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## Electron Paramagnetic Resonance in Some Molecular Charge Transfer Complexes

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Electron paramagnetic resonance studies have been carried out on several new electron transfer molecular complexes in solid and liquid states. A paramagnetic complex is formed when triphenylamine, a strong donor, interacts with acceptors such as iodine, trinitrobenzene, or tetracyanoethylene. The system triphenylamine  $[(C_6H_5)_3N]$ -iodine was studied in more detail. Both in the solid and liquid state the donor positive ion radical of  $(C_6H_5)_3N$  was identified by a characteristic hyperfine structure due to the interaction of the paramagnetic electron with the nucleus of  $N^{14}$ . Further, the state of the  $[(C_6H_5)_3N]^+$  in solution, molten or solid, was ascertained through changes in the hyperfine structure corresponding to changes in the physical state. The integrated intensity of the  $[(C_6H_5)_3N]^+[I_2]^-$  complex in the solid state was found to increase with increasing temperature. The results can be described in general by the Curie-Weiss law which indicates the state of spins to be a ground doublet paramagnetic state with a  $g$ -value of  $2.0025 \pm 0.0002$ . The relaxation parameters  $T_2$  and  $T_1$  were found to be  $1.8 \times 10^{-9}$  and  $1.6 \times 10^{-5}$  sec., respectively, at room temperature. In solutions of these complexes where the paramagnetic electrons were identified by hyperfine structure, characteristic ultraviolet absorption bands were found. These bands can now be ascribed to electron-transfer transitions.

## Introduction

During the past decade a number of investigations have been concerned with the electric and paramagnetic properties of molecular complexes. Such complexes can be formed by the interaction of a number of molecules with a low ionization potential (donors) with a variety of molecules of high electron affinity (acceptors). A theory describing the interaction of donor and acceptor in the complex was formulated by Mulliken.<sup>1</sup>

For weak donors and acceptors, the molecular complex AD is formed by nonbonding van der Waals type forces and is at first approximation a singlet state with a slight admixture of a state in which electron transfer takes place giving rise to an ionic species  $A^-D^+$ . A typical property of the adduct AD is its characteristic optical absorption spectrum which is found in neither the donor nor acceptor molecule alone. An electron transfer process is assumed to be responsible for the optical absorption which leads to the first excited level in which the contribution of the ionic state is greater. However, for molecules with great donating and accepting power a complete electron transfer can take place in the ground state. The system, then, is paramagnetic and is expected to show free radical behavior; e.p.r. is observed in such systems and indicates the presence of unpaired electrons in such crystalline systems. However, the spectra obtained do not exhibit in general a hyperfine structure. Because of the lack of this information, it has been difficult to identify paramagnetic electrons. Since impurities, particularly carbonaceous material, give a single line spectrum there is always a possibility that the signal may be due to some species other than the complex.

Matsunaga,<sup>2</sup> Singer and Kommandeur,<sup>3</sup> and Bloemgren and Kommandeur<sup>4</sup> have observed e.p.r. absorption in solid complexes which are formed between polynuclear hydrocarbons as donors and halogens or antimony pentachloride as acceptors. Singer and Kommandeur<sup>3</sup> showed that these systems exhibit electrical conductivity. They further found that on raising the temperature of the system, the e.p.r. absorption increases, whereas at low temperatures it is independent of temperature. Singer and Kommandeur identified the unpaired electrons with charge carriers which could be thermally excited at high temperatures or frozen in traps at low temperatures.

Eastman, *et al.*,<sup>5</sup> observed e.p.r. signals in hydrocarbon-quinone complexes while Bijl, *et al.*,<sup>6</sup> measured a

temperature-independent signal in the arylamine-quinone complex.

We have found that triphenylamine is a strong donor and forms a paramagnetic complex with iodine. Hyperfine structure was observed in both liquid and molten states. Both the temperature dependence and the magnetic characteristics of the system (spin-lattice and spin-spin relaxation times) were examined. Furthermore, electron donor-acceptor complexes related to the above system were prepared and their paramagnetic properties investigated.

## Experimental

**A. E.p.r. Measurements.**—The e.p.r. measurements were performed in a Varian spectrometer (model V 4500) operating at 9.5 kMc./sec. and using a cavity operating at a TE<sub>102</sub> mode. The magnetic field was modulated at 100 kc./sec. Usually, the sample tubes were filled with the powder to a height greater than that of the resonant cavity. Because of the variation of the  $H_1$  field and the modulation amplitude over the length of the sample, the cavity was calibrated along the  $Z$ -axis using a very small crystal of DPPH. Accordingly, an effective length was determined to be 7 mm. This length of the sample would give the same signal intensity if the  $H_1$  and modulation fields were uniform along the  $Z$ -axis of the resonant cavity.

The technique developed by Singer<sup>7</sup> was used to determine spin concentrations. A single crystal of ruby was used as an internal standard, which remained in the cavity at all times. This ruby was then calibrated with a single crystal of  $CuSO_4 \cdot 5H_2O$  of known susceptibility.

The external magnetic field was modulated at 100 kc./sec. and the absorption derivative was recorded. Special care was taken to avoid saturation of the resonance line by using a sufficiently low microwave power. The modulation was less than 1/20 of the peak-to-peak measured line width.

Varian-designed temperature equipment was used. The samples were placed in a dewar in the maximum microwave field and the temperature was varied by controlling the flow of hot or cold gas. The magnetic field was measured by determining the frequency of the proton magnetic resonance with a Nuclear Magnetics Corp. precision gaussmeter. The frequency of the microwaves was determined by a heterodyne frequency meter.

The optical absorption spectra were obtained with a Cary model 14 recording spectrophotometer.

**B. Sample Preparation.**—The e.p.r. was measured on powders or solutions. Reagent grade chemicals were used for the preparation of complexes. Generally, the reactants were mixed in a solvent and then evacuated in order to exclude oxygen; the samples mixed in the solid state were also evacuated. Pyrex sample tubes were used for strong resonance absorption and pure quartz for weak absorptions. For the complexes where hyperfine structure was observed, the concentration of the complex in solution was varied in order to obtain good resolution. Solvents such as carbon tetrachloride, chloroform, dioxane, *n*-heptane, and tetrahydrofuran were used. Since the solubility of the reactants varied in the various solvents, solvents giving maximum solubility were used. The triphenylamine (reagent grade) was further purified by vacuum sublimation and the dioxane by distillation over sodium metal.

## Results and Discussion

**A. Temperature Effect on the Hyperfine Structure of  $(C_6H_5)_3N-I_2$  Complex.**—A mixture of 0.05 g. of tri-

(7) L. S. Singer, *J. Appl. Phys.*, **30**, 1463 (1959).(1) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).(2) Y. Matsunaga, *J. Chem. Phys.*, **30**, 855 (1959).(3) L. S. Singer and J. Kommandeur, *ibid.*, **34**, 133 (1961).(4) G. E. Bloemgren and J. Kommandeur, *ibid.*, **34**, 137 (1961).(5) J. W. Eastman, *ibid.*, **36**, 1197 (1962).(6) D. Bijl, *et al.*, *ibid.*, **30**, 765 (1959).

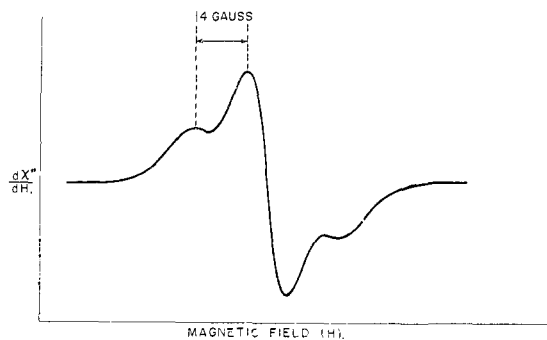


Fig. 1.—E.p.r. absorption of  $(C_6H_5)_3N$ -iodine complex at room temperature. The  $N^{14}$  hyperfine splitting is about 14 gauss.

phenylamine and 1.0 g. of iodine was allowed to react at room temperature in an evacuated tube. The reaction at room temperature was rapid and the homogeneity of the product was favored by vigorous shaking. Electron spin resonance was observed and could be used to follow the rate of interaction of triphenylamine and iodine. Equilibrium was established after 24 hr. The number of spins present, assuming a spin of  $1/2$ , was  $(4 \pm 0.5) \times 10^{18}$  per gram. The nature of the e.s.r. spectrum depended on the temperature of the preparation. At room temperature, Fig. 1, the sample showed three peaks with a splitting constant of 14 gauss. The effect of temperature is shown in Fig. 2.

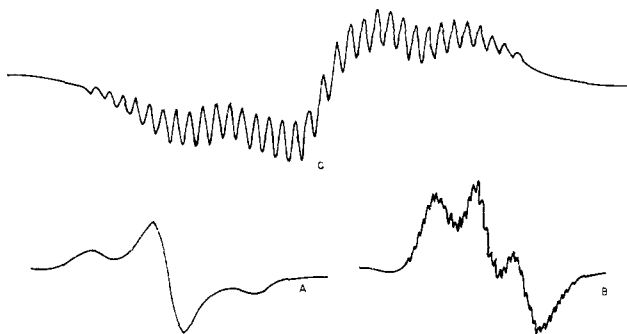


Fig. 2.—The effect of raising the temperature on the e.p.r. absorption of the  $(C_6H_5)_3N$ -iodine complex: A, e.p.r. absorption at  $75^\circ$ ; B, at  $130^\circ$ ; and C, at  $150^\circ$ . These spectra were obtained in the absence of oxygen. The superhyperfine splitting constant in spectrum C is 1.18 gauss.

At a temperature of  $75^\circ$  (A) the resonance line becomes broader and at about  $130^\circ$  (B) the three peaks are further split into a superhyperfine structure with each of the three peaks giving eleven lines with a hyperfine separation of 1.18 gauss. Raising the temperature to  $150^\circ$  (C) produced a better resolution of the superhyperfine structure, and the original three hyperfine peaks were overshadowed by the superhyperfine thirty-three peaks. At temperatures of  $180^\circ$  and higher, the superhyperfine structure disappeared and a broad band was observed. When a higher concentration of triphenylamine was used, a single line corresponding to  $(1 \pm 0.5) \times 10^{19}$  spins per gram was observed at room temperature. These effects are reversible on lowering the temperature.

The following is offered as an explanation for these observations. The three peaks observed at room temperature are undoubtedly associated with the interaction of the hole in the  $[(C_6H_5)_3N]^+$  radical cation with the nuclear magnetic moment of the nitrogen which has a spin of 1. The other component of the electron transfer complex, the electron associated with iodine, was not observed. A similar situation was also found for

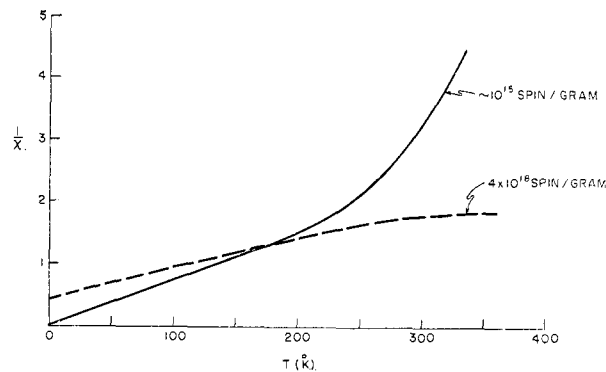


Fig. 3.—Variation of the reciprocal spin susceptibility with temperature for two different concentrations of  $(C_6H_5)_3N$  in iodine.

triphenylamine adsorbed on molecular sieves,<sup>8</sup> where the triphenylamine radical cation could be observed but the corresponding anion radical was not seen in e.p.r. measurements. Three explanations are possible: The electron may exchange so rapidly among the various acceptor iodine atoms and molecules present in the system that its e.p.r. line is broadened by the indeterminacy principle. Another possibility is that the electron may be trapped on such a variety of sites in the iodine system having a wide distribution of local magnetic fields resulting in such a broad e.p.r. signal that it was not observable. Finally, this may be due to short relaxation times of the electron associated with the iodine. It is interesting to note that in the case of semiconductors it is difficult to observe paramagnetic resonance from acceptors unless one applies a uniaxial stress to the crystals.<sup>9a,b</sup>

The appearance of the superhyperfine structure of 33 lines as the temperature of the system is raised probably is due to the weak association of the neutral iodine molecules with the positive triphenylamine cation radical which would give  $4 \times (5/2) + 1$  lines. This effect is not due to iodine atom interaction since the number of superhyperfine lines would be  $2 \times (5/2) + 1$ , or 6. It cannot be due to the iodine molecule or atom anion, since the 11 or 6 lines would be superimposed on a total of 3 lines due to the nitrogen and not appear as a superhyperfine structure. Above  $180^\circ$  the disappearance of the superhyperfine structure is due to the volatilization of the iodine and the breaking up of the electron transfer complex. On cooling, the original hyperfine structure with three bands reappears, showing that the formation of the complex is reversible.

The negative ion radical was neither observed in the case of polynuclear hydrocarbons in sulfuric acid nor in the perylene-iodine systems. Another explanation for the superhyperfine structure of 33 lines may be due to the partial resolution of the hydrogens on the phenyl groups which would have given 39 lines if the *ortho* and *meta* hydrogen atoms interacted and 48 lines if all the hydrogens were involved. We hope to clarify further this point by using deuterated triphenylamine with iodine.

The appearance of the superhyperfine structure of 33 lines as the temperature of the system is raised must be due to the weak association of the radical cation with the iodine molecule or, less likely in our opinion, to the partially resolved superhyperfine structure due to the phenyl hydrogens.

**B. Temperature Variation of E.p.r.**—The temperature dependence on the e.p.r. for two concentrations of the  $[(C_6H_5)_3N]^+[I_2]^-$  complex is shown in Fig. 3, where

(8) D. N. Stamires and J. Turkevich, to be published.

(9) (a) G. E. Pake, "Paramagnetic Resonance," W. A. Benjamin, New York, N. Y., 1962, p. 156; (b) W. Kohn, "Solid State Physics," Vol. 5, F. Seitz and Turnbull, Ed., Academic Press, Inc., New York, N. Y., 1957.

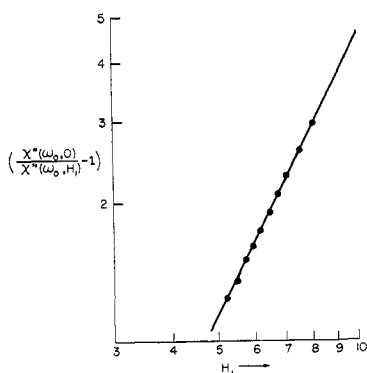


Fig. 4.—The saturation parameter  $Z$  is plotted as a function of  $H_1$  field. The saturation experiment was performed at room temperature on a  $(C_6H_5)_3N$ -iodine complex ( $\sim 10^{18}$  spins/gram).

the reciprocal of the e.p.r. signal in arbitrary units is plotted as a function of the absolute temperature. The e.p.r. measurements were carried out at a sufficiently low microwave power to avoid saturation effects. In both samples, the signal increased on lowering the temperature.

The sample with the high concentration of triphenylamine follows the Curie-Weiss law with a Weiss constant of  $-86^\circ K$ . This is taken to indicate that the triphenylamine free radicals interact with each other, which is consistent with the lack of a hyperfine structure in the resonance signal.

The sample with the lower concentration of the triphenylamine obeys the Curie law below  $200^\circ K$ . The absence of a Weiss field also is reflected in the appearance of a hyperfine and superhyperfine structure in e.p.r. Above  $200^\circ K$ , there was a marked decrease in the number of spins, which is what one would expect if the Curie law curve were extrapolated. A plot of the logarithm of the ratio of spins observed to the spins expected against the reciprocal of the absolute temperature produces a straight line of the Arrhenius type. This indicates an endothermic process which decreases the number of spins and has an energy requirement of 3.7 kcal. The process observed may be one of several types. It may be a combination of the triphenylamine radical anion with the unobserved iodine cation radicals. It is also possible that the sample contained impurities which combined to give a diamagnetic product.

Another approach to the interpretation of the temperature variation is to assume that the system consists of a low lying triplet and a high lying diamagnetic singlet at energy  $E$ .<sup>8</sup> Then, the temperature would change the population between these states and the susceptibility would vary according to

$$\chi = \frac{A}{T(\exp^{-E/ki} + 3)}$$

Our data on the triphenylamine-iodine system cannot be described by this formulation.

Published data on the temperature variation of the e.p.r. for other types of electron transfer complexes are of little help, since they indicate varied behavior for each particular complex examined. Thus, in the arylaminequinone complexes,<sup>6</sup> and in the hydrocarbonquinone complexes,<sup>5</sup> the e.p.r. is independent of temperature. On the other hand, in hydrocarbon halogen complexes the e.p.r. decreases exponentially with decreasing temperature and reaches a constant value at low temperature. The situation is more complex in the diaminodurene-chloranil complex and the sodium tetracyanoethylene complex.<sup>10</sup> In the first system,

(10) D. B. Chestnut and W. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1961).

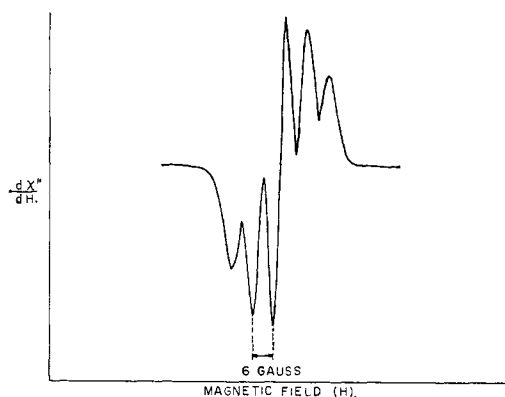


Fig. 5.—E.p.r. absorption of  $(C_6H_5)_3N$ -iodine complex in dioxane solution at room temperature in the absence of oxygen. The hyperfine splitting is 6 gauss for the five lines. The same spectrum is obtained when chloroform or benzene is used as solvent.

the e.p.r. absorption correspondingly decreased with temperature, where the high temperature part of the curve corresponds to a singlet triplet model for pairwise correlation of the ground singlet state and to an excited triplet state having a definite energy separation. In the second system of sodium tetracyanoethylene, the absorption first decreased as the temperature was decreased from  $175$  to  $0^\circ$  and then increased as the temperature was lowered to  $-180^\circ$ . The high temperature part of the curve is interpreted as due to the transition from the triplet to the singlet state with an energy separation of 6 kcal. The low temperature part of the curve is attributed to a doublet state from a very small amount of impurity.

Further work is necessary on various systems in order to present a consistent picture from the existing data.

**C. E.p.r. Saturation Measurements.**—The progressive saturation method developed by Bloembergen, *et al.*,<sup>11</sup> was used to measure  $T_1$  of a highly concentrated triphenylamine-iodine complex at room temperature. The saturation parameter  $Z$  was plotted (Fig. 4) in the form of a logarithm as a function of the

$$Z(\omega_0, H_1) = \frac{\chi''(\omega_0, H_1)}{\chi''(\omega_0, 0)} = \frac{1}{1 + \frac{1}{4}\gamma^2 H_1^2 T_1 T_2}$$

$$\log \left[ \frac{\chi''(\omega_0, 0)}{\chi''(\omega_0, H_1)} - 1 \right] = 2 \log H_1 + \log \left[ \frac{\gamma^2}{4} T_1 T_2 \right]$$

radiofrequency field intensity  $H_1$ . It gives a straight line from which the value of the product  $T_1 T_2$  can be obtained. The values of  $H_1$  were obtained using samples of ruby with known  $T_1$  and  $T_2$  as standards. A detailed account of this method for obtaining  $T_1$  will be given in another communication. By using the line width of 36 gauss as measured between the extreme slope points of the e.p.r. curve and by assuming a Lorentzian shape for the line, a value of  $1.8 \times 10^{-9}$  sec. was obtained for  $T_2$ , the spin-spin relaxation time. The value of  $g$  was  $2.0025 \pm 0.0002$ . The spin-lattice relaxation time  $T_1$  was then calculated to be  $1.6 \times 10^{-5}$  sec. This rather long value of the spin-lattice relaxation time shows that the interaction of the widely scattered ( $10^{18}/g$ ) spins with the lattice of iodine is rather weak. The value of  $g$  close to that of a free electron indicates that the hole is localized in the triphenylamine molecule. However, the fact that there is an unresolved structure in the e.p.r. indicates that the magnetic levels of the electron in the  $[(C_6H_5)_3N]^+$  radical are rather strongly coupled to the  $N^{14}$  nuclear levels. Some dipolar broadening and inhomogeneity in the dis-

(11) N. Bloembergen, *et al.*, *Phys. Rev.*, **73**, 679 (1948).

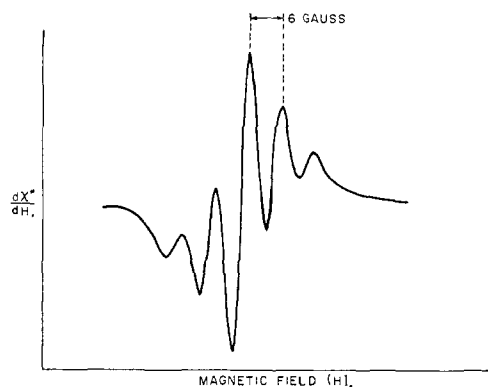


Fig. 6.—E.p.r. absorption of  $(\text{C}_6\text{H}_5)_3\text{N}$ -trinitrobenzene complex in dioxane at room temperature and in the absence of oxygen. The hyperfine splitting of the five lines is 6 gauss.

persion of spins could produce some broadening of the line.

#### Formation of Paramagnetic Complexes in Solution.—

A paramagnetic complex is formed if one mixes solutions of triphenylamine and iodine in one of a variety of solvents: chloroform, benzene, dioxane. The choice of solvent is limited by the solubility of the reactants. The solutions were evacuated to avoid the broadening effect of oxygen on the hyperfine structure. The e.p.r. absorption of triphenylamine and iodine in chloroform mixed in equimolecular amounts is shown in Fig. 5. The over-all line is symmetrical and has a  $g$ -value of  $2.0025 \pm 0.0002$ , which is the same as that of the complex formed in the solid state or in molten iodine. The hyperfine structure, however, consists of five lines having a splitting constant of 6.0 gauss. This hyperfine structure is unexpected. It cannot be due to the interaction of the hole with the one nitrogen nucleus of the triphenylamine since the number of peaks would be three ( $2 \cdot 1 + 1$ ). This type of hyperfine structure was observed in the system of triphenylamine in both solid iodine and molten iodine.

A plausible explanation for this hyperfine structure is the formation of a bimolecular triphenylamine radical ion  $[(\text{C}_6\text{H}_5)_3\text{N}:\text{N}(\text{C}_6\text{H}_5)_3]^+$  in which the hole is localized to an equal extent on the two nitrogen nuclei, each with a spin of one. This gives the observed hyperfine structure of five lines ( $2 \cdot 2 \cdot 1 + 1$ ). The following observations support the existence of a true complex. First, a proper dilution must be made to observe this hyperfine structure, because in the more concentrated solutions the individual lines became broader. There was no appearance of colloid particles as was noted in the hydrocarbon  $\text{SbCl}_5$  case.<sup>4</sup> Also, the presence of dissolved oxygen, if not removed by evacuation, broadens the line.

In order to understand more thoroughly the electron transfer that takes place between the triphenylamine and iodine, analogous systems were studied involving triphenylamine with acceptors other than iodine and iodine with donors other than triphenylamine.

Triphenylamine will transfer electrons to a number of acceptors. When dissolved in chloroform or dioxane, it will react with a solution of trinitrobenzene to give a deep green solution and an e.p.r. signal (Fig. 6) of 5 hyperfine lines with a separation constant of 6 gauss and a value of  $g$  of 2.0025 for the center of the hyperfine multiplet. The e.p.r. spectrum is identical with that which is obtained with iodine as an acceptor. It will also react with a chloroform solution of tetracyanoethylene, a strong acceptor. In this case, a green color develops with an e.p.r. spectrum of five poorly resolved lines. Triphenylamine will react with tetrachloro-

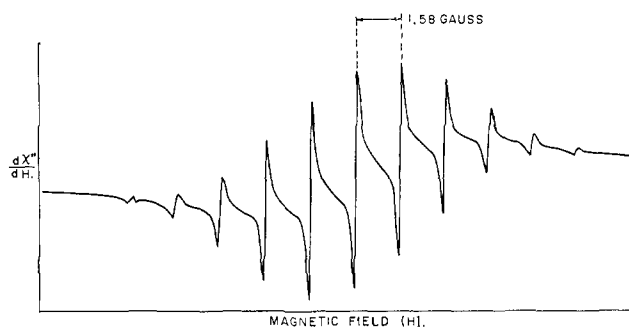


Fig. 7.—E.p.r. absorption of  $\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$ -tetracyanoethylene electron transfer complex in dioxane at room temperature. The 11 lines have a hyperfine splitting constant of 1.58 gauss.

quinone in chloroform to give a strong e.p.r. spectrum with no resolvable hyperfine structure. In all cases but the last, the identity of the hyperfine structure indicates that this signal observed is due to the same donor radical cation which strengthens the point of view that there must be a dimerization of the triphenylamine in the radical cation.

Another set of experiments was set up to investigate the acceptor properties of the iodine molecule. Previous work has shown that iodine was an acceptor which gives paramagnetic complexes with polycyclic aromatic hydrocarbons such as violanthrene, perylene, pyrene, pyranthrene, while  $\alpha, \alpha, \beta, \beta$ -tetra-(4-dimethylamino-phenylethylene)<sup>12</sup> gives no spin resonance. However, the species responsible for the e.s.r. were not identified by resolving their hyperfine structure. In contradistinction to the rather uniform and consistent behavior of triphenylamine with various acceptors, the spin resonance behavior of iodine-donor complexes varies widely with the nature of the donor. Thus, with perylene, a distinctly resolved hyperfine spectrum is obtained in molten iodine. It is identical with that obtained with sulfuric acid. If one interacts perylene with iodine in  $\text{CCl}_4$ , a precipitate is formed which gives a single sharp line. This system of perylene-iodine is not too different from that of triphenylamine-iodine. On the other hand, no spin resonance is observed in solutions of iodine and the donors aniline, diphenylamine, and 1,4-diazabicyclo[2.2.2]octane,  $\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$ . However,  $p$ -phenylenediamine and iodine in  $\text{CCl}_4$  form a precipitate which shows a single line resonance. On the other hand, the precipitate formed with  $\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$  is diamagnetic. However, in the solid reactions of iodine, either at room temperature or slightly elevated temperatures, with aniline, diphenylamine, and phenylenediamine, an e.s.r. signal was observed. In none of these cases was the hyperfine structure of the acceptor anion radical of the iodine species detected. It should be noted that solid iodine or molten iodine is a better acceptor than dissolved iodine.

Iodine differs markedly as an acceptor from another strong acceptor, tetracyanoethylene. When  $\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$  in chloroform or dioxane solution is treated with a tetracyanoethylene in the same solvent, an e.p.r. signal is obtained with a well resolved hyperfine structure of 11 lines with a separation of  $1.58 \pm 0.02$  gauss and an intensity ratio of 1:4:10:16:19:16:10:4:1 (shown in Fig. 7). The  $g$ -value of the center of this complex is close to that of a free electron. In this case, the e.p.r. measurement discloses the spectrum of the anion radical. The appearance of the spectrum is the same as that reported for the product of the interaction of sodium and tetracyanoethylene in tetrahydro-

(12) G. Briegleb, "Electronen-Donator-Acceptor Komplexe," Springer, Berlin, 1961.

furan.<sup>13</sup> The hyperfine spectrum finds a theoretical explanation for both number and intensity of the components in the interaction of the electron with the four nitrogen atoms of ( $N^{14}$ ) to give 9 lines and with a small amount of  $C^{13}$  to give the first and eleventh line of the complex.

Thus, the e.p.r. spectrum of the anion radical can be detected in the particular case of sodium or  $N(CH_2CH_2)_3N$  and tetracyanoethylene. We did not succeed in finding the appropriate donor, solvent, and concentration required to find the e.p.r. spectrum of the iodine anion radical. The iodine can be seen indirectly, by using e.p.r. in the high temperature interaction of triphenylamine and iodine. It appears there as a superhyperfine structure of 11 lines of the iodine molecule superimposed on 3 hyperfine lines of the nitrogen of triphenylamine.

A variety of factors determine both the electron transfer tendency of the donor-acceptor system and the stability of the resultant complex. The energy involved is certainly the resultant of at least the energy of ionization of the donor, the electron affinity of the acceptor, and the energy of solvation when it is different from that of the reactants. Undoubtedly, the resonance energy of the hole in the donor and the electron in the acceptor must play a role. Steric effects may hinder a sufficiently close approach of the two partners which would be required for electron transfer to take place. The insolubility of the complex may remove it from solution, and the insoluble precipitate may or may not give an e.p.r. line. When it does give one, it is in the form of a single line which gives little information about the nuclear environment of the unpaired electron or hole. It may unexpectedly give none, as in the case of  $N(CH_2CH_2)_3N$  and iodine, where the former is a good donor and the latter a good acceptor, but interact to give a diamagnetic species. Another situation may arise in which the scavenging by impurities, particularly of the colloidal type, or a rapid interchange with structurally similar nonradical species, may so broaden the line and thus reduce its intensity, that it becomes undetectable. It should be noted that systems which are considered to form electron transfer complexes such as pyridine-iodine, triethylamine-iodine, with equilibrium constants of 2,110 and 43,100, respectively, show no e.p.r. signals in solutions, which indicates little electron transfer *per se*, from the nitrogen base to the iodine.<sup>12</sup>

Only further research will show what factors dominate electron transfer, but triphenylamine-iodine and related compounds offer a convenient system for exploring these factors.

#### Optical Spectra of Electron Transfer Complexes.—

For a number of years, evidence of the existence of electron transfer complexes has been presented by indicating the appearance of new absorption bands or the shift of existing absorption bands when donor molecules interact with acceptor molecules either in the pure form or solution.<sup>12</sup>

These bands were interpreted by Mulliken to be due to charge transfer transition which takes place in the  $\pi$ -complexes which are formed, for example, when polynuclear hydrocarbons as donors react with good  $\pi$ -acids

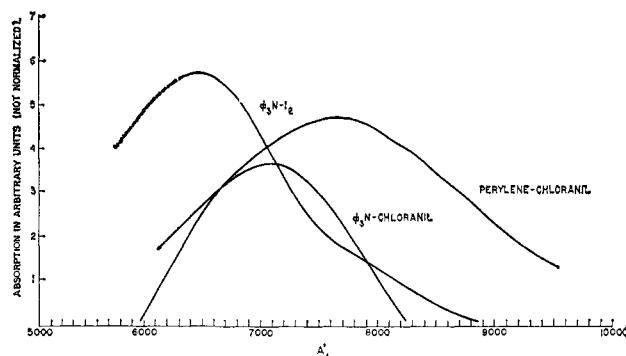


Fig. 8.—Electron-transfer absorptions of  $(C_6H_5)_3N$ -iodine,  $(C_6H_5)_3N$ -chloranil, and perylene-chloranil complexes in  $CHCl_3$  solution. The absorption scale is in arbitrary units. The shift in frequency of the electron-transfer transitions is illustrated for the  $(C_6H_5)_3N$ -iodine and  $(C_6H_5)_3N$ -chloranil complexes.

such as tetracyanoethylene. McConnell, *et al.*,<sup>14</sup> were able to correlate the wave length of the absorption band to the ionization potential of the electron donors and the absorption intensities to the properties of the acceptor.

However, most of the complexes so formed are diamagnetic. Thus,  $I_2$  interacts to form complexes with benzene to give a band at 2980 Å. and with naphthalene at 3590 Å. Yet the chloroform solution of these complexes shows no e.p.r. signal. Thus, the interaction in these cases, and in most others reported, does not lead to a separation of charge. The interaction in these cases must be assumed to be rather weak with the electrons, which in the aromatic ring interact weakly with the vacant antibonding orbital in the iodine molecule. Because of the spatial configuration of this antibonding orbital due to its large radius, an overlap of the orbital can be expected between the hydrocarbon and the iodine. The resulting interaction is responsible for the electronic absorption which may lead to a true charge transfer in the excited state. The interaction between the donor and acceptor must be considerably stronger to give rise to a charge separation in the ground state, since this can be detected by the sensitive methods afforded by e.p.r.

The system of  $(C_6H_5)_3N-I_2$  in chloroform shows strong absorption at  $\sim 6500$  Å. (Fig. 8) which can be assigned to an electron transition associated with ion radicals formed in the ground state, since the system shows an e.p.r. signal with a hyperfine structure identifiable as the radical ion  $[(C_6H_5)_3N]^+$ . Similar absorption bands were observed in the case of the triphenylamine-chloranil system and the perylene-chloranil system, both of which show a true electron charge transfer which gives an e.p.r. signal. The latter system was shown earlier to be a paramagnetic complex,<sup>5</sup> and its spectrum was reported by Eastman.

At present, we are continuing our investigation of the relation of the absorption spectra of the donor-acceptor complexes to the electron spin resonance of such systems.

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