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CHARGE-TRANSFER ASSOCIATION AND PARAMAGNETISM OF SOME ORGANIC SYSTEMS

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CHARGE-TRANSFER ASSOCIATION AND PARAMAGNETISM OF SOME ORGANIC SYSTEMS

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PREFACE

By 1959 there were sufficient experimental data to justify proposing a mechanism for the primary act of photosynthesis. At that time, Tollin, Sogo and Calvin reviewed new evidence obtained in this laboratory (1). They proposed a mechanism by which oxidizing and reducing entities could be separated in plants. It was shown how the chemical oxidation and reduction reactions of photosynthesis could proceed independently by way of these separated species. The separation itself required electron donors and acceptors. Thus photoinduced excitation may be transferred to chemical potential by way of these ionizing donor and acceptor molecules.

At this time very little is known about the mechanism of ionized electron transfer between organic molecules. It was our general purpose to examine electron transfer between organic donors and acceptors in general. We wanted to determine the conditions for which electronic ionization and electron transfer occur in organic systems. Questions about the mechanism of photosynthesis stimulated us to initiate this research. We were originally motivated too by the results of work carried out in laboratories at Tokyo and Oxford.

In 1954 Akamatsu, Inokuchi and Matsunaga at the University of Tokyo discovered the paramagnetism of hydrocarbon-halogen solids (2). These homogeneous solids were prepared stoichiometrically from polycyclic-aromatic-hydrocarbons and halogens. Independently at Oxford in 1954 Kainer, Bijl and Rose-Innes observed electron spin resonance in arylamine-quinone solids (3).

Both of these complex organic solids are composed of electron donors and acceptors. The fact that paramagnetism was observed may mean that electron transfer and concomitant unpairing does occur in these donor-acceptor combinations. The pioneering work at Tokyo and Oxford paved the way for the present investigation. The present work is partly a continuation of the research begun in those laboratories.

Specifically the purpose of the present work was to determine the conditions for which unpaired electrons could be produced by excitation or ionization in donor-acceptor systems. Previously in our own laboratory Kearns (4) demonstrated that laminated combinations of alternating donor and acceptor solids generally contain unpaired electrons. Our purpose was to examine the homogeneous solids and liquid solutions of donors and acceptors such as those investigated at Tokyo and at Oxford.

Because quinones have been found in plants, we decided to limit the choice of acceptor molecules to quinones. Both arylamines and aromatic hydrocarbons have been used as donors. These particular donor-acceptor combinations have been examined both in solids and liquids.

Results and their interpretations are presented first. Experimental methods are described in Chapter V. For conclusions derived from this work, refer to Chapter VI. Structural formulas for the organic compounds used, analyses of the experimental methods, and other details are presented in the appendix.

It is hoped that the experiments described in this work illuminate the essential observable features of charge-transfer association and paramagnetism. No attempt has been made to review the existing theories of donor-acceptor interaction or electron spin resonance.

ABSTRACT

When p-xylene was combined with chloranil in n-heptane, charge-transfer optical absorption was observed. The magnitude of this absorption is used to calculate an equilibrium constant for the formation of a donor-acceptor complex containing one p-xylene and one chloranil molecule. When p-xylene was combined with carbon tetrabromide and with carbon tetrachloride in n-heptane, no charge-transfer absorption was observed.

Reactions of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) with chloranil ($pQCl_4$) have been observed in ethylene dichloride and acetonitrile. In both solvents adduct formation occurs initially, as observed by its charge-transfer absorption. In acetonitrile time-dependent electron spin resonance (ESR) absorption was observed, and it is identified with the positive and negative radical ions of TMPD and $pQCl_4$, respectively. In this case a completely ionized electron transfer has occurred.

Chloranil and other quinones were found to react with N,N-dimethylaniline forming a crystal violet salt. The diamagnetic donor-acceptor complexes and also semiquinone radicals are intermediates which have been observed. Some physical measurements of the kinetics of this reaction are described and correlated. When fluoranil was allowed to react with dimethylaniline, the hyperfine splitting by the fluorine atoms of the fluoranil radical was not resolved. Characteristics of the ESR absorption by this radical in dimethylaniline

are discussed in terms of an electron transfer between the semiquinone and quinone, and between the semiquinone and hydroquinone ion.

Paramagnetism has been discovered in hydrocarbon-quinone solids. ESR absorption is assigned to imperfections in the solid which is normally diamagnetic. The preparation of these solids and some of their physical characteristics are described.

I. INTRODUCTION

A. A description of donor-acceptor complexes.

The association of certain organic molecules in solution generates a color which is present in neither of the individual components. The color is produced by excitation of an adduct or complex which is formed by the association of charge-donor molecules with charge-acceptors. Molecules which have low ionization potentials, the charge-donors, generally do combine with molecules which have high electron affinities, the charge-acceptors. The donor-acceptor adduct itself is colored. The adduct is called a charge-transfer complex[≠] and its electronic excitation causes charge-transfer absorption.

Mulliken has shown that a simple bonding scheme which approximates the bond between a donor (D) and an acceptor (A) is

$$(D{:}A) = \underline{D\ldots A} \longleftrightarrow D^{+} - A^{-}.$$

D:A is the complex; D...A, the no bond part, represents bondingly London forces; $D^{+} - A^{-}$, the dative part, represents bonding by exchange and ionic forces. Experimental evidence indicates that usually the ground state of the donor-acceptor bond is mostly just London attraction, as indicated by the underlining in the bonding scheme. Of course, this illustration is a simplification; Briegleb and Czekalla (5,6), Booth (7) and McGlynn (8) have recently reviewed the nature of charge-transfer bonding in detail.

The corresponding excited state of the complex $(D{:}A)^{*}$ may be written

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≠ In this thesis, the terms charge-transfer complex, donor-acceptor complex and polarization complex are used synonomously.

$$(D:A)^* = D...A \longleftrightarrow \underline{D^+ - A^-},$$

where the bonding is mostly ionic. According to Mulliken's theory, the singlet-singlet excitation, $(D:A) \longrightarrow (D:A)^*$ causes charge-transfer from the donor to the acceptor molecule within the adduct. It is this charge-transfer absorption which gives the complex its characteristic color.

Charge-transfer adducts have dipole moments in the ground state. This is because the donor becomes positive and the acceptor negative in the complex. Indeed, the dipole moments have been used to calculate the percentage of dative $(D^+ - A^-)$ character in the bond (8).

The infrared spectra of the complexes frequently are very similar to superpositions of the spectra of the individual components. In some solutions measurable differences do occur; these changes of intensity and frequency are adequately explained by the theory of charge-transfer bonding (9).

When donors and acceptors are combined in solution, the electronic spectra, the dielectric polarization, and the infrared spectra of these solutions are observable physical properties which depend intimately upon adduct formation. Interpretation of these data provides a detailed insight into the nature of bonding between charge-donors and charge-acceptors.

In solution donors and acceptors may exist in equilibrium with their adducts, if the adduct is a thermodynamically stable species. Equilibrium constants and heats of formation have been determined for many donor-acceptor complexes. Heats of formation are usually between one and 10 kcal/mol (5).

There is no *a priori* reason why charge-transfer complexes or solids should be paramagnetic. As a matter of fact, no one complex has ever been determined unequivocally to be magnetic itself. However, electron spin resonance absorption has been observed in a few solids composed of donor-type and acceptor-type molecules (10,11,12). It has never been demonstrated whether the magnetism is due to the donor and acceptor properties of the individual molecules directly, to a new kind of donor-acceptor association, or to donor-acceptor interaction of the familiar type which we have been discussing here. It is with this problem that the present work is concerned.

B. Hexamethylbenzene-chloranil as an example.

The adduct hexamethylbenzene-chloranil has been investigated in a number of laboratories and serves as an interesting historial example of donor-acceptor association. Briegleb and Czekalla measured the association constant, $K = 9.25\ (\frac{mol}{l})^{-1}$ in carbon tetrachloride (13). The heat of formation $\Delta H = -5.15$ kcal, and the entropy factor, $T\Delta S = -3.8$ kcal. Foster, Hammick and Parsons obtained $K = 28.9\ (\frac{mol}{l})^{-1}$ in cyclohexane (14). The charge-transfer absorption frequency of this complex is 19,350 cm^{-1} in carbon tetrachloride and 19,800 cm^{-1} in cyclohexane (13,14).

Briegleb and Czekalla (13) measured the dipole moment of the hexamethylbenzene-chloranil adduct. The dipole moment, 1.00 D, was used to calculate 4.4% ionic character in the ground state (5).

Harding and Wallwork (15) determined the crystal structure of the one:one solid complex of hexamethylbenzene-chloranil. Hexamethylbenzene and chloranil molecules are stacked alternately in columns. The direction of bonding along the stack is perpendicular to the rings which are nearly parallel.

Nakamoto measured the optical dichroism of this solid (16). Absorption of light polarized perpendicular to the aromatic planes was greater than absorption polarized in the plane. The frequency of maximum absorption was lower for perpendicularly polarized light than for light polarized in the aromatic plane.

The infrared spectrum of the solid can be approximated by superimposing the individual spectra of the donor and the acceptor (17).

C. The present work.

Our aim has been to characterize the magnetic species observed in systems which also contain charge-transfer complexes. In Chapter II we first discuss new results concerning the charge-transfer association of some molecules in solution. This is a general investigation from which we progress to the specific observations of paramagnetism. The transfer of electrons from N,N,N',N'-tetramethyl-p-phenylenediamine to chloranil has been studied and the results are presented at the end of Chapter II.

The oxidation-reduction reaction of chloranil with N,N-dimethylaniline has been studied. The free radicals, charge-transfer complexes and ions present in this reaction are discussed in Chapter III.

Chapters II and III are concerned with the production of paramagnetic species in solution. The paramagnetism of some solid complexes is the subject of Chapter IV. In that chapter are presented the ESR absorption and other physical properties of donor-acceptor solids formed by polycyclic-aromatic-hydrocarbons and tetrahalogenated quinones.

Each chapter is reviewed and discussed independently, and conclusions derived from the entire work are presented in Chapter VI.

II. INTERACTION OF DONORS AND ACCEPTORS IN LIQUID SOLUTIONS

A. Association of p-xylene

The charge-transfer association of p-xylene with chloranil, carbon tetrabromide and carbon tetrachloride in n-heptane solutions has been studied by optical absorption spectroscopy from 240 mμ to 1200 mμ.

1. p-xylene-chloranil. If C is the electron acceptor, chloranil, and X is the donor, p-xylene, in n-heptane, the two are in equilibrium with a one:one molecular complex which is observed by its unique charge-transfer absorption spectrum (14).

$$C + X = CX$$

$$K = \frac{(CX)}{(C)\ (X)}$$

If p-xylene is present at a concentration, (X), much higher than that of chloranil, (C), the association constant K is

$$K = \frac{(CX)}{[(C_o) - (CX)]\ (X_o)} .$$

(C_o) and (X_o) are the total concentrations of all species containing C and X molecules respectively. If D is the observed optical density of the solution, d is the length of the absorption cell, and ϵ is the extinction coefficient of the charge-transfer absorption by the complex,

$$\frac{d(C_o)}{D} = \frac{1}{\epsilon} + \frac{1}{\epsilon K(X_o)} .$$

When $\frac{d(C_o)}{D}$ is plotted as a function of $1/(\xi_{X_o})$, a straight line results whose intercept and slope may be used to calculate the extinction coefficient and association constant. This is the familiar Benesi-Hildebrand relation.

Because the charge-transfer optical absorption maximum occurred at the same wavelength as an absorption by unassociated chloranil, the calculation was made at wavelengths longer than the absorption maximum. The extinction coefficient at the maximum was determined by subtracting the chloranil absorption after the equilibrium concentration of chloranil was determined.

Table 1 and Figure 1 give the experimental data and calculated functions used to determine the association constant, $K = 1.35\ mol^{-1}$ $\pm$ 5% at 27°C.

The absorption spectra of chloranil and of the p-xylene-chloranil complex are illustrated in Figure 2. $\lambda_{max} = 420$ mμ, $\epsilon_{max} = 1380 \left(\frac{mol}{l}\right)^{-1} cm^{-1}$ in n-heptane. Foster (18) has reported a $\lambda_{max} = 395$ mμ in carbon tetrachloride. Foster, et al. (14) report that chloranil and m-xylene have an association constant in cyclohexane of 2.9 $(mol/l)^{-1}$ (18°-20°C) and exhibit charge-transfer absorption at 395 mμ. The results of the present work are in qualitative agreement with the work of Foster, et al. Why the charge-transfer frequencies should differ by as much as 25 mμ is uncertain.

2. p-xylene-carbon tetrabromide. A saturated solution of CBr_4 in p-xylene showed no electronic absorption between 400 mμ and 1200 mμ. Below 400 mμ both CBr_4 and p-xylene themselves absorb so that special methods had to be employed in the search for charge-transfer absorption.

Table 1

Calculation of the association constant of p-xylene-chloranil

$(C_o) \times 10^4$	(X_o)	D $\lambda = 460$ mμ	D $\lambda = 470$ mμ	D $\lambda = 480$ mμ
3.35	1.26	0.414	0.327	0.240
3.41	0.457	0.271	0.215	0.163
4.00	0.583	0.351	0.279	0.207
4.02	0.242	0.181	0.147	0.109
5.02	0.328	0.289	0.229	0.169
5.00	0.1001	0.120	0.094	0.069
10.0	0.442	0.755	0.602	0.450
Intercept x 10^4		5.1	6.1	8.0
Slope x 10^4		3.60	4.35	6.44
K		1.42	1.40	1.24

$K = 1.35 \pm 5\% \ (\frac{mol}{l})^{-1}$

Temperature = $27^oC \pm 2^oC$

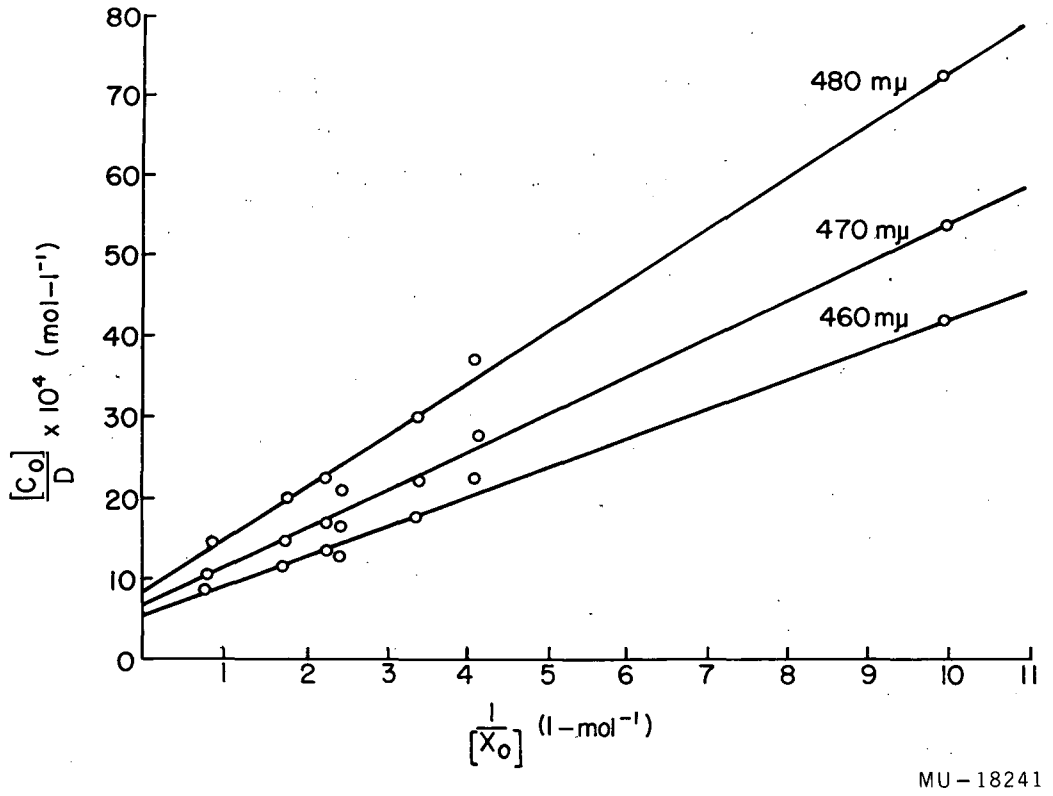

Fig. 1. Charge-transfer absorption at 460 mμ, 470 mμ and 480 mμ by p-xylene-chloranil in n-heptane as a function of the xylene concentration.

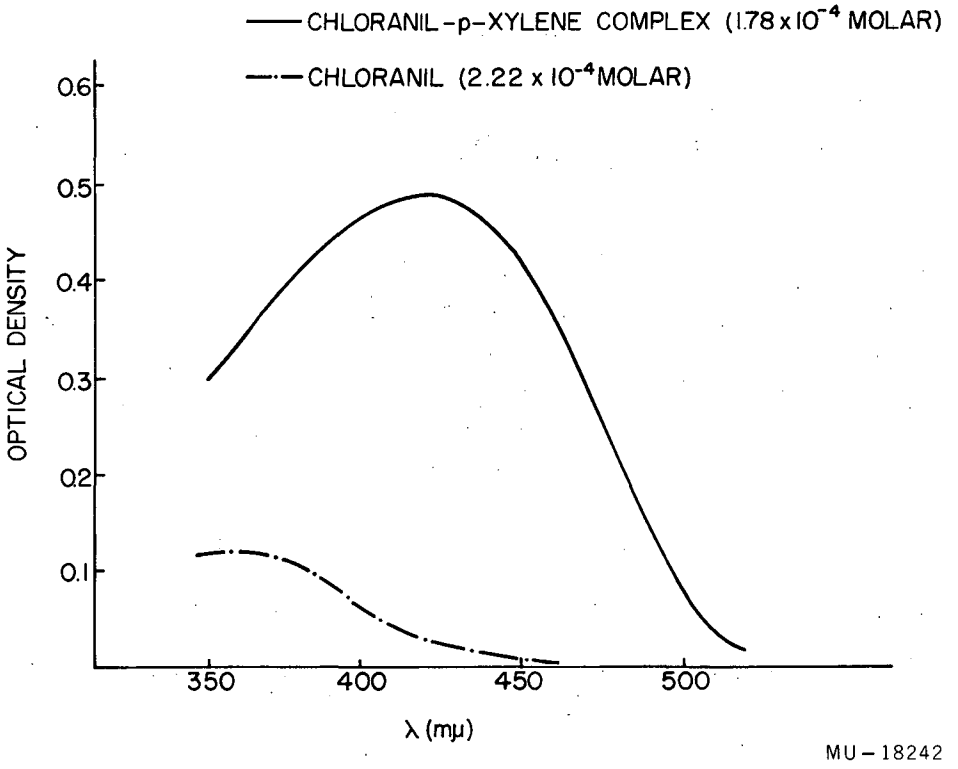

Fig. 2. Absorption spectrum in n-heptane of p-xylene-chloranil using a 2 cm cell.

The method of Landauer, McConnell and Lawrey (19) has been used to place an upper limit on the association constant for CBr_4 and p-xylene, if any complexing occurs.

In a solution containing CBr_4, C, and p-xylene, X, there is the possibility of forming a complex, CX. As before, the association constant, K, is

$$K = \frac{(CX)}{[(C_o) - (CX)]\ (X_o)}$$

when the total concentration of species containing X is much greater than the concentration of species containing (C). The optical density, D, measured in cell of length d, is

$$\frac{D}{d} = \epsilon_x(X) + \epsilon_c(C) + \epsilon_1(CX)$$

The adduct (ϵ_1) will be observed only if its absorption spectrum is measurably different from the spectra of the components (ϵ_x and ϵ_c). When the solution is flooded with xylene the concentration of CX is

$$(CX) = \frac{K\ (C_o)\ (X_o)}{1 + K(X_o)}$$

and

$$\frac{1 + K(X_o)}{(\epsilon_1 - \epsilon_c)K} = \frac{d\ (X_o)(C_o)}{D - d\epsilon_x(X_o) - d\epsilon_c(C_o)}$$

When the right hand function, to be called Q, is experimentally determined and plotted as a function of (X_o), the slope and intercept of the straight line may be used to determine the association constant, K.

Between 300 mμ and 400 mμ the observed optical density, D, was just the sum of the initial optical densities of the components themselves, $D_a = d\epsilon_x(X_o) + d\epsilon_c(C_o)$ (Table 2).

The denominator of the function

$$Q = \frac{d(X_o)\ (C_o)}{D - d\epsilon_x(X_o) - d\epsilon_c(C_o)} = \frac{d(X_o)\ (C_o)}{D - D_a}$$

is no greater than about 0.01, Q itself is $Q \geq .06$. Therefore,

$K \leq \dfrac{1}{.06(\epsilon_1 - \epsilon_c) - (X_o)}$. In this wavelength region $\epsilon_c \leq 50$, and (X_o) is negligible compared to reasonable guesses for $\epsilon_1 \sim 1000$.

$$K\epsilon_1 \leq 17\ \text{mol}^{-2}\text{-l}^2\text{mm}$$

$$K \leq .02\left(\frac{\text{mol}}{\text{l}}\right)^{-1}$$

A more detailed study was made between 250 mμ and 300 mμ where the accuracy was limited by stray absorption by xylene. Tables 3 and 4 show that within about 10% the absorption, D, by solutions of both p-xylene and CBr_4 was just the sum, D_a, of the absorptions by the independent components, $D_a = d\epsilon_x(X_o) + d\epsilon_c(C_o)$. The large variation in the actual differential (-1% to 58%) is attributed to the instrumental difficulties of measuring accurately and rapidly the optical density in this highly absorbing and highly peaked region.

In this case $Q \geq .03$ and $K \leq \dfrac{1}{.03\ (\epsilon_1 - \epsilon_c) - (X_o)}$

For wavelengths between 260 mμ and 300 mμ, considering the usual width of charge-transfer absorption bands and taking $\epsilon_c \ll \epsilon_1 \approx 10^3$, $K \leq .03\ \left(\frac{\text{mol}}{\text{l}}\right)^{-1}$, which is the same limit assigned at higher wavelengths.*

---

* Because ϵ_c becomes appreciable between 250 mμ and 300 mμ it may be difficult to estimate a maximum K value. This is especially true because the extinction coefficient of the complex may be the same as that of CBr_4, in which case there might be no change in the observed optical density if xylene were added. Addition of p-xylene would cause a decrease in the absorption by unassociated CBr_4 but a proportional increase in absorption by the complex so that the optical density would remain the same. Based upon the extinction coefficients reviewed by McConnell, Ham and Platt (20), between about 250 mμ and 260mμ it may not be possible to estimate K by optical methods.

Table 2

Search for p-xylene-CBr_4 complex in n-heptane solution between 300 mμ and 400 mμ

$(X_o) = 0.100$ mol-l^{-1}; $(C_o) = 3.09 \times 10^{-3}$ mol-l^{-1};

d = 2.0 cm

λ(mμ)	$d\epsilon_x X_o$	$d\epsilon_c C_o$	D_a	D	$D - D_a$
310	0.033	0.347	0.380	0.393	0.013
330	0.009	0.058	0.067	0.058	-0.009
350	0.009	0.008	0.017	0.006	-0.011
370	0.007	0.002	0.009	0.000	-0.009

Table 3

Search for p-xylene-CBr_4 complex in n-heptane solution

Wavelength dependence

λ(mμ)	$d\epsilon_x X_o$	$d\epsilon_c C_o$	D_a	D	$D - D_a$	$\frac{100\ (D - D_a)}{D}$
Experiment 1. 0.403 molar p-xylene. 0.0307 molar CBr_4. d = 0.05 mm						
320'	0.000	0.001	0.001	0.000	-0.001	0 %
300	0.000	0.015	0.015	0.022	0.007	32
280	0.080	0.055	0.135	0.158	0.023	15
272	0.521	0.092	0.613	0.667	0.054	8.1
262	0.766	0.160	0.926	1.024	0.598	58
250	0.311	0.223	0.534	0.632	0.098	16
235	0.064	0.700	0.764	0.816	0.052	6.4
Experiment 3. 0.087 molar p-xylene. 0.00761 molar CBr_4. d = 0.5 mm						
280	0.135	0.011	0.146	0.160	0.014	8.8
267	1.820	0.026	1.846	1.820	-0.026	-1.4
262	1.318	0.035	1.353	1.379	0.026	1.9
250	0.581	0.043	0.624	0.666	0.042	6.4

Table 4

Search for p-xylene-CBr_4 complex in n-heptane solution

Concentration dependence

λ(mμ)	X_o	$d\epsilon_x X_o$	$d\epsilon_c C_o$	D_a	D	$D - D_a$
Experiment 2: C_o = 0.0077 molar. d = 0.25 mm						
264	ϵ_x = 32.8 mol^{-1}-l mm^{-1},		ϵ_c = 84.1 mol^{-1}-l mm^{-1}			
"	0.0796	0.654	0.163	0.817	0.849	0.032
"	0.0730	0.600	"	0.763	0.763	0.000
"	0.0614	0.504	"	0.667	0.664	-0.003
"	0.0492	0.404	"	0.567	0.569	0.002
"	0.0398	0.327	"	0.490	0.504	0.014
"	0.0306	0.251	"	0.414	0.434	0.020
255	ϵ_x = 23.3 mol^{-1}-l mm^{-1},		ϵ_c = 10.9 mol^{-1}-l mm^{-1}			
"	0.0796	0.462	0.212	0.676	0.713	0.037
"	0.0730	0.425	"	0.637	0.643	0.006
"	0.0614	0.358	"	0.570	0.578	0.008
"	0.0492	0.286	"	0.498	0.503	0.004
"	0.0398	0.232	"	0.444	0.349	-0.095
"	0.0306	0.178	"	0.390	0.410	0.020
Experiment 3: C_o = 0.00761 molar. d = 0.05 mm						
262	ϵ_x = 32.6 mol^{-1}-l mm^{-1},		ϵ_c = 93.0 mol^{-1}-l mm^{-1}			
"	0.402	0.655	0.035	0.690	0.660	-0.030
"	0.474	0.774	"	0.839	0.766	-0.073
"	0.557	0.909	"	0.944	1.216	0.272
"	0.642	1.048	"	1.083	1.059	-0.024
"	0.721	1.176	"	1.211	1.213	0.002
"	0.807	1.318	"	1.353	1.379	0.026
267	ϵ_x = 45.2 mol^{-1}-l mm^{-1},		ϵ_c = 69.01 mol^{-1}-l mm^{-1}			
"	0.402	0.908	0.026	1.169	0;854	-0.315
"	0.474	1.07	"	1.096	0.995	-0.0266
"	0.557	1.26	"	1.286	1.578	0.026
"	0.642	1.45	"	1.476	1.392	-0.026
"	0.721	1.63	"	1.656	1.595	-0.026
"	0.807	1.82	"	1.846	1.820	-0.026

Keeping in mind that a weak charge-transfer absorption by the complex may possibly be buried in the spectrum of the individual components and that there may be absorption at higher energies than at 240 mμ, the results of these experiments show that charge-transfer complexing by CBr_4 and p-xylene in n-heptane solution is negligible. If charge-transfer absorption occurs at wavelengths greater than 240 mμ, the equilibrium constant for association is estimated as $K \leq 0.02\ (\frac{mol}{l})^{-1}$.

3. p-xylene-carbon tetrachloride. The results of this experiment are the same as for the p-xylene-CBr_4. The results summarized in Table 5 have been used to determine an upper limit for association, $K \leq 0.01\ mol^{-1}$-l.

Discussion

The results of this work indicate that association of p-xylene and CBr_4 does not occur in n-heptane. This is in contrast with the association of p-xylene with bromine which does occur, as is already well known. In solution CBr_4 does not appear to form complexes with xylene although bromine does. p-Xylene-bromine absorbs optically at 306 mμ and the adduct has a formation constant $K = 2.26\ (\frac{mol}{l})^{-1}$ (21).

Benzene itself, as well as p-xylene, forms a donor-acceptor adduct with bromine. Charge-transfer absorption by the benzene-bromine adduct occurs at 292 mμ (21). It has a formation constant $K = 1.04\ (\frac{mol}{l})^{-1}$.

These two examples show what is well known, that bromine does form adducts with benzene-like donors, in general. On the other hand, we have found that association of CBr_4 with p-xylene is very small, if it occurs at all. Thus bromine acts as an acceptor much more effectively than does CBr_4.

Table 5

Search for p-xylene-CCl_4 complex in n-heptane solution.

Wavelength dependence

C_o = 0.00471 molar; X_o = 0.402 molar; d = 0.05 mm

λ(mμ)	$d\,\epsilon_x X_o$	$d\,\epsilon_c C_o$	D_a	D	$D - D_a$	$\frac{100\,(D-D_a)}{D}$
280	0.070	0.000	0.070	0.059	-0.011	-16%
272	0.454	"	0.454	0.412	-0.042	- 9.2
267	0.909	"	0.909	0.820	-0.089	- 9.8
264	0.711	"	0.711	0.632	-0.079	-11.1
262	0.672	"	0.672	0.609	-0.063	- 9.4
255	0.490	"	0.490	0.448	-0.042	- 8.6
250	0.290	"	0.290	0.263	-0.027	- 9.3
240	0.089	"	0.089	0.079	-0.010	-11.2
280 - 1200	0.000	"	0.000	0.000	0.000	0.0

Comparison of the acceptor properties of bromine and CBr_4 in liquid solution does not apply evidently to their acceptor properties in the solid. The crystal structure of the one:one solid complex p-xylene-CBr_4 was solved by Strieter (22). It is very similar to the structure of benzene-bromine, which was reported by Hassel and Stromme (23). The intermolecular bond distances are, in fact, nearly identical. In both cases, the bromine atoms are aligned along the six-fold axis of the benzene ring, located 3.36 Å from the plane.

If we assume there is a relation between bond energy and bond distance it appears that in the solid, Br_2 and CBr_4 associate with benzene-like compounds equally well. However, the similarities of the solids p-xylene-CBr_4 and benzene-Br_2 disappear when the solids are dissolved.

Because of uncertainties in the optical method of detecting complex formation, it would be wise to investigate CBr_4 association in solution by other methods and with other donors. Then the general validity of the conclusions arrived at here may be tested.

B. Ionization in solutions of donors and acceptors.[f]

So far we have considered only that kind of donor-acceptor interaction which results in the formation of a colored complex. As we noted earlier, there is no evidence that any of the adducts studied up to now are paramagnetic. However, radical ions may be produced if the donor has a very low ionization potential and the acceptor has a high electron affinity. The ions are formed by the transfer of an electron from the donor to the acceptor. We have tried to produce

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[f] We consider here only cases in which electron transfer, not ion transfer, produces ionized species.

just this kind of ionization in a variety of systems. Before presenting our results, we will review all of the experimental evidence obtained prior to our work which shows that ionized electron transfer is possible in solutions of organic donors and acceptors.

1. Experimental evidence. Kainer and Uberle (24) observed the optical absorption spectra of the radical ions $TMPD^+$ and $pQCl_4^-$ when solid TMPD-$pQCl_4$ was dissolved in acetonitrile. TMPD is N,N,N',N'-tetramethyl-p-phenylenediamine; $pQCl_4$ is tetrachloro-p-benzoquinone (chloranil). Kainer and Uberle proposed that a complete electron transfer from donor to acceptor occurs in these solutions. It is plausible to assume that charge-transfer complexes are intermediates in this overall ionization. Ionization of TMPD-$pQCl_4$ did not occur in dioxane and benzene which have lower dielectric constants than acetonitrile.

Also electrons may be donated from TMPD to the acceptor tetracyanoethylene, and ions are produced (5).

The formation of intermediate complexes, radicals and ions have been observed in the reaction of trinitrobenzene (an acceptor) with various donors (25,26,27,28,29). ESR absorption was observed in the reaction of trinitrobenzene with trimethylamine (30).

The initial reaction of bromine and $\alpha,\alpha',\beta,\beta'$-tetrakis-(4-methoxyphenyl)-ethylene produces a blue paramagnetic solution in nitroethane, a brown diamagnetic solution in carbon tetrachloride as observed by ESR (31). The effect of dielectric constant on ionization was again demonstrated. Paramagnetism was observed in the polar nitroethane

but not in nonpolar carbon tetrachloride.[7]

At this preliminary stage, the chemical literature contains few quantitative studies of electron transfer between organic molecules in solution (as opposed to charge-transfer). However there is plenty of experimental evidence to show that charge-transfer complexes, ions, and radicals to appear together in many reactions. The phenomenon of ionization has been reviewed by Briegleb and Czekalla (5) with some specific reference to dielectric effects.

2. N,N,N',N'-Tetramethyl-p-phenylenediamine-chloranil (TMPD-$pQCl_4$). We have somewhat extended the work of Kainer and Uberle (24), who observed the optical spectra of the radical ions $TMPD^+$ and $pQCl_4^-$ in acetonitrile. They showed that in solvents of high enough dielectric constant an ionized electron transfer from TMPD to $pQCl_4$ takes place. We have qualitatively investigated the conditions under which this ionization occurs.

We have found that solutions of TMPD and $pQCl_4$ are not stable, even in the absence of air. When equimolar quantities of TMPD and $pQCl_4$ were dissolved in acetonitrile, two distinct ESR absorptions were observed (Figure 3a). A narrow single line, which we have assigned to the chloranil semiquinone, was superimposed on a set of thirteen triplets attributed to the TMPD positive ion. The latter has been characterized by Tuttle (35), Hausser (36) and others. The narrow $pQCl_4^-$

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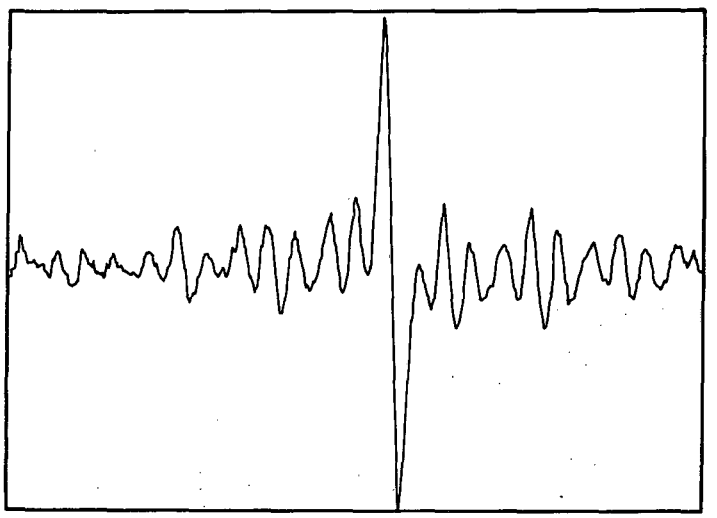
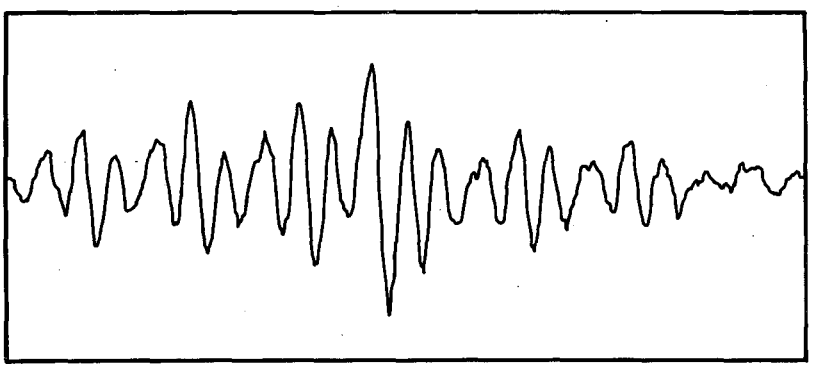
[7] SO_3, $SbCl_5$ and BF_3 have been used to accept electrons from aromatic hydrocarbons (32,33). ESR of the aromatic positive ions produced have been investigated in some detail (34). These inorganic acceptors appear to form sigma complexes rather than pi charge-transfer complexes as intermediates in the ionization reaction (32).



A



B

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Fig. 3. Derivative of the ESR absorption observed by dissolving equimolar amounts of TMPD and $pQCl_4$ in acetonitrile. Reaction time: (a) 25 min; (b) 1 hour.

resonance began decreasing rapidly and the $TMPD^+$ resonance increased proportionately as soon as the original solution was prepared (Figure 5b). Simultaneously the optical absorption by the semiquinone at 4500 Å decayed, and the absorption by the positive radical ion at 6000 Å increased. The charge-transfer absorption at 9240 Å disappeared altogether.

After these rapid changes were complete additional reactivity was observed, but the product is unknown. Both the initial rapid reaction and the slower one were not dependent upon the presence of air.

The characteristics of these reactions in acetonitrile are summarized in Table 6ab. TMPD, the donor (D), and $pQCl_4$, the acceptor (A), immediately form charge-transfer complexes (AD). In acetonitrile it appears that a two-electron transfer may occur, producing the dinegative quinone ion ($A^=$) and the TMPD positive ion radical (D^+). The dinegative ion was not observed, however. Intermediate in the reaction is the semiquinone, A^- (Figure 3a). After several days, further reaction produces an unknown product (X_1).

In the nonionizing solvent ethylene dichloride, a charge-transfer complex (AD) is formed rapidly. An unknown product (X_2) is formed in one hour (Table 6c,d). No radical ions were observed in this reaction.

If X_1 and X_2 are the same product there occur two independent reactions of TMPD with $pQCl_4$. If this is true, one reaction is nonionic and is accelerated in nonionizing solvents. The other reaction, producing radical ions, is accelerated in ionizing solvents. The nonionic reaction occurs in one hour in ethylene dichloride ($\epsilon = 10.4$); it takes ten days in acetonitrile ($\epsilon = 37.5$). However, the ionization occurs rapidly only in acetonitrile.

Table 6

Reaction of TMPD (D) with p-chloranil (A)

Solvent and Condition	Reaction	Time for Complete Reaction
a		
Acetonitrile (ϵ = 37.5)	$A + D \rightleftarrows AD$	< 1 min
air	$A + 2D \rightarrow A^{=} + 2D^{+}$	60 min (longer reaction not studied)
b		
Acetonitrile	$A + D \rightleftarrows AD$	< 1 min
high vacuum	$A + 2D \rightarrow A^{=} + 2D^{+}$	30 min
	$A + D \rightarrow X_1$	10 days
c		
Ethylene dichloride (ϵ = 10.4)	$A + D \rightleftarrows AD$	< 1 min
air	$A + D \rightarrow X_2$	60 min
d		
Ethylene dichloride	$A + D \rightleftarrows AD$	< 5 min
N_2	$A + D \rightarrow X_2$	60 min

In another series of experiments the ionization of tetramethylbenzidine-chloranil was observed in ethanol, not in carbon tetrachloride. Both ESR and optical spectra of the ions were found. Also complexes of some phenothiazine derivatives were examined by ESR and optical spectroscopy, but their donor properties are more complex.

Discussion

We have not discovered any radical ions in solutions of hydrocarbon quinone complexes, such as perylene-chloranil. The work here and elsewhere shows, however, that arylamine donors such as TMPD do form radicals when combined with quinones. The arylamines used have lower ionization potentials which probably arise because of their nonbonding electrons (37). No hydrocarbons with as low ionization potentials have been investigated.

Note that a chemically stable electronic ionization has yet to be clearly established in a donor-acceptor system in solution. At least two kinds of reactions occur between TMPD and $pQCl_4$. As the product of one of these reactions in acetonitrile, the radical ions have been identified by their ESR absorption spectra. An ionized electron transfer from TMPD to $pQCl_4$ is therefore definitely established in this system even though it is unstable.

III.

FREE RADICALS, IONS, AND DONOR-ACCEPTOR COMPLEXES IN THE REACTION: CHLORANIL + DIMETHYLANILINE $\longrightarrow$ CRYSTAL VIOLET

A. Introduction

An ionized electron transfer from TMPD to $pQCl_4$ was discussed in Chapter II. We wanted to extend this kind of work to another donor-acceptor system. To study the mechanism of this kind of electron transfer we chose the liquid solution of chloranil ($pQCl_4$) in N,N-dimethylaniline (DMA). Indeed, Eley had shown that under some conditions the complex solid DMA-$pQCl_4$ was partially paramagnetic (38). Note, however, that we have investigated solutions of $pQCl_4$ in liquid DMA rather than the solid complex. First of all we wanted to see if the solutions were at all paramagnetic, and then to see if an ionized electron transfer from DMA to $pQCl_4$ could be established as it has been from TMPD to $pQCl_4$.

There was another incentive to investigate this particular liquid system. Eley reported that DMA-$pQCl_4$ solid had a relatively high electronic conductance, $\sigma = 2 \times 10^{-8}$ (ohm-cm)$^{-1}$. We have tried to find out if electronic conduction occurs in the solutions as well.

From the very first it was known that the solution of $pQCl_4$ in DMA was not perhaps an ideal case for the study of electron transfer. One might, for example, anticipate the presence of complicating side-reactions which do not involve electron transfer at all. As a matter of fact, DMA is not itself stable in air, but can be slowly oxidized by

air to crystal violet (39). Buckley, Dunstan and Henbest had already attempted to observe a reaction between DMA and $pQCl_4$ in dilute solutions (40). They observed no reaction, and we hoped that no irreversible reactions would occur in the course of our experiments either.

This turned out not to be the case. We now know that $pQCl_4$ does react with DMA to form the familiar crystal violet cation. We have studied this reaction in some detail to see if an electron transfer from DMA to $pQCl_4$ occurs at any time.

The results of this work are correlated in sections B and D, interpreted in section C and summarized in section F. Some rather detailed measurements of ESR absorption are discussed in section E.

B. Results

1. Product identification (41). The infrared and visible spectra (Figure 4) of the isolated compound were identical to the spectra of crystal violet, a familiar dye. Simultaneous chromatography on paper, both with a mixture of ethyl acetate and butyl alcohol and with chloroform alone as eluents, has confirmed that our reaction product is the cation of crystal violet.

The crystal violet precipitated mainly in the form of a chloranil hydroquinone salt. When the reaction takes place in the presence of air, the product is crystalline and is nearly 100% crystal violet salt. The integral ratio of crystal violet cation to hydroquinone which best fits the analysis is one:one. However, the product contains somewhat more crystal violet cation than a one:one ratio predicts.

Found: C, 63.52; H, 5.87; N, 8.58; Cl, 17.98.

Calc.: C, 60.10; H, 5.08; N, 6.79; Cl, 22.8.

Carried out under nitrogen, the reaction led to a product with a glassy appearance. This consisted of about 30% crystal violet, the remainder being one or more colorless compounds.

2. Optical absorption. Optical absorption spectra of the reacting solution of chloranil and dimethylaniline are reproduced in Figure 5. Initially, a charge-transfer absorption occurs at 650 mμ because of formation of the well known dimethylaniline-chloranil complex (42). The complex then reacted to produce an intermediate which absorbed near 400 mμ and which rapidly disappeared when exposed to the atmosphere. The spectrum of the final product, crystal violet, has an absorption peak at 590 mμ (Figure 4).

3. Conductivity. The conductivity of dimethylaniline was 2×10^{-9} $ohms^{-1}$ ± 25% (cell constant about $10^{-1} cm^{-1}$). When chloranil was dissolved in the dimethylaniline the conductivity was time dependent and could always be divided into three periods (Figure 6). An initial fast rise (period one, ten minutes) to about $9 \times 10^{-8} ohm^{-1}$ was followed by a slower increase to about $3 \times 10^{-7} ohm^{-1}$. The rate of this rise decreased until a period of very small change was reached (period two, one day). After this period of relatively small change, a gradual increase to $1.5 \times 10^{-5} ohm^{-1}$ (period three, four days) was observed, at which time the product salt precipitated from the solution.

Thus, there occurred a rapid increase in conductivity by a factor of 100 (period one) followed by a period of little change (period two) and finally a period of product salt formation (Period three).

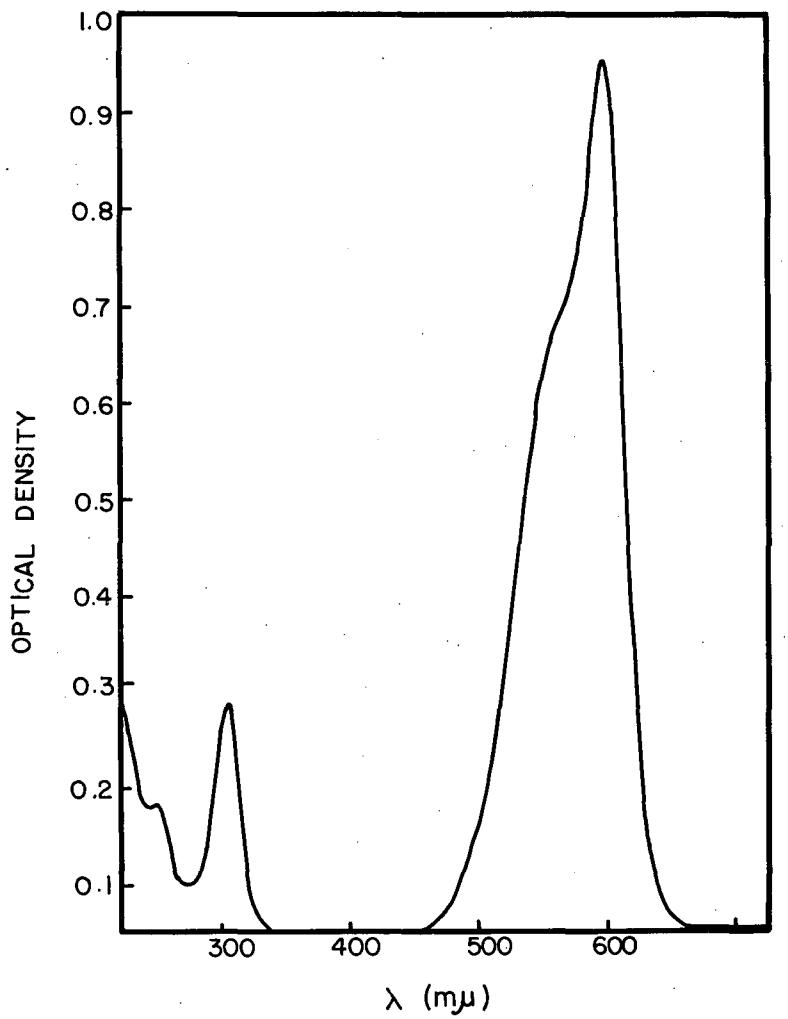

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Fig. 4. Optical absorption spectrum of the unpurified crystalline final product in $CHCl_3$, 0.13 g/l, cell length, 0.05 cm. It is the same as the spectrum of crystal violet (79).

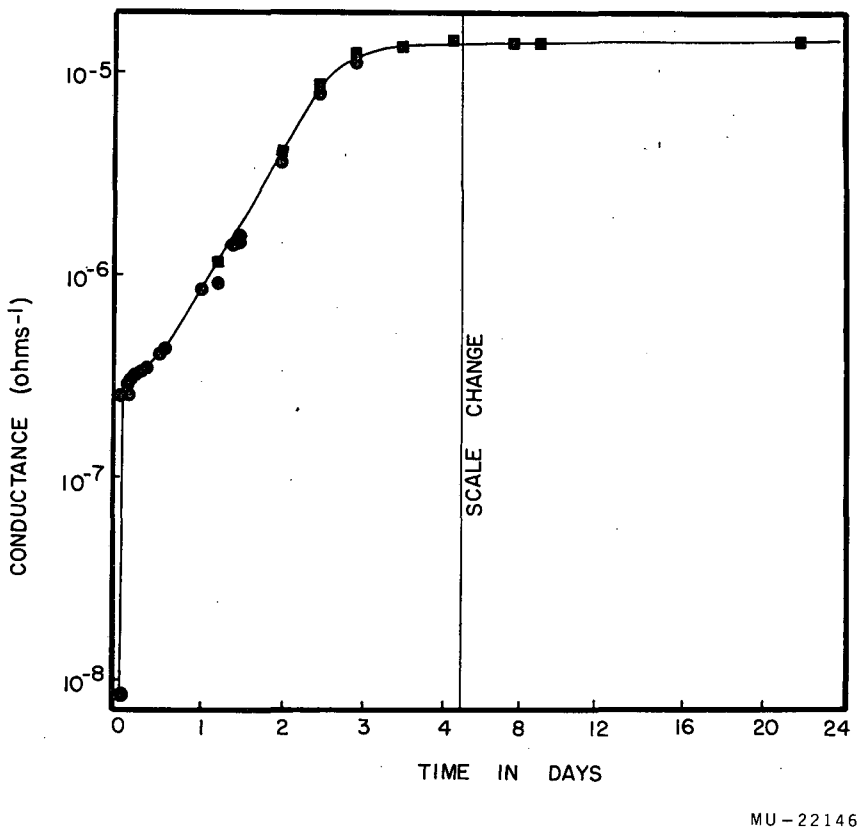

Fig. 6. Conductance of the reacting solution of dimethylaniline initially containing 0.14 molar chloranil. The cell constant was about $10^{-1}cm^{-1}$. Circles: D. C.; Squares: A. C.

When the conductivity approached the factor of 100 increase and intermediate constancy (within period two), its temperature dependence was measured. A logarithmic plot of conductivity as a function of reciprocal absolute temperature gave a straight line above 2.5°C, the melting point. Below -30°C, the function could be approximated by a straight line, but the slope was many times greater than the slope above 2.5°C. If one interprets the slope as an activation energy, evidently the energy requirements of conduction are much greater in the solid than in the solution.

Also, the conductivity of the solid at 2.5°C was 1/20 that of the liquid at 2.5°C. Although it was impossible to distinguish between ionic and electronic conductivity, it is assumed that this decrease of conductivity on freezing is due to the fixing of conducting ions.

4. Electron spin resonance (ESR). A typical time dependence of ESR is illustrated in Figure 7. Apparently the intermediate free radical is preceded by other species as is shown by the slow initial rate of formation. Eleven measurements of the reaction kinetics by ESR showed that the length of this initial period was very irreproducible. The reaction proceeded to completion in a few hours if the dimethylaniline was exposed to air for a prolonged period (several months) before chloranil was added. Even in the absence of air (O_2 <0.1% by volume) the reaction proceeds, but the product is less crystalline. On the other hand, the concentration of free radicals observed always decreased on exposure to air at any time during the course of the reaction.

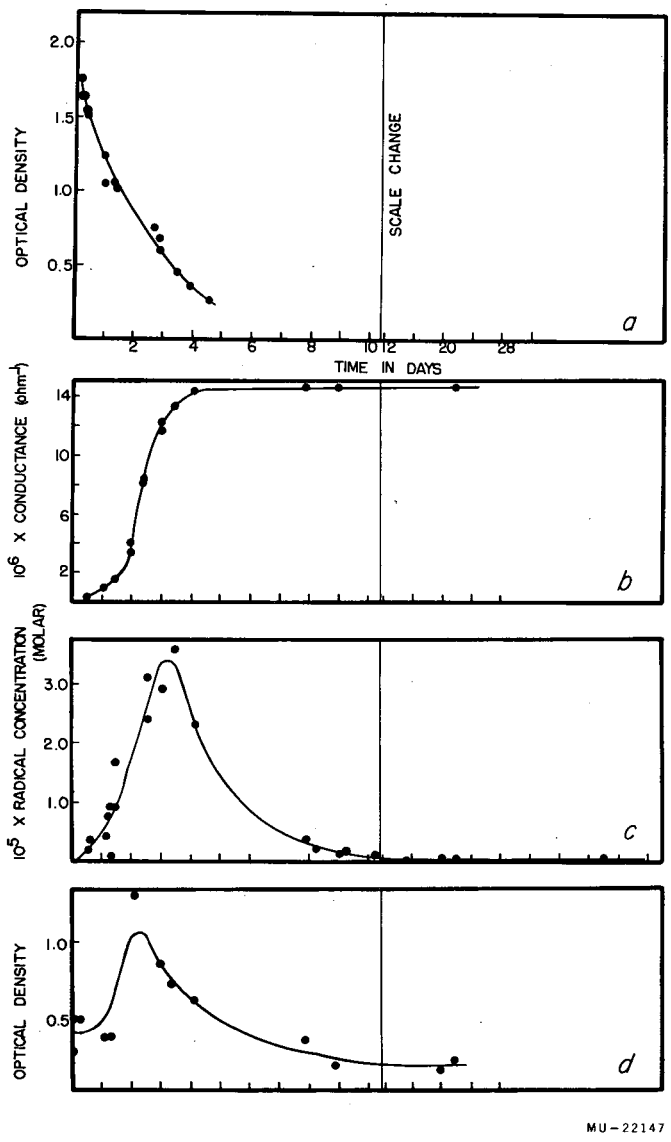

Fig. 7. The reaction in a nitrogen atmosphere of 0.14 molar chloranil in dimethylaniline. a) Charge-transfer absorption at 650 mμ (using a 0.005 cm optical cell). b) Conductivity (cell constant $\sim 10^{-1}$cm^{-1}). c) Radical concentration by ESR. d) Intermediate absorption at 410 mμ. The abcissas are all time in days. Because of the scale in Figure 7b, the initial rapid rise in conductivity does not appear.

The g-value of the intermediate radical was measured, $g = 2.0056 \pm 0.0002$. This agrees with the value $g = 2.0058$ determined for the familiar chloranil semiquinone (43). Below is given additional evidence which shows that the semiquinone is the intermediate radical(See III.D.2.)

The ESR absorption curve is asymmetric, and it is more nearly Lorentzian than Gaussian, indicating that the radical is not present as an ideal dilute solute.

The solutions were centrifuged to see if the radicals were present in aggregates. The solutions contained the same radical concentration before and after centrifugation. Making the usual assumptions concerning density and viscosity, the maximum particle diameter for uncharged particles left in solution would be 200 mμ.

5. Simultaneous measurements. The reaction of DMA and $pQCl_4$ was followed simultaneously by three physical measurements. The results are reproduced in Figure 7. The charge-transfer absorption by the dimethylaniline-chloranil complex decreases (Figure 7a). The ionic product is obserbed by its conductivity to increase (Figure 7b), after a slow initial period. The intermediate radical (Figure 7c) and optically observed species (Figure 7d) follow similar delayed kinetics. The absorption at 410 mμ is not yet assigned, but it is not due to semiquinones.

A second experiment correlating optically observed decay with ESR absorption showed that the ESR absorption did not increase until after considerable chloranil had reacted.

6. Comments. The mechanism of the chloranil-dimethylaniline reaction will yield abundantly to more extensive research. The results should be viewed in light of the fact that the exact relationship between the presence of air and the reaction yield and mechanism is not established. Also we have no information about the dependence of this reaction on acidity, nor have any byproducts been identified.

C. Interpretation of results

It has been found that charge-transfer complexes form immediately when chloranil is dissolved in dimethylaniline. Very quickly a rise in solution conductivity occurs. The reaction proceeds for a few days as observed by the decrease in the charge-transfer optical absorption. After a time the semiquinone is observed by ESR. The ESR eventually decays while salt formation is observed by a second rise in conductivity. The product crystal violet cation had been identified.

Because there is no information about the oxidized intermediates, it is impossible to suggest a definite mechanism, but some general characteristics of the reaction may be discussed. For convenience we divide the reaction into six periods (Figure 8). Each period includes one, or several, intermediate reactions.

In the solvent dimethylaniline essentially all the chloranil is complexed (step 1). (The complex formation constant is $K = 3.34$ $(mol/l)^{-1}$ for the formation of one:one complexes in carbon tetrachloride (42)). The reaction has been followed by the decay of the optical absorption of this charge-transfer complex.

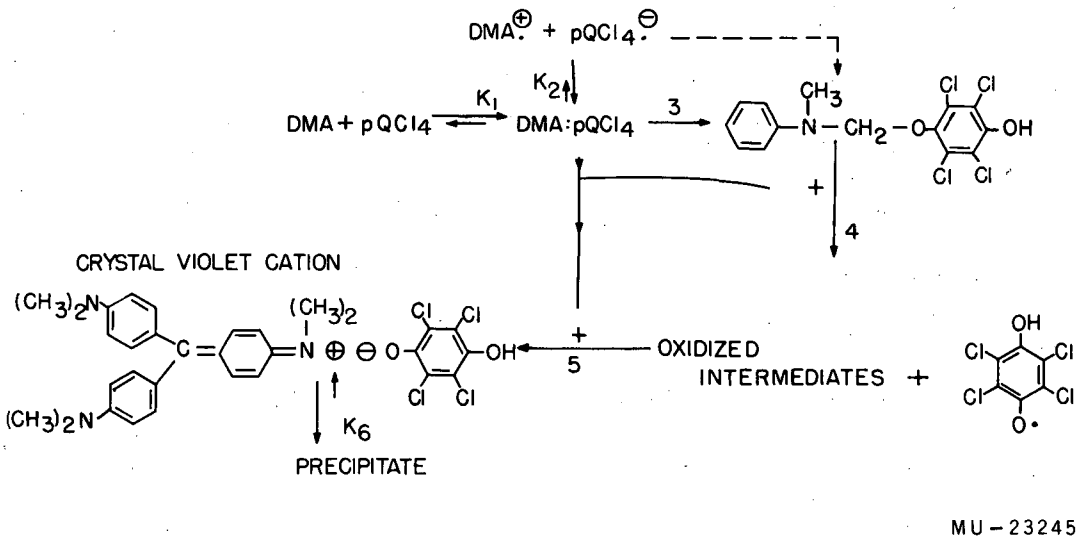

Fig. 8. Schematic of the reaction, chloranil + dimethylaniline ⟶ crystal violet.

The ions observed by the rapid initial rise in conductivity may be the products of the ionized complex (step 2). If one assumes an equivalent conductance of $\Lambda = 100 \frac{cm^2}{equivalent\text{-}ohm}$ for the hypothetical organic radical ions produced, the ionization constant $K \sim 10^{-13}$ mole/l is estimated from a measurement of conductivity. If this ionization does occur, the concentration of radicals would be barely detectable directly by ESR, and we have not observed any. Note, however, that only 10^{-7} molar ions are necessary to produce the sharp initial increase in conductivity. If the ions are impurities in the chloranil, only 10^{-6} mol ions per mol of chloranil are necessary to cause this increase. In view of this consideration, the ionization hypothesis may be untenable. After this initial increase the conductivity remains fairly constant until semiquinone and product salt formations begin.

Once the initial equilibria have been established (step 1 and perhaps step 2), there follows a period of oxidation initiation in which apparently no olarge concentration of semiquinone is produced (step 3). No evidence has been observed for the intermediate suggested as the product of step 3. However, it is a model which satisfies the criterion that, although quinone has reacted considerably, neither radicals nor ions are produced in this step. In any case, it is likely that a hydrogen atoms transfer takes part in the limiting reaction. No electron transfer could be established.

During a fourth period radicals are produced in quantity.After the chloranil is expended, the semiquinones are reduced further to the hydroquinones (period 5). At no time in this sequence do any

product radicals other than semiquinones reach an observable concentration. If there are arylamine radicals, they must react quickly (see D.2. below).

An increase in conductivity occurs during the final oxidation periods after which the solid salt is precipitated (period 6). The optical density (assuming $\epsilon = 87{,}000\ (\frac{mol}{l})^{-1}cm^{-1}$) and conductivity (assuming $\Lambda = 50\ \frac{cm^2}{equivalent\text{-}ohm}$) have been used to estimate a solubility product approximately $K \sim 10^{-8}(\frac{mol}{l})^2$.

D. The reaction of other quinones dissolved in dimethylaniline.

1. Charge-transfer absorption and reaction rates. We have studied the reaction of dimethylaniline (DMA) with fluoranil (pQF_4), bromanil ($pQBr_4$), o-chloranil ($oQCl_4$) and o-bromanil ($oQBr_4$) as well as chloranil. The charge-transfer frequencies (Table 7) may be taken to be a measure of the effective electron affinities of the quinones in the DMA medium (see Chapter VI) (44). They are nearly all the same. Briegleb and Czekalla give $15.4 \times 10^3 cm^{-1}$ as the absorption frequency of DMA-$pQCl_4$ in carbon tetrachloride (42).

Orthoquinones reacted with DMA at a rate one hundred times faster than the paraquinones. The limiting reaction (Figure 8, period 3), may be accelerated sterically if, for example, a hydrogen atom transfer is important, as has been suggested in the discussion above.

2. g-values. The g-values of radical intermediates (Table 8) may be compared with the g-values of semiquinones prepared by other

Table 7

Frequency of maximum charge-transfer absorption by quinones dissolved in dimethylaniline

Quinone	Frequency x 10^{-3}(cm^{-1})
pQF_4	15.55
$pQCl_4$	15.6
$pQBr_4$	15.1
$oQCl_4$	15.9
$oQBr_4$	15.7

Table 8

Comparison of g-values

Semiquinones of the quinone	Method of Preparation: This Work* — Quinone + dimethylaniline in dimethylaniline	This Work* — Quinone + sodium iodide in acetonitrile	Other Work — Air oxidation of hydroquinone in ethanolic KOH	Other Work — Quinone + sodium iodide precipitate (45)**
pQF_4	2.0054		2.0048 ± 0.0006 (46)	
$pQCl_4$	2.0056	2.0055	2.0058 (43)	2.0044 ± 0.0008
			2.00568 ± 0.00002 (47)	
$pQBr_4$	2.0085	2.0085	2.00875 ± 0.0002 (47)	2.0068 ± 0.0010
$oQCl_4$	2.0058			
$oQBr_4$	2.0094			2.0077 ± 0.0008

* Usual average deviation of individual measurements from recorded value is ± 0.0002

** We have obtained for solid $NapQCl_4$, g = 2.0057, demonstrating a systematic error in these measurements. Add 0.0015 to numbers in this column

methods.* The radicals observed in dimethylaniline have g-values identical to the g-values independently observed for semiquinones. In fact, it is this comparison which we have used to identify the radical intermediates as semiquinones.

E. Electron spin resonance of the fluoranil radical

1. Linewidth and saturation. Previously the semiquinone of pQF_4 had been produced in ethanol by Anderson, Frank and Gutowsky (46). By ESR they observed five hyperfine component lines, each separated by four oersteds. We hoped to further identify the semiquinone of pQF_4 in DMA by also observing the hyperfine splitting. However, when pQF_4 was dissolved in DMA (in air), only one line, six oersteds wide, was observed (Figure 9).

The observed semiquinone itself is present inconcentrations 5×10^{-5} to 5×10^{-4} molar. On the other hand there are high concentrations of quinone and hydroquinone in the solution. The solutions were initially between about 0.15 and 1.5 molar fluoranil. The narrowing of the ESR absorption or collapsing of hyperfine splitting may be due to electron transfer between the semiquinone and the quinone, or the dinegative hydroquinone ion. The transfer reaction envisioned here occurs also in solutions of naphthalene negative ion and naphthalene (48). Venkataraman, Segal and Fraenkel have, in fact, suggested that ESR linewidths of semiquinones in dilute solution may be caused by just such an electron transfer mechanism (49).

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* In the late stages of reaction, after the semiquinones disappear, a second radical has been observed in the $pQCl_4$ and $oQCl_4$ reactions with dimethylaniline. The latter has $g = 2.0049 \pm 0.0002$. The g-value of the secondary radical derived from $pQCl_4$ is also less than that of the primary radical. The g-value was not measured because absorption of the two radicals overlapped.

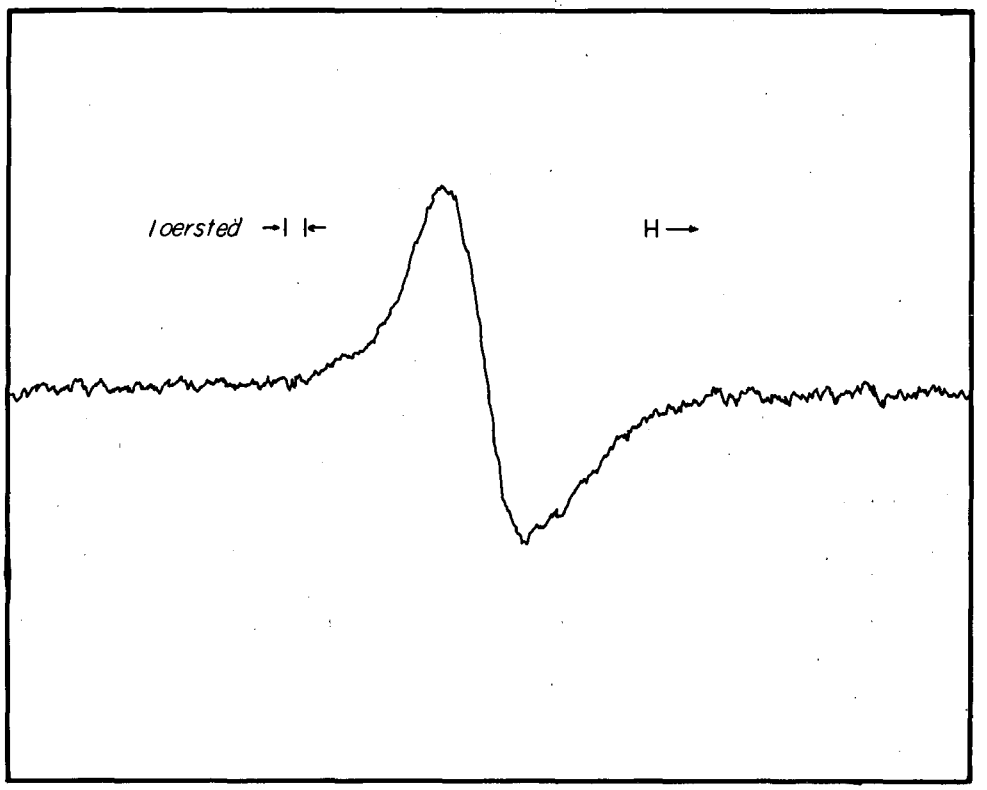

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Fig. 9. ESR absorption derivative of the radical intermediate in the reaction of pQF_4 with DMA. At 25°C after 2-1/2 hours at 61°C initially 1.3 M fluoranil. Minimum saturation.

Pines and Slichter write, for narrowed ESR absorption of this kind, the linewidth $W = (\delta\omega)^2 \tau_{eF}$ (50). $(\delta\omega)$ is the total width of the hyperfine splitting observed in dilute solution. τ_{eF} is the mean lifetime of the electrons in a given fluorine environment. This relation gives an estimate for the mean time between electron transfers, $\tau_{eF} \lesssim 1 \times 10^{-9}$ sec. This is a lower limit because greater narrowing may become masked by other broadening effects.

At elevated temperatures the linewidth is time dependent. At 110°C the width changes from 3.8 to 5.2 oersteds as the oxidation proceeds. Perhaps the quinone is replaced by hydroquinone in the transfer reaction as the DMA oxidation proceeds. That is, after the quinone becomes exhausted, enough hydroquinone has been formed to allow an electron transfer with the semiquinone to continue. If the energy barrier to transfer is different, and the rate of transfer different, then the linewidth will depend upon the time as quinone is transformed to hydroquinone.

Above 25°C, the linewidth was not dependent upon the incident microwave power within experimental error, even though the resonance was highly saturated. Therefore, the solution may be classed as an inhomogeneous spin system. Evidently there are different species absorbing microwave energy over a spread of frequency. These entities may differ in their nuclear environment. The fluorine hyperfine splitting may not have coalesced completely. (Incidentally, the linewidth of the flurine multiplets observed by Anderson et al. appears to be about 4 oersteds, or about 2 oersteds broader than the linewidth observed at 25°C in DMA.) The protons of DMA may be responsible for the inhomo-

geneity of the spin system if DMA and the semiquinone are complexed in some manner.

Below the freezing point, the linewidth is dependent upon the degree of saturation of the resonance and the spin system may be classed as homogeneous. In Figure 10 the linewidth is graphed as a function of saturation at -150°C.

Linewidth measurements as a function of temperature are illustrated in Figure 11. Below 6°C the widths are plotted as a function of saturation. Above that temperature, the time dependence of the width creates an uncertainty, as shown. Neglecting these two complications, it is apparent that the linewidth decreases with increasing temperature, from 7.5 oersteds at -150°C to about 5.0 oersteds at 150°C. Consistent with the interpretation of transfer-narrowing, this means that the transfer rate increases with increasing temperature. As the electron transfer more rapidly at elevated temperatures, the hyperfine structure collapses more, and the line becomes more narrow. There is no discontinuous change of width when the solution is frozen. The electron transfer may proceed almost equally well in the solid and in the solution.

At -150°C, the ESR absorption becomes saturated at very much lower power levels than it does at 25°C. Thus, the spin-lattice relaxation time increases as the temperature of the system is reduced. Putting this within the framework of our model, the electron transfer which dominates the spin-lattice interaction occurs less frequently at reduced temperatures. As the electron transfer occurs less frequently the spin-lattice relaxation time increases, and the spin resonance saturates more easily.

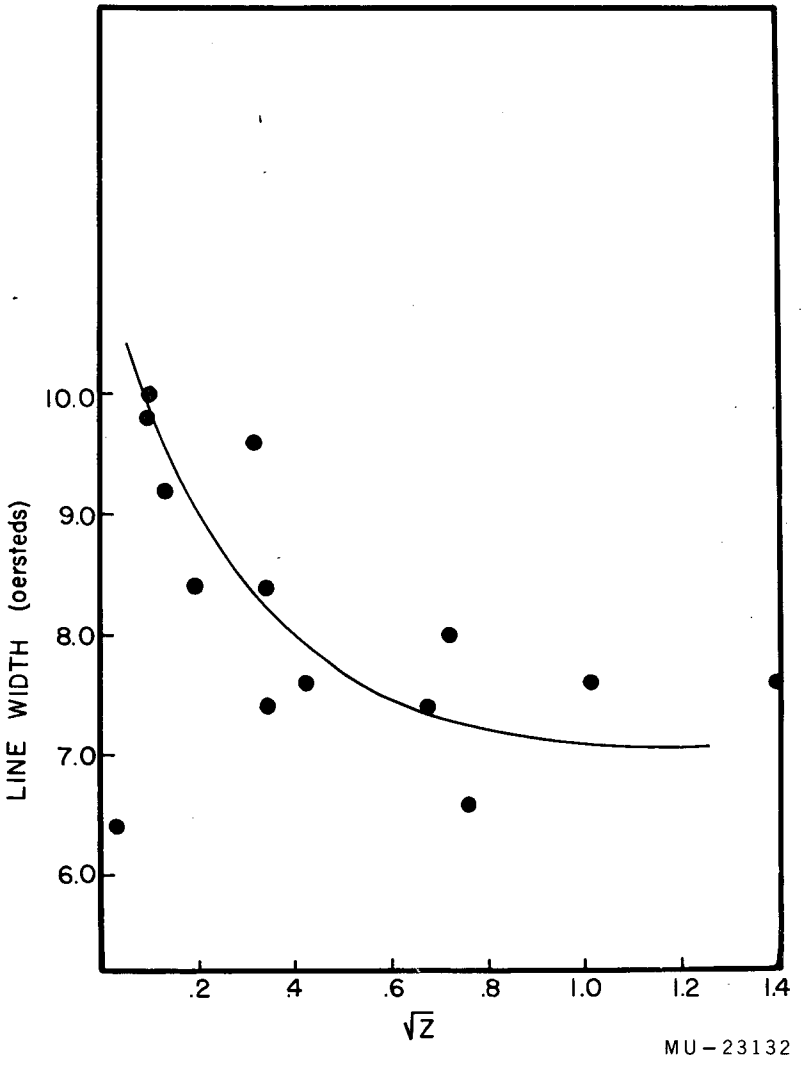

Fig. 10. Saturation dependence of the width at -150°C. ESR absorption by the radical intermediate in the reaction of pQF_4 with DMA. Saturation parameter, $\sqrt{Z_{et}}$ is defined in Chapter V. A. 5. For no saturation, $Z_{et} = 1$.

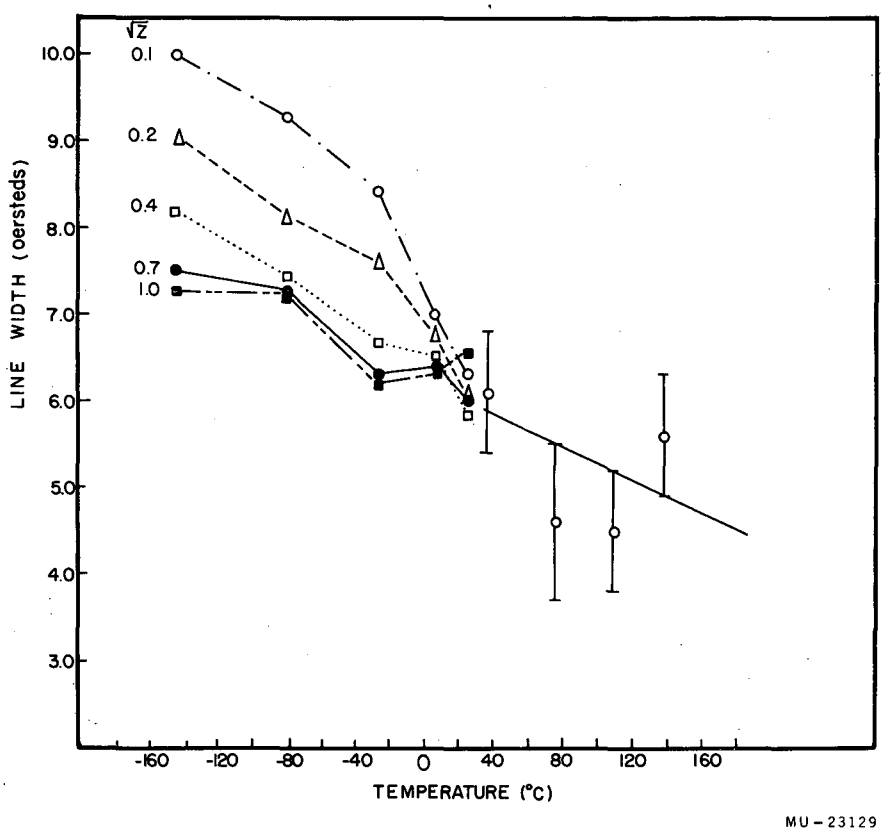

Fig. 11. Temperature dependence of the width, including the dependence on the saturation parameter $\sqrt{Z_{et}}$. ESR absorption by the radical intermediate in the reaction of pQF_4 with DMA.

From the temperature dependence of the linewidth (Figure 11), we deduce that line broadening at reduced temperatures results from increased spreading out of the fluorine hyperfine structure. If this is true, the spin system should become more inhomogeneous. In fact the system becomes more homogeneous. The saturation dependence of the linewidth is greater at reduced temperatures, which contradicts the hypothesis. On the other hand, the linewidth does not increase with saturation nearly as much as might be expected for a perfectly homogeneous system.

2. Line shape. The fact that the ESR absorption is more nearly Lorentzian than Gaussian is consistent with our interpretation. As in the case of $pQCl_4$, ESR absorption of the semiquinone of pQF_4 was asymmetric (Figure 9). In Figure 12 the asymmetry is illustrated as a function of temperature. The voltage recorded at the derivative maximum was greater on the low field side than on the high field side of the resonance. An approximate absorption curve is sketched in the figure. The asymmetry decreases at elevated temperatures. It may be due to anisotropy of the g-value as reflected in the hyperfine component widths and observed width (51). As the temperature increases the solvent fluidity increases and the anisotropy is averaged which is observed.

However, with respect to this interpretation, the saturation dependence of the asymmetry appears anomalous. We suggested that unresolved hyperfine components have different widths which reflect an anisotropic g-value. Then these multiplets should each saturate differently and asymmetry of the unresolved envelope should change on satura-

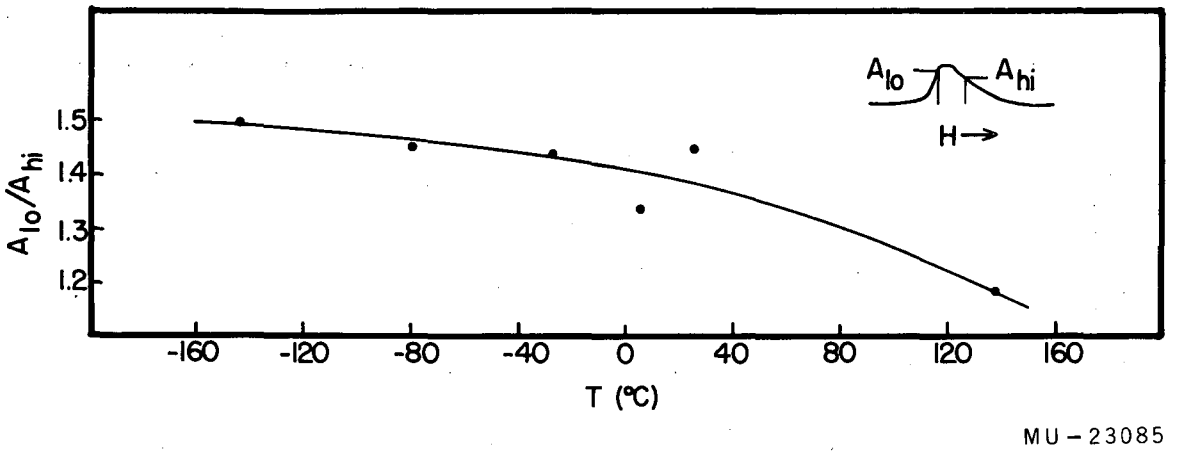

Fig. 12. Asymmetry as a function of temperature. ESR absorption by the semiquinone intermediate in the reaction of pQF_4 with DMA.

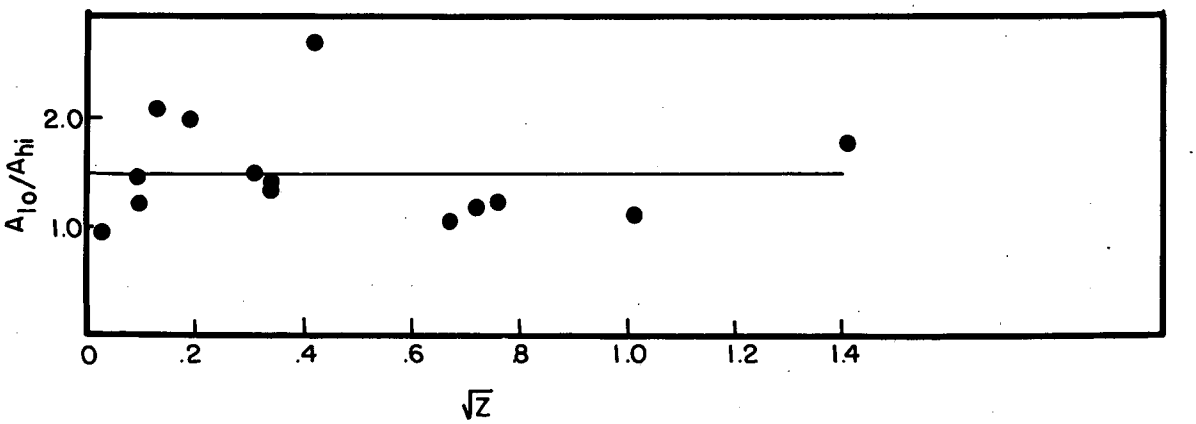

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Fig. 13. Asymmetry as a function of saturation, $\sqrt{Z_{et}}$, at -150°C. ESR absorption by the semiquinone intermediate in the reaction of pQF_4 with DMA.

tion (52,53). This is not observed. Within experimental error the asymmetry did not change when the ESR absorption was saturated (Figure 13). The error may be too great to detect the expected change.

3. Temperature dependence of the concentration. In the frozen reaction mixture the temperature dependence of ESR did not obey Curie's law. The semiquinones are reactive intermediates, and their steady-state concentration may be temperature-dependent, even in the frozen mixture. The species are not just trapped radicals.

F. Summary

Chloranil reacts with dimethylaniline to yield a crystal violet salt. The diamagnetic dimethylaniline-chloranil charge-transfer complexes and paramagnetic semiquinones are two observed intermediates. A reaction scheme has been proposed which is consistent with the observations of optical absorption, conductivity and ESR. A hydrogen atom transfer has been invoked in initial rate-determining sequence. Whatever the initial step may be, a simple transfer of an electron from DMA to $pQCl_4$ could not be established.

We have assumed that only one kind of magnetic species is present, namely, the semiquinone. Five different tetrahalogenated quinones were allowed to react with DMA. In every reaction the observed g-value agrees well with the known g-values of semiquinones.

The reaction of DMA with pQF_4 was studied extensively by ESR. The g-value, temperature dependence, line shape, linewidth and saturation were measured.

The g-value shows that the observed species is probably the fluoranil semiquinone. The semiquinone concentration is temperature

dependent. A rapid electron transfer among the semiquinone, quinone and hydroquinone ion is likely, as deduced from the linewidth. Evidently the electron transfer occurs more rapidly at elevated temperatures than it does at low temperatures. Thus also it is found that the spin-lattice relaxation time decreases markedly as the temperature is increased.

Above the freezing point, the ESR absorption saturates inhomogeneously. Below that temperature, the absorption saturates homogeneously. The ESR absorption is asymmetric. Within experimental error the asymmetry is independent of saturation, and it decreases somewhat at higher temperatures.

IV. HYDROCARBON-QUINONE SOLIDS

The outline of this chapter, which deals with solids, follows the pattern of Chapter II which deals with liquid solutions. In the first section we describe the preparation of some solid donor-acceptor adducts. Most attention is directed to the solid prepared from perylene and quinones. Their chemical and physical properties are discussed and related to the donor character of perylene and the acceptor character of the tetrahalogenated quinones. Finally, once the nonmagnetic properties are fairly well established, an investigation by ESR is presented.

A. Preparation

When o-chloranil was dissolved with an equivalent amount of perylene in hot ethylene dichloride ($EtCl_2$), shining black needles were precipitated on cooling. Chemical analyses for carbon and chlorine gave results which agreed well with the composition predicted for a one:one complex of perylene with o-chloranil.

By somewhat more complicated recipes, black needles of the following have been prepared: pyrene-o-chloranil (pyrene-$oQCl_4$), pyrene-$oQBr_4$, perylene-$oQCl_4$, perylene-$oQBr_4$, coronene-$oQCl_4$, and the para-quinone complexes, perylene-$pQCl_4$ and perylene-$pQBr_4$. In almost all cases, the solids are one:one combinations of hydrocarbon and quinone. The analyses of carbon and chlorine were used to calculate the actual ratios, which are recorded in Table 9.

There are several ways of recovering the components of the complex solids, as observed by visual inspection. A rapid (flash) sublimation of the complex in a thermal gradient produces separation. The more volatile oQBr and oQCl have been separated from perylene in this way.

Table 9

Composition and concentration of unpaired electrons in some hydrocarbon-quinone solids. The molar ratio quinone/hydrocarbon and the estimated spin concentration in the solids within 24 hours of preparation

Complex Donor	Acceptor	Composition based upon analysis of C	Cl or Br	Unpaired electrons per gram	Method of precipitation	Crystalline appearance
Pyrene	$oQCl_4$	1.000	0.986	10^{17}	Equimolar ratios in hot, dry $EtCl_2$	Yes
	$oQBr_4$	1.02	1.01	--	Evaporation of equimolar ratios in $EtCl_2$	No
Perylene	$pQCl_4$	--	--	$< 10^{15}$	Equimolar ratios in saturated hot dry $EtCl_2$	Yes
		1.072	1.042	10^{15}	Equimolar ratios in hot CCl_4	Yes
	$pQBr_4$	--	--	$< 10^{15}$	Equimolar ratios in saturated hot dry $EtCl_2$	Yes
	$oQCl_4$	1.038	--	10^{17}	Equimolar ratios in saturated hot $CHCl_3$	No
		1.05	0.990	10^{16}	Equimolar ratios in hot CCl_4	Yes
		1.02	0.972	10^{15}	Previous sample recrystallized from hot CCl_4	Yes
		1.011	1.012	$< 10^{15}$	Equimolar ratios in hot dry $EtCl_2$	Yes
	$oQBr_4$	1.018	0.980	10^{16}	Equimolar ratios in hot CCl_4	Yes
		1.92	1.92	10^{16}	Large excess of $oQBr_4$ in hot $EtCl_2$	Yes
		1.11	1.07	$< 10^{15}$	2 parts $oQBr_4$ to 1 part perylene. Saturated hot 25% $EtCl_2$, 75% CCl_4	Yes
		1.013	0.982	5×10^{15}	Ditto, using 10% $EtCl_2$	Yes
Coronene	$oQCl_4$	0.996	0.994	10^{17}	3 parts $oQCl_4$ to 1 part coronene in hot dry $EtCl_2$	No

Perylene and oQCl have been separated on a silicic acid column using ethylene dichloride and petroleum ether as the solvents. Also, chloroform leaches oQBr from the perylene-$oQBr_4$ complex.

B. Nonmagnetic properties

1. Crystal structure. Crystal structures have been determined for many solids composed of donor and acceptor molecules. In all cases the donors and acceptors alternate throughout the crystal. As an example, the structure of hexamethylbenzene-chloranil was described in Chapter I.

The crystal structures of polynuclear-aromatic-hydrocarbon-quinone complexes are unknown. We have assumed that the donors and acceptors alternate in the general fashion. In the course of the present investigation, x-ray patterns have been obtained for a single crystal of perylene-chloranil, proving that the material is indeed crystalline (54). The symmetry is monoclinic or triclinic, having 7 x 17 x 16 Å per unit cell. The unit cell contains about two donor-acceptor pairs.

The essential feature of donor-acceptor adduct formation in solution is charge-transfer. That is, the association of donors and acceptors depends upon partial dative-bond formation. Although bonding in the solid is no longer a pair-wise phenomenon, we assume that donor-acceptor charge-transfer interaction dominates other forces.

We have already noted (See II.B.) that the crystal structure of a donor-acceptor solid may have no relation to the configuration of the one:one complex which occurs in solution. However, the known alternating structures of solid complexes are quite inkeeping with our knowledge about one:one adducts in solution.

2. Infrared spectra. The infrared spectra of solid perylene complexes with $pQCl_4$, $pQBr_4$, $oQCl_4$ and $oQBr_4$ are very similar to the superimposed spectra of the individual components. There are slight shifts in frequency and some alterations in intensity which reflect the molecular association. The characteristic quinone frequency of 1690 cm^{-1} remains essentially unchanged. The maximum absorption (1690 cm^{-1}) of complexed quinones occurs at frequencies 5 to 10 cm^{-1} lower than the maxima observed in the unassociated quinones. Evidently no intramolecular bonds have been greatly changed during formation of the complex. Kainer and Otting (17) observed the same result for the hexamethylbenzene-chloranil solid.

Physical appearance of the crystals, their chemical analyses, recovery of the initial entities, the definition of x-ray photographs and infrared spectra, all five observations indicate that the crystals are homogeneous molecular solids of well-defined constitution and structure. The association is one in which none of the original chemical bonds have been altered.

3. Charge-transfer spectra. The perylene-quinone solids do exhibit charge-transfer optical absorption, some examples of which we measured and are recorded in Table 10. An example spectrum is illustrated in Figure 14, showing the doublet nature of the absorption. In Figure 15 the frequencies of absorption by the solid are compared to the frequencies observed in solution. There are at least three possible explanations of the difference between charge-transfer frequencies of one:one adducts in solution and the frequencies of the solids. First, multiple interaction in the solid between arrays of

Table 10

Frequencies of maximum charge-transfer absorption in some perylene-quinone solids as observed in KBr

Acceptor	Frequencies x $10^{-3}cm^{-1}$ in $CHCl_3$	Solid in KBr A	Solid in KBr B
$pQCl_4$	13.4	13.35	12.3
$pQBr_4$	13.1	13.05	12.05
$oQCl_4$	12.3	11.95	11.0
$oQBr_4$	11.9	11.65	10.7

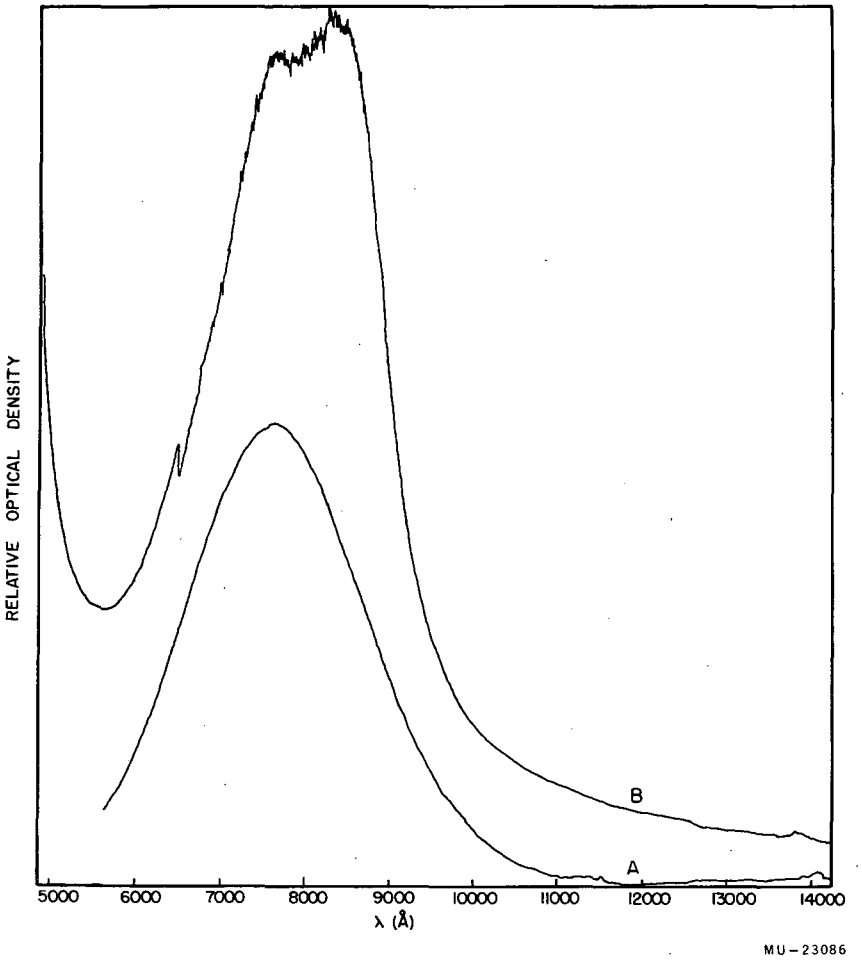

Fig. 14. Charge-transfer absorption by perylene-$pQBr_4$. a) One:one complexes in $CHCl_3$; b) powdered solid in KBr_4.

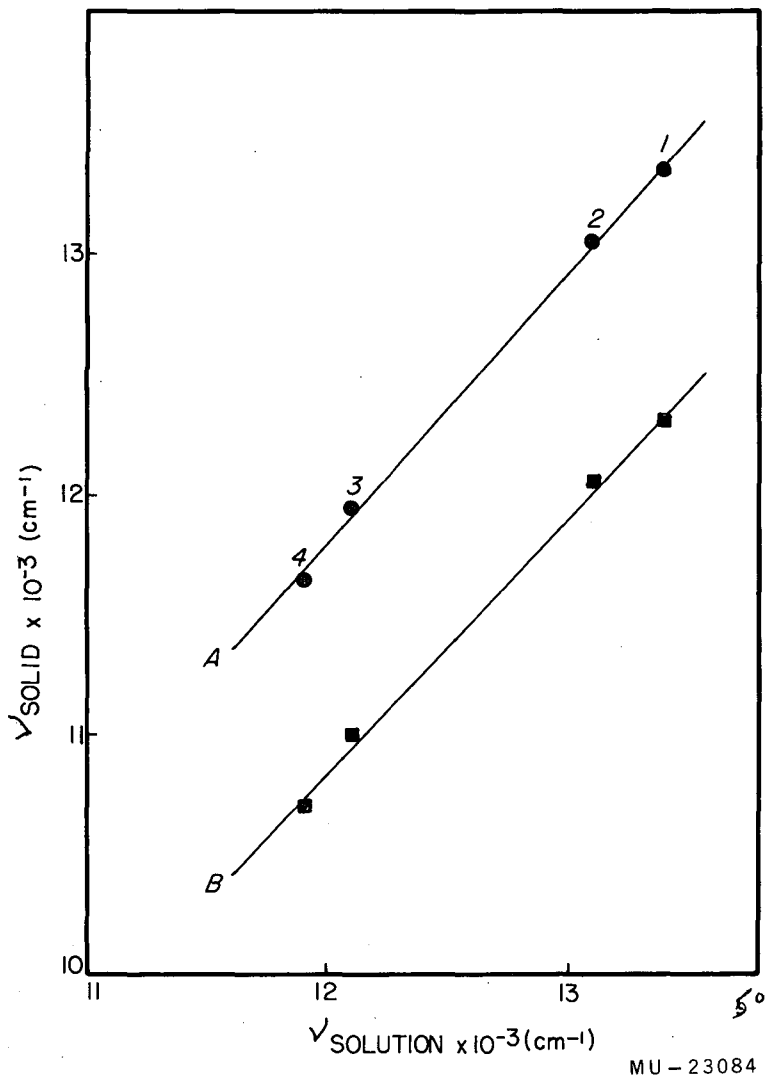

Fig. 15. Frequencies of charge-transfer absorption by perylene-quinone complexes in $CHCl_3$ and in the solid. A and B are two maxima observed in the solid. Quinones are: (1) $pQCl_4$, (2) $pQBr_4$, (3) $oQCl_4$, (4) $oQBr_4$.

alternating donors and acceptors is different from one:one interaction in solutions. Secondly, the configurations in solid and solution may differ. Thirdly, the dielectric constant of the solid is different from that of the solution.

The optical dichroism is undetermined. (see Chapter I) Powdered samples were used in the determination of frequencies reported in Table 10. The doublet nature of the maximum might be attributed to the random orientation of anisotropically absorbing particles. Then again there may be two independent excitations in the solid configuration. In general, however, the optical properties of solid complexes are a natural extrapolation of the optical properties of one:one complexes in solution.

4. Semiconductivity. Labes, Sehr and Bose (55) have measured the conductivity of perylen-chloranil solid. The room temperature conductivity is 10^{-8}ohm^{-1}cm^{-1}. In general donor-acceptor solids have higher conductivity than other organic materials. The electrical properties of charge-transfer solids have been studied extensively by Eley, Inokuchi and Willis (38), Akamatsu, Inokuchi and Matsunaga (56), Kommandeur and Hall (57), and Labes, Sehr and Bose (55).

5. Summary. Stoichiometric one:one solids have been prepared from aromatic hydrocarbons and quinones. The solids are crystalline. The component entities may be recovered. Intramolecular bonding is essentially unaltered in the solids. Charge-transfer absorption has been determined. From these nonmagnetic properties we conclude that the crystals are near-perfect, ordered, homogeneous solids of well-defined composition and structure.

C. Electron spin resonance

1. Introduction. Bijl, Kainer and Rose-Innes have studied the paramagnetism of arylamine-quinone solids (10). In these systems the concentration of unpaired electrons was found to be temperature independent. Therefore the authors suggested that trapped in the solid are free radicals which give rise to the observed ESR absorption. Matsunaga and McDowell have more recently reported that the ESR absorption by the solid complex TMPD-$pQCl_4$ may be resolved into two component absorptions, one by the cation radical $TMPD^+$, the other by the anion radical $pQCl_4^-$ (58). These component species were identified by their characteristic g-values. Exactly how the radicals are formed and trapped in the solid has not been determined. However, in chapter II.B. we have shown how these two radical ions are formed in solution. Because of their instability in solution we ourselves did not investigate the solid adduct of TMPD and $pQCl_4$.

Matsunaga (58,59) and more recently Singer and Kommandeur (11) investigated the paramagnetism of hydrocarbon-halogen solids. The temperature dependence of the unpaired-spin concentration in these donor-acceptor solids was resolved into two components by Singer and Kommandeur. At low temperatures the concentration was constant, and the magnetic species is tenatively presumed to be a free radical trapped in the solid. At high temperatures, the concentration of unpaired electrons increased logarithmically as the reciprocal of the absolute temperature decreased. The unpaired electrons were identified as charge carriers in a thermally populated electronically conducting state.

We observe that in both of the two solid donor-acceptor complexes studied so far free radicals are apparently trapped in the solid. Using our knowledge about the formation of radicals in solutions of donors and acceptor we may suggest how radicals are formed during precipitation of the solids. To start with the donor must have a low enough ionization potential and the acceptor must have a high enough electron affinity. Once these requirements have been met, the medium must have a large enough dielectric constant to accommodate the ionic charge of the radicals. So far we have no experimental information at all concerning the mechanism by which free radicals are trapped in organic solids.

It appears that homogeneous donor-acceptor solids are frequently paramagnetic because of imperfections rather than because of an intrinsic property of the regular crystal. A trapped free radical is one kind of imperfection which has been observed. Of course the argument may be reversed. The absence of 100% paramagnetism in a given material might be due to the presence of diamagnetic imperfections.

The excited state observed by Kommandeur and Singer may be an intrinsic property of the hydrocarbon-halogen solids. However it is conceivable that the excitation occurs at the site of an imperfection. Actually the reproducibility of the ESR and its excellent correlation with conductivity measurements make the hypothesis of an imperfection appear less plausible.

Before proceeding to the results of the present investigation, we wish to clarify one point. That is, use of the term <u>imperfections</u> is strictly our invention, and we have used it as an attempt to generalize the work of others. We ourselves have made no measurements

on the systems which have just been reviewed. To consider the trapped radicals as imperfections is a convenient generalization which contributes no new knowledge. The point is that the solids are not completely regular. Solids which are formed by the combination of charge-donors and charge-acceptors may or may not be intrinsically paramagnetic. In two cases studied, trapped radicals occur (according to information available now) and the donor-acceptor solids are imperfect.

The word, imperfections, has been used in the very most general sense. We avoid a more specific definition now, partly because the properties of imperfections in these organic materials may be quite different from the properties of imperfections in inorganic materials (60).

In the present work we have examined the ESR absorption by some new complexes. We have used aromatic hydrocarbons as donors, but have used only tetrahalogenated quinones as the acceptors.

2. Results and discussion. In our work, ESR absorption was observed in nearly all hydrocarbon-quinone solids prepared. However, quantitative measurements have shown that the concentration of unpaired spins was very irreproducible and time dependent (see also 61). The observed concentrations of unpaired spins are catalogued in Table 9. With certain recipes it is possible to prepare some complexes free of detectable ESR. Therefore we conclude that the hydrocarbon-quinone complex solids are not themselves paramagnetic.

Evidently imperfections are the cause of ESR absorption in the hydrocarbon-quinone solids. The imperfections could conceivably be defects in the crystal structure or trapped impurities such as free radicals.

No change in the ESR was observed when large crystals were finely powdered. Thus surface effects seem to be eliminated as sources of paramagnetism once the solid has been formed.

In solids initially free of ESR, the concentration of imperfections in ortho-quinone complexes ($oQCl_4$ and $oQBr_4$) was increased several orders of magnitude by heating the complex solid (see also 62). The width and g-value of the ESR absorption were the same as those observed on crystallization. ESR absorption by the para-quinone complexes did not increase when the solid was heated for several hours at 125°C. Para-quinones have higher melting points, and in complexes they may have less tendency to migrate and introduce imperfections.*

An example spectrum is reproduced in Figure 16. The acceptor molecules do affect the g-value. Imperfections in perylene-$oQCl_4$ have $g = 2.00270$ ($\pm$ 0.00005 reproducibility); $g = 2.00348$ ($\pm$ 0.00010) for perylene-$oQBr_4$. Linewidths are about 5 oersteds. Line shapes are symmetric. The high symmetry of the absorption suggests that the observed resonance is not caused by multiple species. On this basis we believe that hydrocarbon positive ions and semiquinones are not both present independently in the solid. For the ESR observed, the g-value is probably not an average, but a characteristic of a single entity.

Relative to solid 1,1-diphenyl-2-picrylhydrazyl (DPPH, $T_1 = T_2 =$ 38 mμ sec (63)) the resonance was very easily saturated. Between 40°C and -80°C the concentration of unpaired spins in perylene-$oQCl_4$ was

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* Prolonged heating of the $oQCl_4$ and $oQBr_4$ complexes produces a second radical species which has a linewidth about one-fifth that of the first.

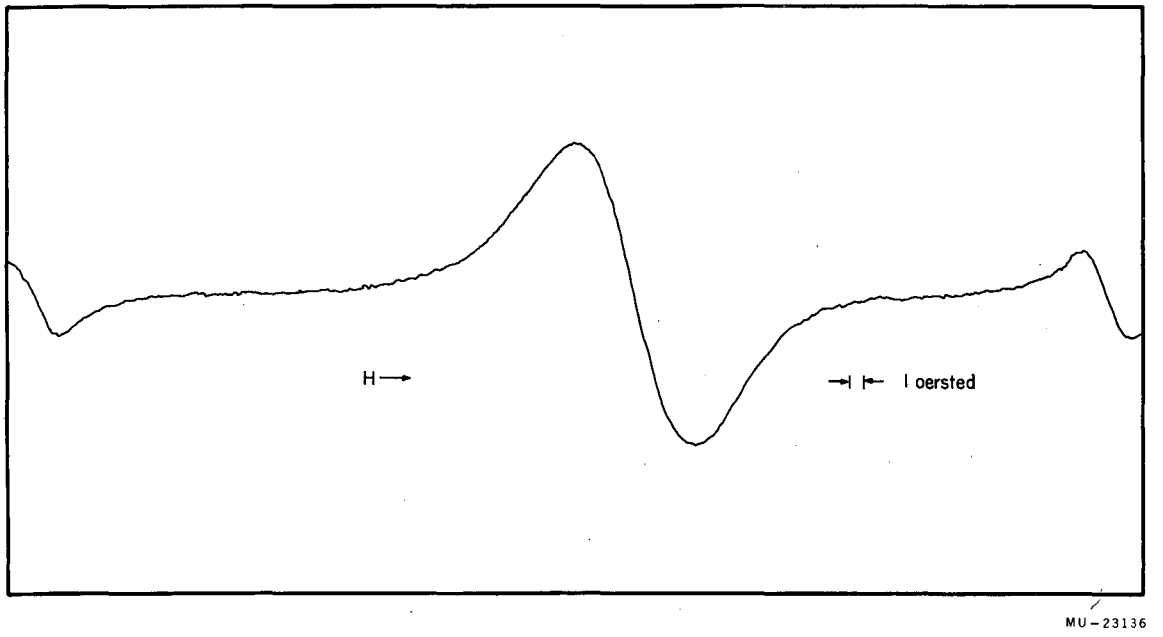

Fig. 16. ESR absorption derivative of the imperfections in perylene-oQBr4 at 100°C. The two peaks at each side are the Mn^{++} standard.

fairly constant, within ± 40%. If one assumed an activation energy, E, for production of unpaired spins, then $E \leq 0.05$ ev.

An increase in the ESR absorption was observed when the solid perylene-$oQCl_4$ was illuminated at temperatures above 80°C. Only wavelengths greater than 700 mμ were effective (see also 64). Probably this photoinduced ESR is the result of heating, although the effect appears to be reversible.

3. Summary. ESR absorption has been observed in hydrocarbon-quinone complexes which are themselves diamagnetic. The unpaired electrons occur as imperfections. Some characteristics of their ESR absorption have been described.

No detailed description of the imperfection is possible now. For example, among the many possibilities not yet eliminated, the imperfections may be free radicals trapped in the solid.

V. EXPERIMENTAL METHODS

A. Electron spin resonance

1. General characteristics. An X-band spectrometer with transmission cavity and barretter detector was used. It was constructed by P. G. Sogo. The external magnetic field was modulated at 200 cps and the ESR absorption derivative recorded. Microwave absorption was observed by detecting the decrease in barretter resistance. Unbalance of the barretter bridge at 200 cps was amplified conventionally and passed to a phase sensitive detector whose dc output was recorded. The recorded voltage change with paramagnetic absorption is analyzed in Appendix II.A.

Frequency of the klystron was automatically controlled at the cavity resonance. Possibly the recorded noise was caused by limitations in frequency control.

Two kinds of transmission cavities were used, a cylindrical TE_{011} and a rectangular TE_{103}. Q-values varied from 3000 to 5000 in different experiments.

Practical sensitivity of the spectrometer was 10^{14} unpaired-electron-oersted^2. 10^{15} radicals of DPPH gave a signal-to-noise ratio of 10 for rapid and undistorted detection.

Two 6-inch diameter magnets were used, both having gaps of 2-1/4 inches. Attempts of high resolution were probably limited by the field modulation amplitudes. At practical signal-to-noise ratios, 0.1 oersted is an estimated limit of resolution.

In a few cases where higher sensitivity was required, a 100 kc reflection spectrometer was used. It incorporated a Varian modulation

and control unit, Model V4560, and had a sensitivity about fifteen times better than the above machine.

2. Concentrations of unpaired electron spins. Singer and Kommandeur discussed some of the practical problems encountered in concentration measurements (11). Singer has also described a method for determining the concentration of unpaired spins (65). A ruby was fixed permanently on the cavity wall. Orientation of the ruby was adjusted so that its resonance absorption was displaced from the resonance position of the radicals, and they did not overlap. The concentration of Cr^{+++} in the ruby was calibrated with known amounts of $CuSO_4 \cdot 5H_2O$, $MnSO_4 \cdot H_2O$, and 1,1-diphenyl-2-picrylhydrazyl (DPPH). At any time the first moments of the ruby and of the radical absorption derivatives could be compared. The main advantage of this method is that it avoids use of organic free radicals which are unstable.

We attempted to use the Mn^{++} ion in MgO as a standard but discovered that the resonance was easily saturated. To avoid saturation difficulties we decided to use a free radical standard in spite of its instability.

All quantitative calculations of the number of unpaired electrons were referred to the DPPH radical. Poirer, Kahler and Benington measured the optical extinction of DPPH at 529 mμ, $\epsilon = 37\ (g/l)^{-1}cm^{-1}$ in chloroform (66). The highest extinction coefficient measured on samples prepared by us was 34. The Aldrich Chemical Company provided one sample (of several) which, when received, had an extinction coefficient of $37\ (g/l)^{-1}cm^{-1}$. This figure decreased with time until reaching a constant value of $32.3\ (g/l)^{-1}cm^{-1}$ after one year.

At any time the fraction of DPPH in the solid was calculated to be the ratio of the measured extinction coefficient to 37. The standards were prepared by weight and dilution, where the measured weight was corrected by this fraction to give the weight of DPPH.

The optical absorption obeys Beer's Law below 10^{-3} molar DPPH. There are numerous reports concerning the effect of oxygen and solvent on the DPPH electron spin resonance absorption (67,68,69,70).

A TE_{103} cavity was employed, following the suggestion of Kohlein and Muller (71). The DPPH standard and the sample were positioned each in a separate maximum of the resonating microwave magnetic field. Except perhaps for the case of water, it was shown that the dielectric constant of the sample did not greatly affect the concentration measurement (Figure 17). Within the experimental error the microwave field intensity apparently was reduced equally throughout the cavity by dielectric loss in the sample. At the position of the standard the cavity was sandwiched between Helmholtz coils. The DPPH absorption was displaced along the field axis by regulating the dc current passing through these coils. Thus the DPPH resonance did not overlap the absorption by the sample. In one sweep of the external field the sample absorption and standard absorption were displayed separately (Figure 18).

If the widths of the two absorptions by sample and DPPH were the same, the amplitudes of the two absorption derivatives were used to compute the ratio of concentrations.

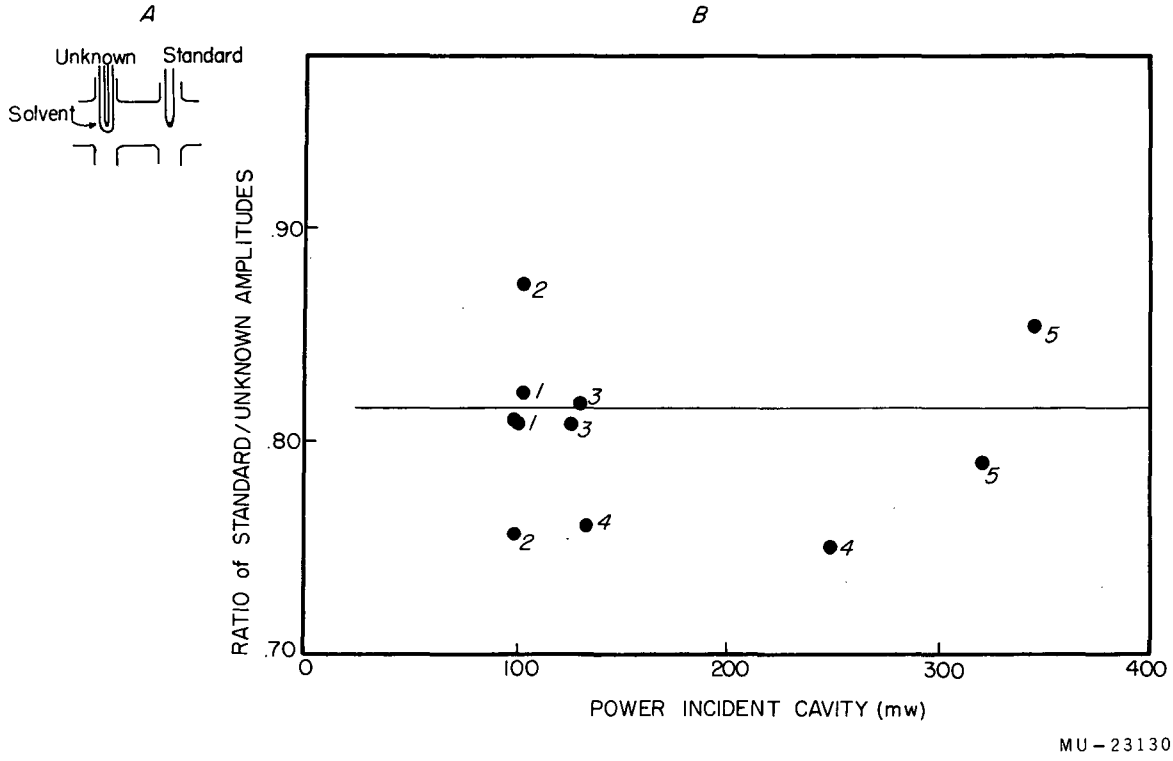

Fig. 17. Dielectric loss of TE_{103} cavity.

a) Geometry. Dielectric loss at the sample was varied by adding solvents of varying dielectric constant.

b) Relative amplitudes at the two positives as a function of the incident power needed to transmit constant power. 1. No solvent. 2. Dimethylaniline (ϵ = 4.91) 3. Acetonitrile (ϵ = 37.5). 4. Water (ϵ = 80). 5. Formamide (ϵ = 110).

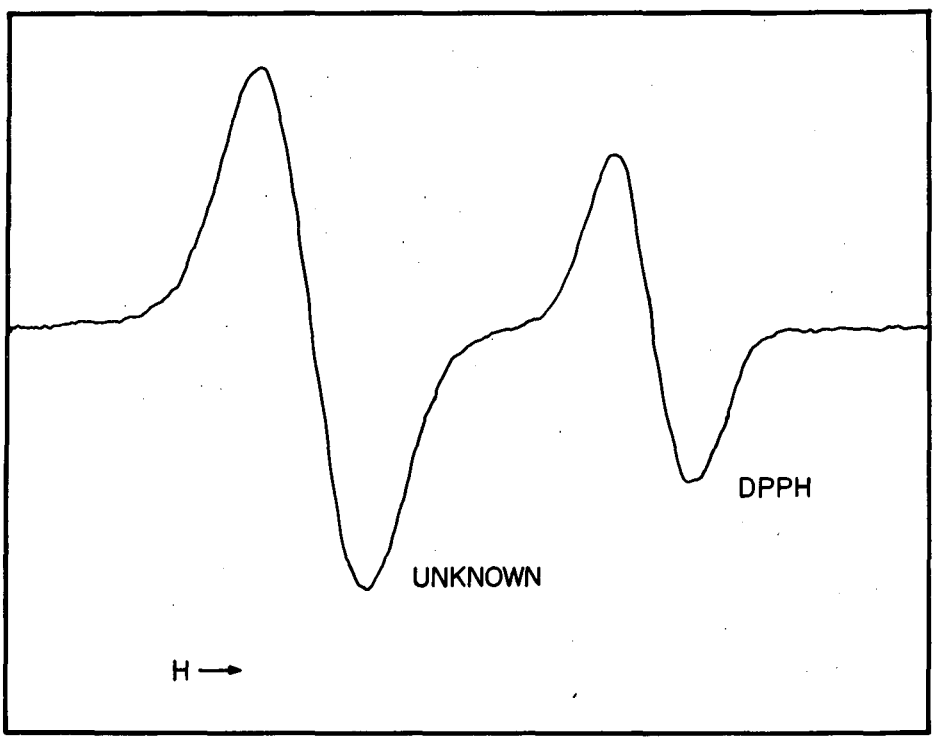

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Fig. 18. Typical concentration measurement using TE_{103} cavity with displaced DPPH resonance. Comparing DPPH with imperfections in perylene-$oQCl_4$. Linewidth of the DPPH absorption is caused by inhomogeneities in the external field.

If the widths differed slightly, by less than a factor of two, a somewhat more complicated computation was made. Ideally, the integrated absorption (double integral of the displayed derivative) should have been determined. Because of noise it was impossible to determine end-points of the absorption tails. The limits of integration on the recorded field axis had to be chosen somewhat arbitrarily. Silsbee showed (72) that the first moment of the absorption derivative was theoretically proportional to the integrated absorption. The simplest approximation to the first moment is the derivative amplitude times the square of the derivative width, $\underline{AW^2}$. For sample and DPPH linewidths not much different from each other, comparison of the approximate first moment, AW^2, may be more accurate than comparison of the integrated absorptions because of the influence of noise on the latter. Therefore in the case of similar linewidths, the AW^2 was used to compute the relative number of spins in the sample and in the standard.

Frequently the sample absorption had too great a linewidth to use either of these relatively simple computations. Then amplitudes and approximate first moments were only used for relative concentration measurements. Where absolute measurements were required, the exact first moment of the derivative had to be determined. The precison of this method was about ± 20% in the absolute concentration of unpaired electrons.

3. Temperature dependence. Sometimes the sample contained a polar solvent. Therefore, at different temperatures there were differ-

ent dielectric losses in the microwave cavity. Temperature dependence of the recorded voltage was caused not only by changes in magnetic absorption but also by changes in dielectric absorption. Therefore the use of an internal standard was essential. The standard DPPH obeys Curie's Law in the temperature region investigated and is a convenient standard, except for its instability. The TE_{103} cavity was used to measure the concentration of unpaired electrons as a function of temperature. When linewidths were temperature dependent, first moments were obtained as well as possible. Otherwise, the amplitudes were compared directly.

4. g-values and widths. An Mn^{++} in MgO standard which could be dispersed in a polyethylene sleeve had been designed by Lindblom as an internal standard (73). Mn^{++} was introduced into MgO, the $Mn^{++}:Mg^{++}$ ratio being about 1:5000. This MgO powder was diluted with polyethylene and molded into sleeves which fit snugly around the sample tubes.

g-Value measurements were made with the aid of this standard. The use of a plastic sleeve enabled one to keep the unknown in a fixed geometry in relation to the standard, i.e., the two were a glass tube and a concentric plastic cylinder, respectively. The Mn^{++} sleeve was calibrated by sliding it over a proton probe and making simultaneous measurements of the electron and proton resonance absorptions. Table 11 gives the results, in g-value units, of the calibration for the six hyperfine components of the Mn^{++} absorption at 9.844 Kmc. The value $\frac{\mu_p \text{ (oil)}}{\beta} = (657.462)^{-1}$ (74) was used with the microwave and radio frequencies to calculate the resonance positions. Frequency measure-

Table 11

Standard for g-value determinations. Hyperfine structure of Mn^{++} in MgO at 9.844 Kmc

Absorption Line (increasing field)	Effective g
1	2.13445 ± 0.00020*
2	2.08216 ± 0.00020
3	2.03114 ± 0.00009**
4	1.98150 ± 0.00009
5	1.93321 ± 0.00020
6	1.88599 ± 0.00020

* m.a.e. ± 100 ppm

** m.a.e. ± 45 ppm

ments were made either with a Hewlett-Packard frequency meter X550A or an HP 540A transfer oscillator and electronic counter 524B with converter.

The two central Mn^{++} lines were swept through at the same time as the free radical line. The g-values for the free radicals were determined by interpolating between the Mn^{++} lines. A characteristic reproduction of this sweep is shown in Figure 19.

Precision g-value measurements have been discussed by Bleis, Brown and Maling (47). We have been interested in a rapid and easy measurement which is suitable for analytical purposes at the frequency of calibration. A precision of $\pm$ 0.0002 was usual. There are low intensity satellite lines of Mn^{++} which absorb in the free radical resonance positions. Therefore, it is necessary to keep the standard small compared to the number of unpaired electrons in the sample. No corrections were made for deviations of the microwave frequency from 9.844 Kmc.

Widths were also determined by this interpolation procedure. The width of a line was calculated from the microwave frequency and the position of derivative maxima between the Mn^{++} lines.

It was convenient to calibrate the Mn^{++} in MgO sleeve as an approximate concentration standard as well as g-value standard. In one sweep, the first moment of both standard and unknown could be compared. The difficulties of this method have been mentioned. g-Value measurements, widths and approximate concentration estimates were made in one sweep of the spectrum. Concentration measurements

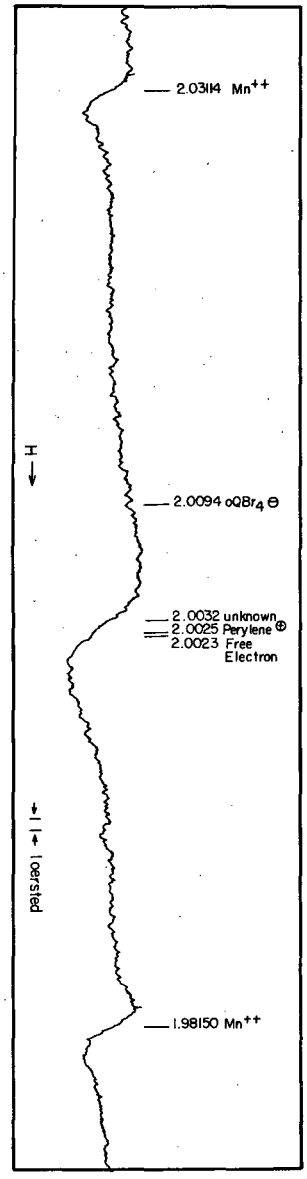

Fig. 19. ESR absorption produced by vigorously mixing perylene solid with $oQBr_4$ solid at 25°C. Typical determination of a g-value, g = 2.0032, and comparison with other known g-values at 9.6 Kmc.

made in this way was reproducible to $\pm$ 20% for 10^{14} radicals. Absolute measurements were good perhaps with in an order of magnitude.

5. Saturation. The degree of power saturation was determined for most of the observations of microwave absorption. The recorded total signal was obtained as a function of the power incident the cavity from 0.5 mw to 250 mw. The degree of saturation was computed from the deviation of this function from linearity at the power level employed.

The theoretical relationships between power, saturation factor Z and width for a homogeneous system having Lorentzian lineshape are reproduced in Appendix II.B. For simplicity we have used a phenomenological definition of the saturation factor Z_e, which is the theoretical Z only under certain conditions. Z_{ea} is the experimental saturation factor determined at the amplitude maxima of the recorded derivative. Including linewidth changes, Z_{et} is the total saturation factor.

$$Z_{ea}^{3/2} = \frac{A}{m_a P_o}$$

and

$$Z_{et}^{1/2} = \frac{AW^2}{m_t P_o},$$

where A is the maximum amplitude of the derivative of ESR absorption; W is the width between derivative maxima; and P_o is the incident microwave power. At low P_o, Z = 1 and $A = m_a P_o$. Thus at low power the

the amplitude increases linearly with power, the slope being m_a. Likewise for m_t. Most measurements were made with about 20 mw incident to the cavity resonator, 8 mw incident to the barretter detector.

Microwave power transmitted through the cavity was determined directly by the barretter detector. If the bias voltage of the barretter bridge was measured when the bridge was balanced, the microwave power at the barretter could be calculated. The power at other points in the waveguide was determined similarly. The absolute power was determined only at the beginning and end of all saturation measurements. Direct reading variable attenuators (Hewlett-Packard 382A) were sufficiently accurate to measure the power once the absolute determination had been made.

B. Other physical measurements

The optical absorption spectra were obtained with a Cary Model 14M recording spectrophotometer. Cells of lengths between 10 cm and 0.005 cm were used.

A Beckman IR7 was used to obtain the infrared spectra. The instrument was used with automatic conditions at 200 cm^{-1}/min sweep.

Dc conductance measurements were made with a vibrating reed electrometer (Applied Physics Corp. Model 31) which recorded the voltage drop across a standard resistor in series with the conductance cell. Ac measurements were made at 60 cps with an Industrial Instruments, Inc. Conductivity Bridge Model RC 16. The cell supplied by Industrial Instruments was a pipette type with shiny platinum electrodes having a cell constant about 0.1 cm^{-1}.

C. Chemical techniques

Chemical operations were done in the atmosphere, in a dry box and in vacuum. The dry box was swept with nitrogen evaporating from a liquid nitrogen reservoir. It contained less than 1 ppm impurity. The sweep rate was such that the box was swept completely about once every hour.

Quinones were recrystallized from carbon tetrachloride. Dimethylaniline and other solvents were purified according to Vogel (75) and Weissberger (76). Tetramethylphenylenediamine and the hydrocarbons were vacuum sublimed at temperatures up to 200°C. Analyses of some starting materials follow. Perylene: Found, C = 94.89, H = 4.85; formula, C = 95.20, H = 4.80. o-Chloranil: Found, C = 29.03, Cl = 57.32; formula, C = 29.30, Cl = 57.70.

VI. CONCLUSION

A. Radicals in solution

Whether or not an electron will be transferred from one organic molecule to another in solution is primarily determined by the ionization potential of the donor molecule and the electron affinity of the acceptor.* No accurate electron affinities of quinones are available now. However, since the ionization potentials of arylamines and hydrocarbons are known (Table 12A), the results may be discussed in terms of these donor molecules which were used. For example, chloranil ($pQCl_4$) hasbeen allowed to react in solution with N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD), with N,N-dimethylaniline (DMA), and with perylene. The results in each of these three systems are now reviewed and their relationships discussed.

For the first time we have observed by ESR the hyperfine structure of the TMPD positive ion in the presence of a transient chloranil semiquinone. This is positive evidence that a completely ionized electron transfer from TMPD to $pQCl_4$ does occur in acetonitrile to produce free radicals.

Free radicals were also observed when $pQCl_4$ was dissolved in DMA even though the ionization potential of DMA is about 0.7 ev greater than that of TMPD. However, a simple electron transfer is not observed. In this case the radical semiquinone of chloranil is an unstable intermediate in the reaction of $pQCl_4$ with DMA, whose produce

---

* The effects of ionic solvation, ion-pair formation and the tendency to form covalent bonds are arbitrarily assumed to be the same for all compounds under investigation.

Table 12

A. Ionization potentials (77)

N,N,N',N'-tetramethyl-p-phenylenediamine	6.6 ev
Perylene	7.15
N,N-dimethylaniline	7.3

B. Relative electron affinities*

Iodine	1.8 ev
Chloranil	2.72
Bromanil	2.76
o-Chloranil	2.87
o-Bromanil	2.91

C. Dielectric constants (76,78)

	ϵ	$1/\epsilon \times 10^2$
N,N-dimethylaniline	4.91	20.4
Ethylene dichloride	10.36	9.65
Nitrobenzene	34.82	2.87
Acetonitrile	37.5	2.66

---

* The value for iodine $E_A \geq 1.8$ ev, was taken from the work of Ferguson and Matsen (9). The other values were estimated assuming a linear function for the charge-transfer frequency, ν_{CT}. $\nu_{CT} = C \approx E_A$. For a given donor, in this case perylene, C is a constant. Exactly, a more complex function holds in which case the electron affinities estimated for quinones are somewhat lower, relative to iodine, than the values reported here (5). Note also that the effects of polarizability on ν_{CT} have been neglected.

is crystal violet. The kinetics of the reaction may be explained if it is assumed that a hydrogen atom transfer is the limiting step in the reaction, rather than an electron transfer. The semiquinone is produced subsequently.

Perhaps the ionization potential of DMA is not low enough for an electron to transfer from DMA to $pQCl_4$, as it did in the reaction of TMPD with $pQCl_4$. We have used a donor having an ionization potential nearer that of TMPD, hoping that again we would observe an electron transfer. Perylene has an ionization potential between those of TMPD and DMA, but still over 0.5 ev greater than TMPD. However, no ESR absorption was observed when perylene-$pQCl_4$ was dissolved in nitrobenzene. With $pQCl_4$ as the acceptor, it appears that 6.6 ev, the ionization potential of TMPD, may be near an upper limit for which ionized electron transfer can be observed in solution.

We have attempted to produce ionization by using other quinones which are stronger acceptors than $pQCl_4$. Some approximate electron affinities of the tetrahalogenated quinones used are tabulated in Table 12B. Still no ESR absorption was observed when perylene-$oQCl_4$ was dissolved in nitrobenzene. When $oQCl_4$ was allowed to react with DMA the rate of reaction was much greater than the reaction rate of DMA with $pQCl_4$. However, in DMA there is not much difference between the electron affinities of these two acceptors. The difference in rate has tentatively been assigned to a steric factor. The reaction of TMPD with $oQCl_4$ was so fast that no quantitative measurements were made.

The kind of reaction which will occur between a donor and an acceptor quinone is obviously determined by what kind of donor mole-

cule is used. An electron will be transferred directly from donor to acceptor only when the ionization potential of the donor is sufficiently low. Although the kind of reaction depends upon the donor, the rates of these reactions depend upon the kind of tetrahalogenated quinone used. It has not been established whether the difference in the rates is a result of small differences in electron affinity, less than 0.2 ev, or is the result of steric factors.

The dielectric constant, ϵ, of the medium was a controlling factor in the transfer of an electron from TMPD to $pQCl_4$. In addition to the potential for complete electron transfer, the medium must be able to accommodate the ionic charge of the radicals for the transfer to occur in preference to other reactions. The transfer from TMPD to $pQCl_4$ occurred in acetonitrile, $\epsilon = 37.5$, not in ethylene dichloride, $\epsilon = 10.36$.

DMA has a low dielectric constant (Table 12C) and we tried to induce an electron transfer to $pQCl_4$ by adding solvents of higher polarity to the DMA. It was found, however, that addition of solvents to the DMA solution of $pQCl_4$ changed the characteristics of this reacting system. In general the addition of solvents destroyed the observed ESR absorption.

Also, no electron transfer from perylene to $oQCl_4$ was observed in solution by ESR, even in nitrobenzene. The dielectric constant of nitrobenzene is $= 34.82$, which is similar to the dielectric constant of acetonitrile in which electron transfer has been observed from TMPD to $pQCl_4$. Of course there may be some specific local solvent coordination which invalidates comparison of the macroscopic dielectric constants of acetonitrile, and nitrobenzene

In solution we have studied two reactions in which both donor-acceptor complexes and free radicals are observed. An electron transfer from TMPD to $pQCl_4$ occurs in acetonitrile. $pQCl_4$ also oxidizes DMA However, only in the first case does the electron appear to transfer directly from the donor to the acceptor.

In the reaction of quinones with DMA, the semiquinones were identified by their g-values. We wanted additional evidence that the observed radicals were semiquinones. The fluoranil semiquinone normally has an ESR absorption spectrum consisting of five hyperfine components. Observation of this hyperfine splitting in the reaction of fluoranil with DMA would have aided considerably in identifying the intermediate radical. However, in the presence of a high concentration of fluoranil, which were the conditions of the experiment, the fluorine hyperfine pattern was not resolved. Apparently the semiquinones exist in a complex environment in which rapid electron transfer among quinone, semiquinone and hydroquinone ion is likely.

B. Imperfections in solids

ESR absorption was discovered in hydrocarbon-quinone solid complexes. The paramagnetism could not be correlated with any other properties of the solids which we determined, and it is quite irreproducible. Apparently the observed ESR is caused by an imperfection in the general sense; that is, the donor-acceptor solids are not themselves paramagnetic.

There are general characteristics in the ESR absorption by the perylene-quinone solids which will be used to assign a more specific structure to the imperfection in the future.

C. Discussion

The positive results obtained by this research have been related to the charge-donor properties of aromatic hydrocarbons and arylamines and to the charge-acceptor properties of tetrahalogenated quinones. We point out that in none of the cases studied were the donor-acceptor complexes or solids themselves intrinsically paramagnetic. Rather the donor and acceptor properties of the organic materials result in two observations. One observation is that the donors do associate with the acceptors to form diamagnetic adducts. Secondly, these donors and acceptors frequently react to form paramagnetic species, that is, radicals and imperfections. Indeed these observations may be related if the donor-acceptor complexes are precursors of the magnetic species.

ACKNOWLEDGMENTS

The author thanks Professor Melvin Calvin for his imaginative supervision. His stimulating insight made this work entertaining. His relevant and demanding criticisms caused it to be more significant.

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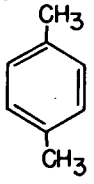
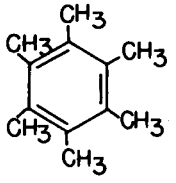
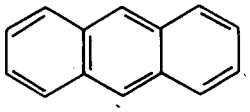
P-XYLENE



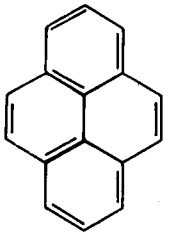
HEXAMETHYLBENZENE



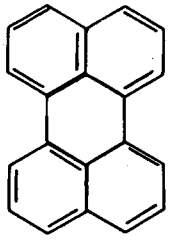
ANTHRACENE



PYRENE



PERYLENE



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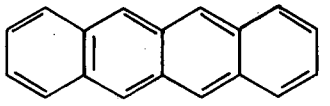

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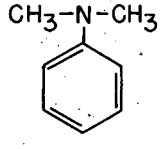
N,N- DIMETHYLANILINE (DMA)



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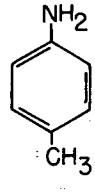
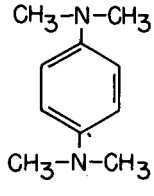


N,N,N',N'-TETRAMETHYL-P-PHENYLENEDIAMINE (TMPD)



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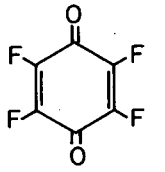
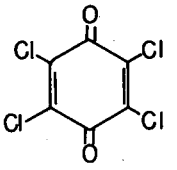
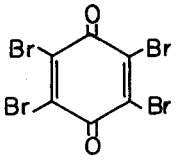


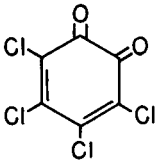
2,3,5,6-TETRACHLORO-1,4-BENZOQUINONE
FLUORANIL (pQF_4)



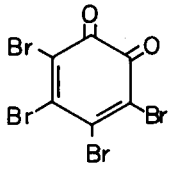
CHLORANIL ($pQCl_4$)



BROMANIL ($pQBr_4$)



O-CHLORANIL ($oQCl_4$)



O-BROMANIL ($oQBr_4$)

MU-23244

APPENDIX II.

A.

The recorded voltage change with ESR absorption, as a function of the microwave frequency, ω, is ΔV_r.

$$\Delta V_r = G \eta Q_{uo} P_o H_s \frac{dX''}{d\omega}$$

where G is a numerical factor including the barretter constant and instrumental gain; η is the filling factor; Q_{uo} is the unloaded quality factor without magnetic absorption; P_o is the power incident the cavity; H_s is the amplitude of magnetic field modulation; and X'' is the absorptive magnetic susceptibility.

$$X'' = \frac{N_o g^2 \beta^2 S(S+1)}{3kT} \omega_o \pi \left[\frac{g(\omega - \omega_o)}{1 + 1/4 \left(\frac{g\beta}{\hbar}\right)^2 H_1^2 T_1 g(\omega - \omega_o)} \right]$$

where $g(\omega - \omega_o)$ is the shape factor and the other familiar constants are defined in Appendix III.

B.

The recorded voltage of Appendix II.A may be written for a Lorentzian lineshape factor as a function of frequency.

$$\Delta V_r = \frac{2CN_o T_2^3}{\pi T} P_o \frac{(\omega - \omega_o)}{\left[1 - (\omega - \omega_o)^2 T_2^2 + 1/4 \left(\frac{g\beta}{\hbar}\right)^2 H_1^2 T_1 T_2\right]^2}$$

C is an instrument constant. The maxima of the recorded derivatives are,

$$\pm(\Delta V_r)_{max} = \frac{9CN_o T_2^2}{8\sqrt{3}\pi T} P_o Z^{3/2}$$

where

$$Z = \frac{1}{\left[1 + 1/4 \left(\frac{g\beta}{\hbar}\right)^2 H_1^2 T_1 T_2\right]}$$

The width of this Lorentzian line between derivative maxima is

$$W = \frac{2}{\sqrt{3}\ T_2} Z^{-1/2}$$

C.

The following working equation was used to calculate the microwave magnetic field maxima in the TE_{10S} cavity:

$$H_1^2 = 1.6 \times 10^5 \frac{P_o}{V\nu} (1 - T)Q_L$$

where H_1^2 is oersted^2, maximum of the total linear polarized field,

P_o is milliwatts power incident the cavity,

T is the cavity transmission coefficient,

Q_L is the loaded quality factor,

V is the cavity volume in cm^3,

ν is the microwave frequency in cps.

APPENDIX III

The Gaussian system of units has been used in discussions of molecular properties. The magnetic field and induction have been assumed equal. Magnetic quantities are expressed in oersteds.

When making the transition from measured quantities to molecular interpretations, a mixed system of units was used. Measurements were made in mks units; interpretations were made in gaussin units. The working equations relating experiment to theory contain both mks and gaussian units, with the correct numerical conversion factors.

DEFINITIONS AND NUMERICAL VALUES*

Planck constant	$h = 2\pi\hbar$	6.62491×10^{-27} erg-sec
Bohr magneton	β	0.92732×10^{-20} erg-gauss^{-1}
Magnetic moment of the proton in units of the Bohr magneton	$\left(\frac{\mu_p(\text{oil})}{\beta}\right)$	$(657.462)^{-1}$
Spectroscopic splitting factor	g	
Spectroscopic splitting factor of a free electron	g	2.00229
Effective electron spin	S	
Absolute temperature	T	degrees
Concentration of unpaired electrons per gram	N_o	gram^{-1}
Frequency	ν	cycles-sec^{-1}
Frequency	ω	radians-sec^{-1}
Total amplitude of the microwave magnetic field	H_1	oersted
External dc magnetic field	H_o	oersted
Modulation amplitude of the external field	H_s	oersted
Spin-lattice relaxation time	T_1	sec
Spin-phase coherence time	T_2	sec

* Numerical values obtained from the following references:

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