responsible for the behavior of the CT complex and radical ions or if the water itself interacts with these species (other than by amino proton exchange) to alter their lifetimes.

A detailed consideration of the CT complex PPD–DDQ in CH_3CN will illustrate the usefulness of the flow system in obtaining information about the interaction between the donor and acceptor molecules in a charge-transfer complex in solution over an extended time. Figures 4–6 show a series of spectra recorded during an experimental run with this complex.

In Figures 4B and 4C, the superposition of the spectra of three paramagnetic species becomes evident. Two are immediately identifiable as $PPD\cdot^+$ and $DDQ\cdot^-$. The third species has about the same g value as $DDQ\cdot^-$ (it is centered at the same H-field value), which is higher than that of $PPD\cdot^+$. Its decay rate was found to be faster than that of $DDQ\cdot^-$ but far slower than that of $PPD\cdot^+$. That the third species is not produced by the reaction of either PPD, $PPD\cdot^+$, DDQ, or $DDQ\cdot^-$ with CH_3CN is obviated by its absence when either molecule or radical is dissolved separately in CH_3CN. The presence of the third species was confirmed in three completely separate experiments as described above.

Figure 5 is of value in the identification of the third species because it clearly shows all the absorption lines of the third species which do not lie under the $DDQ\cdot^-$ spectrum. There are several theoretically feasible compositions and structures which the new species may have. (1) It may be composed of a DDQ radical anion and molecule (DDQ has been known to form 1:2 D:A complexes) which are oriented in a coplanar fashion or with their planes parallel. (2) It may be composed of DDQ or $(DDQ)_2$ and PPD, where only one unpaired electron remains on the bi- or trimolecular entity, or where the two unpaired electrons are very far apart and do not affect each other, and in which the planes of the two or three molecules are coincident, or they are parallel.

If the PPD–DDQ complex is a π–π complex, the planes of the constituent molecules would be expected to be parallel. On the other hand, PPD as a donor may have both n and π character so that the two (or three) molecules in the complex might be oriented in a coplanar fashion with the amino nitrogens close to the DDQ entities. If the two (or three) molecular planes are parallel, the molecules may either be free to rotate with respect to each other or they may be fixed. If the molecules are coplanar, it is likely that only one orientation would be assumed.

Although (1) may be dismissed since the esr spectrum produced by either structure would not contain as many lines as that of the new species, there is no way of deciding among the structures in (2) on the basis of present information.

Interactions between $D\cdot^+$ and $A\cdot^-$ under other conditions were not demonstrated in these experiments. The complexes under consideration appeared to dissociate in solvents of high and low polarity, although such properties as lifetime and hyperfine coupling constants varied. Using a flow system such as this combined with esr spectroscopy to study complexes composed of weaker donors and acceptors might possibly shed more light on donor–acceptor interactions, since dissociation might not be complete.

Acknowledgment. The authors wish to thank Mrs. Suzanne S. Toce for her work on the TMPD–DDQ systems done under the Honors Program of Wellesley College.

---

(28) R. G. Lawler and G. K. Fraenkel, *J. Chem. Phys.*, **49**, 1126 (1968).

(29) R. G. Lawler, J. R. Bolton, M. Karplus, and G. K. Fraenkel, *ibid.*, 47, 2149 (1967).

(30) M. R. Das and G. K. Fraenkel, *ibid.*, 42, 792 (1965).

(31) T. Cole, *ibid.*, **35**, 1169 (1961).

(32) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963).