reported to be 0.056 at 65°. This value compares reasonably with that found in the course of this work, *i.e.*, 0.03, which was carried out in the liquid phase. We have some reservation about Holmes and Kutschke's results, which are discussed elsewhere.[18] It seems that these workers did not eliminate the reaction $CF_3(CH_3)\cdot C_6H_5\cdot + CF_3 \rightarrow CF_3(CH_3)\cdot C_6H_4 + CF_3H$. Participation of this step in their reaction might account for their high value of k_3'/k_2.

NOTE ADDED IN PROOF.—The reaction of CF_3 radicals with toluene performed in the gas phase at 65° showed that $CF_3H/N_2 = 0.071$ leading to $k_3/k_2 = 0.037 \pm 0.003$, in agreement with our liquid phase results. In these experiments the concentration of hexafluoroazomethane was varied by a factor of 5 without affecting the CF_3H/N_2 ratio. Only minute amounts of C_2F_6 (less than 0.5%) were observed in the products.

In conclusion, we wish to acknowledge the financial support of this investigation by the National Science Foundation Grant G-19044.

(18) P. S. Dixon and M. Szwarc, *Trans. Faraday Soc.*, in press.

[CONTRIBUTION FROM THE INSTITUTE FOR MUSCLE RESEARCH AT THE MARINE BIOLOGICAL LABORATORY, WOODS HOLE, MASSACHUSETTS]

Solvent Effects in Radical Ion Formation[1]

BY IRVIN ISENBERG AND SPENCER L. BAIRD, JR.

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Electron spin resonance techniques indicate that the interaction of tetramethyl-*p*-phenylenediamine and chloranil will lead to the formation of Wurster's blue and chloranil free radicals in polar solvents but not in non-polar solvents. Presumably, this occurs through the dissociation of a charge transfer complex. Similar results are obtained for the interaction of diethylaniline and chloranil.

Introduction

Mulliken[2] pointed out that solvent effects should alter the nature of donor–acceptor interaction. In general, one may expect polar solvents to increase the amount of charge transferred.[3] In the present note it will be shown, in a rather direct fashion, that changing from a non-polar solvent to a more polar solvent can be accompanied by a change from complex formation in which there is little or no dissociation to form free radicals, to one in which there is appreciable free radical formation.

The complexes studied were tetramethyl-*p*-phenylenediamine/chloranil and diethylaniline/chloranil. Solvent polarity was altered by using various mixtures of chloroform, 1,2-dichloroethane and ethanol.

The use of the tetramethyl-*p*-phenylenediamine/chloranil system has a number of advantages. The charge transfer complex has been previously studied.[4] The free radical ions of each partner have been investigated by spin resonance methods[5–7] and consequently can be identified easily. Furthermore, another rather unexpected advantage, to be described below, also occurs.

Technique.—Optical spectra were run on a Cary Model 14 Spectrophotometer. Electrin spin resonance spectra were run on a Varian Model V-4500 Spectrometer modified to run as a double modulation instrument.[8] A flat quartz specimen chamber of internal dimensions approximately 0.3 mm. × 5 mm. × 25 mm. was used for all spin resonance studies.

N,N,N^1,N^1-Tetramethyl-*p*-phenylenediamine dihydrochloride (Eastman) was dissolved in water, neutralized with KOH and extracted with ether. The ether was pumped away. The residue was redissolved in ether, dried with $MgSO_4$, filtered and dried by pumping. The powder was melted in a molecular still and distilled onto a cold finger. The white crystalline solid thus obtained was kept at approximately −40° until used.

Chloranil (Matheson, Coleman and Bell) was recrystallized twice from acetone.

Ethanol, 1,2-dichloroethane and chloroform were redistilled before use.

Diethylaniline was distilled twice in a Hickman still. After the second distillation it was pale yellow, almost colorless.

Experimental Procedure and Results

A flow system using a four jet nylon mixing chamber and nitrogen pressure was used to mix 10^{-2} *M* chloranil in chloroform and 10^{-2} *M* tetramethyl-*p*-phenylenediamine in ethanol in equal amounts and flow the mixture into the electron spin resonance sample tube. This yielded a signal showing a superposition of the chloranil free radical and the Wurster's blue free radical (Fig. 1). The time for the liquid to flow from the mixing chamber into the flat portion of the sample tube could be varied from about 1 sec. to about 10 sec. without any observable change in the signal. When the flow was stopped the chloranil free radical gradually diminished, dropping about 15% per minute while the Wurster's blue free radical concentration did not change.[9] This rather striking constancy was observed a number of times and permitted a simplification of technique.

Since the Wurster's blue concentration did not change, the effect of the solvent could be observed without the use of a mixing chamber. The tetramethyl-*p*-phenylenediamine and chloranil solutions could thereafter be mixed by hand. The sample chamber could then be filled and a spectrum taken. By observing the hyperfine components on the far wings of the Wurster's blue free radical where they were

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(1) This research was sponsored by grant No. RG-9144(R1) from the National Institutes of Health.

(2) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

(3) (a) O. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer Verlag, Wien, 1961. (b) J. W. Eastman, Thesis, University of California, 1961.

(4) H. Kainer and A. Uberle, *Chem. Ber.*, **88**, 1147 (1955).

(5) J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **23**, 2441 (1955).

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

(7) G. E. Pake, S. I. Weissman and J. Townsend, *Discussion Faraday Soc.*, **19**, 147 (1955).

(8) I. Isenberg, S. L. Baird, Jr., and A. Szent-Gyorgyi, *Proc. Natl. Acad. Sci.* (U. S.), **46**, 1307 (1960).

(9) After about an hour there appears to be a perceptible diminution in the Wurster's blue concentration.

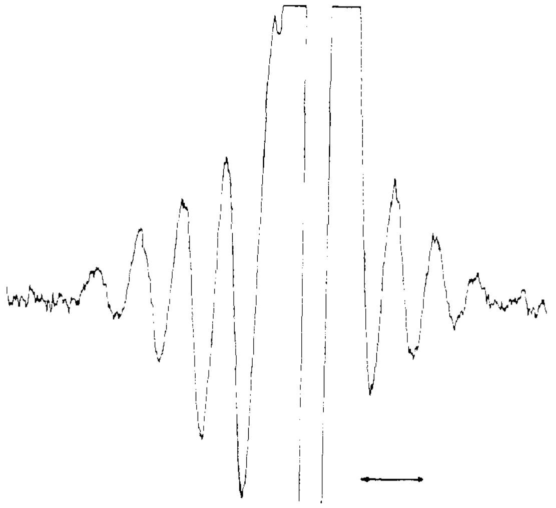

Fig. 1.—Second derivative of the e.s.r. absorption in a flow experiment. 10^{-2} M Chloranil in chloroform and 10^{-2} M tetramethyl-*p*-phenylenediamine in ethanol were forced into a mixing chamber under nitrogen pressure and then into the sample chamber. The central narrow peak which runs off the chart paper is the chloranil free radical while the other peaks are the hyperfine components of the Wurster's blue free radical. The marker indicates 10 gauss. The central peak was retraced.

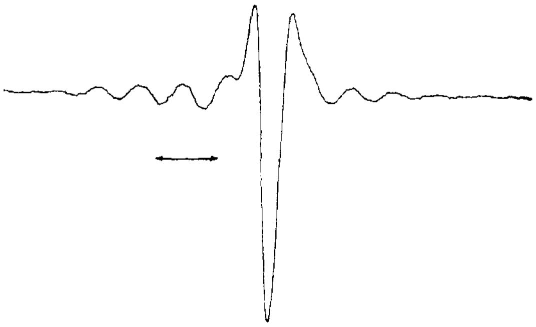

Fig. 2.—Same as Fig. 1 except that the flow system was stopped to permit the chloranil signal to decrease until both signals could be observed on the same scale.

minimally affected by the chloranil spectrum, the effects of various solvents could be noted. In all of the samples run in this fashion it was also noted that, while the chloranil free radical concentration diminished, the Wurster's blue concentration was constant. The same phenomena could be observed using a spectrophotometer in the visible range (Fig. 3) and taking repeated runs on the same sample.[10]

Tetramethyl-*p*-phenylenediamine and chloranil yielded little or no signal in chloroform. In mixtures of chloroform and 1,2-dichloroethane or chloroform and ethanol relatively large resonance signals were observed. Furthermore, the strength of the signal increased with the polarity of the medium (Figs. 4 and 5).

The diethylaniline chloranil system showed similar features. Here, too, there was no detectable free radical formation in chloroform. As the polarity of the solvent increased, an electron spin resonance signal was obtained becoming larger with increasing polarity. The signal yielded no hyperfine structure. It had a g value of 2.0055 ± 0.0004 and a line width of about one gauss. This is apparently the signal of the chloranil free radical.[5] However, in this case the signal did not decrease with time. In fact, there was a slight but definite increase with time. It should also be noted that in this case efforts to observe a superposition of two free radicals with the use of a flow system met with no success.

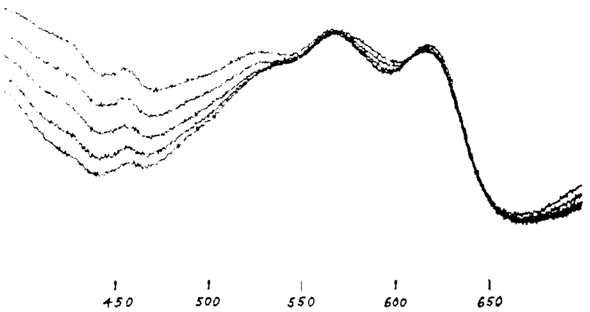

Fig. 3.—Repeated runs in a Cary Spectrophotometer of 5×10^{-3} M chloranil and 5×10^{-3} M tetramethyl-*p*-phenylenediamine in 50–50 chloroform–ethanol. The Wurster's blue absorption remains constant while the low wavelength region shows a decrease on successive runs.

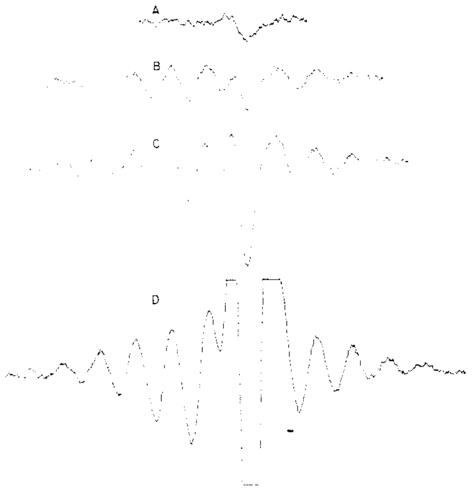

Fig. 4.—3.3×10^{-3} M Chloranil and 3.3×10^{-3} M tetramethyl-*p*-phenylenediamine in mixtures of chloroform and ethanol: A, no ethanol; B, 8.3% ethanol; C, 16.7% ethanol; D, 25% ethanol. Marker shows one gauss.

Discussion

It seems reasonable to assume that radical ions are formed from donor–acceptor interaction *via* a charge transfer complex, namely

$$D + A \rightleftarrows DA$$

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

Probably the most important factor in free radical ion formation is the lowered free energy of the free radical ion state due to ion–solvent interaction. This would tend to stabilize the free radical state with respect to other states of the system.

It is possible that solvent interaction could also influence the first step above, perhaps accompanied by an alteration of charge in the complex. The ground state of the complex is a superposition of a "no bond" state and a "dative" state. Interaction with the solvent could enhance the contribution of the dative state and hence lead to a stronger transfer of charge in the ground state. If an inner complex

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[10] The simplification of technique described here will work only with certain solvents. For example, it has been observed that with dimethyl formamide the Wurster's blue signal starts to decrease after only a short period of time.

in the Mulliken[2] sense existed, the transfer or charge would be greatly enhanced.

The work reported here is consistent with the observations of Bijl, Kainer and Rose-Innes[11] and Kainer and Uberle.[4] These authors noted that the color of a mixture of tetramethyl-*p*-phenylenediamine and chloranil was closer to the color of the free radical in polar solvents than in non-polar solvents. They furthermore showed that a strong paramagnetic component existed in the solid complexes.

In this connection the observations of Miller and Wynne-Jones[12] should be mentioned. Using techniques of electrical conductivity and optical absorption, they obtained evidence for the existence of complexes of an ion pair type ($D^+ A^-$). The interactions were solvent sensitive and the complexes could apparently dissociate in sufficiently polar media into separate ions.

Eastman,[3b] working in Calvin's laboratory, has obtained results paralleling those obtained in our Laboratory. Tetramethyl-*p*-phenylenediamine and chloranil in acetonitrile yielded two superimposed free radical signals in spin resonance, one due to Wurster's blue and the other due to chloranil. He also observed that little or no free radical could be observed in non-polar media.

The enhancement of charge transfer and free radical production by polar solvents probably will turn out to have a rather general significance. As such, it may have biochemical implications. The formation of free radicals in biochemical systems takes place in an aqueous environment and interactions with the medium may be expected to play a significant role.

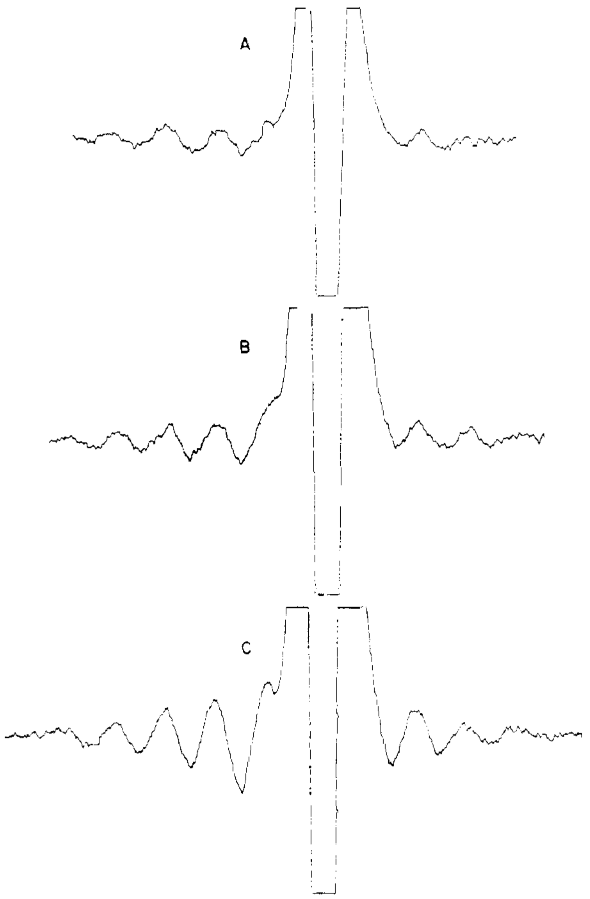

Fig. 5.—3.3 × 10^{-3} *M* Chloranil and 3.3 × 10^{-3} *M* tetramethyl-*p*-phenylenediamine in mixtures of chloroform and 1,2-dichloroethane: A, 67% 1,2-dichloroethane; B, 83% 1,2-dichloroethane; C, 100% 1,2-dichloroethane.

The authors wish to thank S. I. Weissman for discussions on these and related problems and M. Ashraf El-Bayoumi for calling their attention to the thesis by Eastman.

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