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Free Radicals, Ions and Donor-acceptor Complexes in the Reaction: Chloranil + N,N-Dimethylaniline → Crystal Violet

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Chloranil and other tetrahalogenated quinones react with N,N-dimethylaniline to form the crystal violet cation. Diamagnetic donor-acceptor complexes and semiquinone radicals are two intermediates which have been observed in this reaction. Some preliminary physical measurements of the kinetics are described and correlated.

Introduction

We have been interested in the mechanism by which organic compounds are oxidized or reduced.[1a,2,3] In the present work we have focused our attention on the system in which both the oxidizing agent and the reducing agent are organic compounds. We have examined the reaction of chloranil with N,N-dimethylaniline in N,N-dimethylaniline as a solvent.

It is known that chloranil and dimethylaniline (N,N-dimethylaniline in this work) form a blue molecular complex. The equilibrium constant is $K = 3.34$ (mole/l.)$^{-1}$ for the formation of 1:1 complexes in carbon tetrachloride.[4] The blue color is caused by charge-transfer excitation of the complex.[5] The formation of the adduct and the optical absorption within the adduct are the result of charge donor–acceptor interaction of a general kind.

In general, donor–acceptor adducts are formed when compounds which have low ionization potentials, charge-donors, are combined with compounds with high electron affinities, charge-acceptors.[5] There is an extensive literature concerning the kind of donor-acceptor interaction which results in the formation of diamagnetic molecular adducts like dimethylaniline-chloranil. Although a great deal is known about the reversible formation of donor–acceptor complexes, very little is known about donor–acceptor association which might occur during the course of irreversible reactions.

If the ionization potential of the donor is low enough and the electron affinity of the acceptor is high enough, an electron may be transferred completely from the donor molecule to the acceptor molecule. This electron transfer, or electronic ionization, is one process in which donor–acceptor complexes may be intermediates.

In fact, an ionization of this kind has already been demonstrated by the work of Kainer and Überle,[6] who made a solid donor–acceptor complex from N,N,N′,N′-tetramethyl-*p*-phenylenediamine (TMPD), the donor, and chloranil, the acceptor. When this solid was dissolved in acetonitrile, they observed the optical absorption spectra of the positive radical-ion of TMPD and the negative radical-ion of chloranil. They proposed that these radical-ions are products of the complete transfer of an electron from TMPD to chloranil.

Kainer and Überle found that the transfer of an electron from TMPD to chloranil did not occur in dioxane and benzene, solvents with lower dielectric constants.

We have found that solutions of TMPD and chloranil are not stable, even in the absence of air. When equimolar quantities of TMPD and chloranil were dissolved in acetonitrile, two distinct electron spin resonance (c.s.r.) absorptions were observed (Figure 1a). 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,[7] Hausser[8] and others. As soon as the original solution was prepared, the narrow chloranil semiquinone resonance began decreasing rapidly and the TMPD$^+$ resonance increased proportionately (Fig. 1b). Simultaneously optical absorption by the semiquinone at 4500 Å. decreased, and optical absorption by the positive radical-ion at 6000 Å. increased.

When this solution of TMPD and chloranil was first prepared, a donor–acceptor complex was observed by its charge-transfer optical absorption at 9240 Å. As the electron transfer proceeded to completion, the charge-transfer absorption disappeared altogether.

After these rapid changes were complete, additional slower changes followed. The free radicals disappeared completely in the course of one week.

Although the electron transfer occurred in acetonitrile ($\epsilon = 37.5$), it did not occur in ethylene dichloride ($\epsilon = 10.35$). When TMPD and chloranil were dissolved in ethylene dichloride, the charge-transfer absorption of the TMPD chloranil complex was observed, but neither e.s.r. absorption nor optical absorption by the positive and negative radical-ions were observed. These solutions are also unstable and an unknown product is formed in 1 hr.

While the final oxidation level of TMPD is not yet known, it seems certain that an electron transfer from donor to acceptor does occur in the initial steps of the reaction when the dielectric constant of the medium is sufficiently high. The phenomenon of ionization has been reviewed by Briegleb and

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(1) (a) Abstracted from thesis of J. W. Eastman, University of California, Berkeley, June, 1961. UCRL-9722. (b) NATO Fellow, 1960–1961. (c) Organisch Chemisch Laboratorium, Rijks Universiteit, Leiden, The Netherlands; (d) The work described in this paper was supported, in part, by the U. S. Atomic Energy Commission.

(2) Gerrit Engelsma, Thesis, Leiden (1959), G. Engelsma and E. Havinga, *Tetrahedron*, **2**, 289 (1958).

(3) M. Calvin, *J. Theor. Biol.*, **2**, 258 (1961).

(4) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **58**, 249 (1954).

(5) G. Briegleb and J. Czekalla, *Angew. Chem.*, **72**, 401 (1960), and references cited therein; also UCRL Translation 654, 1961.

(6) H. Kainer and A. Überle, *Chem. Ber.*, **88**, 1147 (1955).

(7) T. R. Tuttle, Jr., *J. Chem. Phys.*, **30**, 331 (1959).

(8) K. H. Hausser, *Arch. Sci. Geneva*, **12**, 195 (1959).

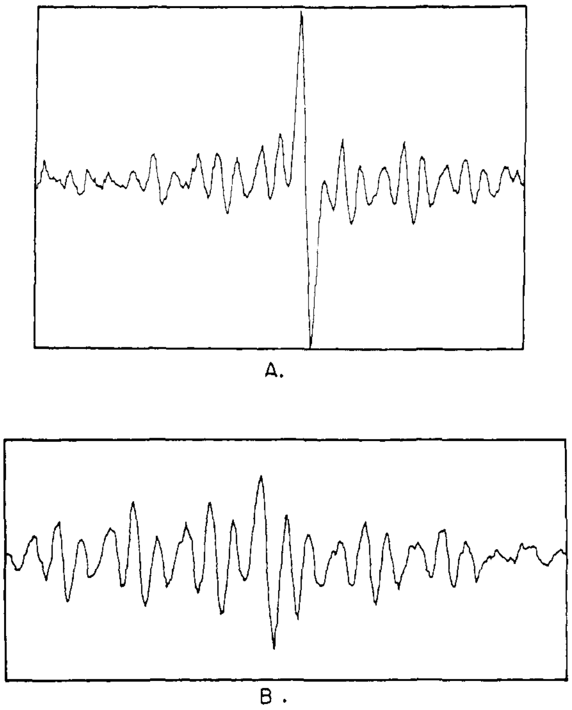

Fig. 1.—Derivative of the e.s.r. absorption observed by dissolving equimolar amounts of TMPD and chloranil in acetonitrile; reaction time: (a) 25 min.; (b) 1 hour.

Czekalla[5] with some specific reference to dielectric effects.

At this time there is insufficient quantitative information to generalize the electron-transfer mechanism to other reactions. However, there is ample experimental evidence to show that donor–acceptor complexes, ions, and radicals do appear together frequently.

Intermediate complexes, radicals and ions have been observed in the reaction of trinitrobenzene (the acceptor) with various donors.[9–13] E.s.r. absorption was observed in the reaction of trinitrobenzene with trimethylamine.[14]

The initial reaction of bromine and $\alpha,\alpha',\beta,\beta'$-tetrakis-(4-methoxyphenyl)-ethylene produced a blue paramagnetic solution in nitroethane and a brown diamagnetic solution in carbon tetrachloride, as observed by e.s.r.[15] This again demonstrated the dependence of ionization on dielectric constant. Paramagnetism was observed in the polar nitroethane but not in nonpolar carbon tetrachloride. SO_3, $SbCl_5$ and BF_3 have been used to accept electrons from aromatic hydrocarbons.[16,17] E.s.r. of the aromatic positive ions produced has been investigated in some detail.[18] These inorganic acceptors appear to form sigma complexes as intermediates in the ionization reaction.[16] These various oxidation–reduction reactions are still under investigation.

Eley has shown that under some conditions the complex solid dimethylaniline–chloranil is paramagnetic,[19] indicating that radical-ions may be present in the solid. He also reported that dimethylaniline–chloranil solid has an electronic conductance, $\sigma = 2 \times 10^{-8}$ (ohm cm.)$^{-1}$. We have tried to determine not only if electron transfer occurs in solution but also if electronic conduction occurs in the solution.

The solution of chloranil in dimethylaniline is not perhaps an ideal case for the study of electron transfer. The dielectric constant of dimethylaniline (4.91) is low compared to the dielectric constants of ethylene dichloride (10.4) and acetonitrile (37.5). Transfer of an electron from TMPD to chloranil occurred in acetonitrile but not in ethylene dichloride. Also the ionization potential (determined by charge transfer absorption) of dimethylaniline (7.3 e.v.) is greater than the ionization potential of TMPD (6.6 e.v.).[20] Thus both the dielectric constant and the ionization potential may be unfavorable in the present reaction for an electron transfer to occur.

Dimethylaniline is not itself stable in air, but it can be slowly oxidized by air to crystal violet.[21] Buckley, Dunstan and Henbest have already attempted to observe a reaction between dimethylaniline and chloranil in dilute benzene solutions.[22] They observed no irreversible 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 chloranil does react with dimethylaniline to form the familiar crystal violet cation. We have studied this reaction to see if the transfer of an electron from dimethylaniline to chloranil occurs at any time during its course.

Experimental

Chemical operations were done in the air atmosphere and in a dry box. The dry box was swept with dry nitrogen evaporating from a liquid nitrogen reservoir. It reportedly contained less than 1 p.p.m. impurities. The sweep rate was such that the box was swept completely about once every hour.

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

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

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(9) R. E. Miller and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 2375 (1959).

(10) R. Foster, *ibid.*, 3508 (1959).

(11) G. Briegleb, W. Liptay and M. Cantner, *Z. Physik. Chem.*, **26**, 55 (1960).

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(20) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959).

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The microwave spectrometer and the method of determining g-values has been described elsewhere.[23] A Mn^{++} standard which could be dispersed in a polyethylene sleeve was designed as an internal concentration standard as described elsewhere.[3]

Concentration measurements on one unknown were reproducible to ± 20% for 10^{14} radicals. Absolute measurements were probably good only to an order of magnitude.

Chloranil was recrystallized once from toluene and once from carbon tetrachloride. Dimethylaniline was purified according to Vogel.[24]

Results

1. **Product Identification.**—The infrared spectrum and the visible spectrum (Fig. 2) of the isolated product were identical to the spectra of crystal violet. 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 1:1. However, the product contains somewhat more crystal violet cation than a 1:1 ratio predicts.

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

Because the reaction proceeds in a very large excess of dimethylaniline, the chloranil may be expended before the reaction has reached completion. That is, the dimethylaniline may be oxidized by chloranil to form arylamine intermediates so that none of the chloranil remains to complete the formation of crystal violet in the final steps. If air is present it may perform the oxidation after the chloranil has been expended or it may regenerate the chloranil by oxidation of the hydroquinone.

2. **Optical Absorption.**—Optical absorption spectra of the reacting solution of chloranil and dimethylaniline are reproduced in Fig. 3. Initially, a charge-transfer absorption occurs at 650 mμ caused by the well known dimethylaniline-chloranil complex. The complex reacted to produce an intermediate which absorbed near 400 mμ and whose absorption disappeared rapidly when exposed to the air. The spectrum of the final product, crystal violet, has an absorption peak at 590 mμ (Fig. 2).

3. **Conductivity.**—The conductivity of dimethylaniline was about 2×10^{-10} ohm^{-1} cm.$^{-1}$. When chloranil was dissolved in the dimethylaniline, the conductivity was time dependent and always could be divided into three periods (Fig. 4), although the lengths of the periods were somewhat irreproducible. An initial fast rise (period one, ten minutes) from 2×10^{-9} ohm^{-1} to about $9 \times$

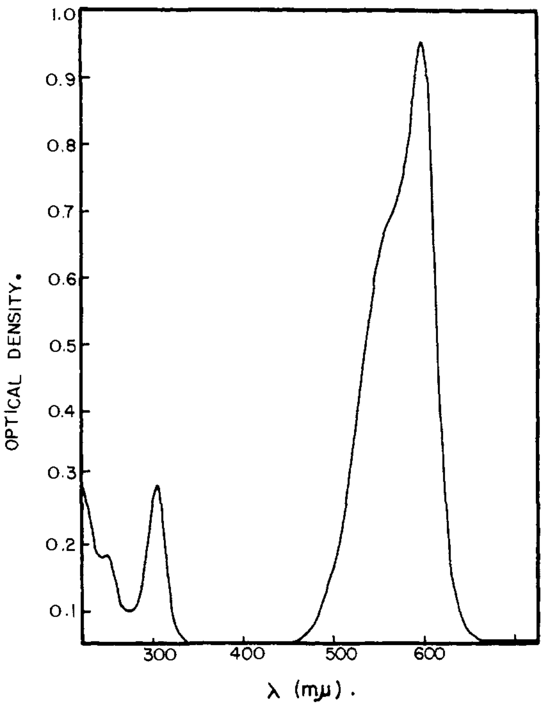

Fig. 2.—Optical absorption spectrum of the unpurified crystalline final product in $CHCl_3$, 0.13 g./l., cell length, 0.05 cm. It is the same as the spectrum of crystal violet.[25]

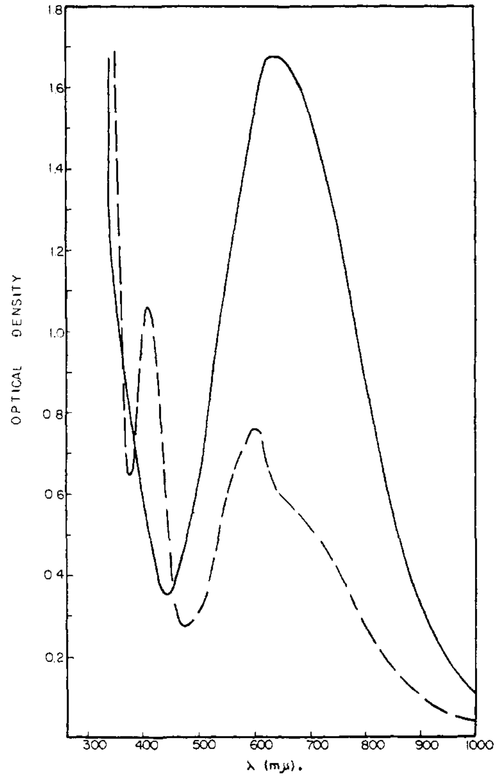

Fig. 3.—Optical absorption spectra of the intermediates in the reaction of 0.14 M chloranil with dimethylaniline in the absence of air, after: ———, 4 hr., shows only C–T complex at 650 mμ and – – – –, 2.5 days, shows three different species, (a) C–T complex, 650 mμ, (b) intermediate, 400 mμ, (c) crystal violet, 590 mμ.

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(23) J. W. Eastman, G. M. Androes and Melvin Calvin, *J. Chem. Phys.*, to be published.

(24) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p. 573.

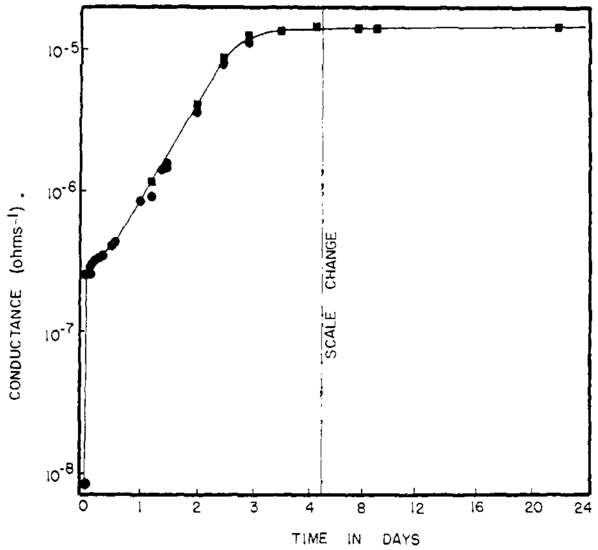

Fig. 4.—Conductance of the reacting solution of dimethylaniline initially containing 0.14 *M* chloranil. The cell constant was about 10^{-1} cm.$^{-1}$; circles, d.c. and squares, a.c.

10^{-8} ohm^{-1} was followed by a slower increase to about 3×10^{-7} ohm^{-1} (cell constant about 10^{-1} cm.$^{-1}$). 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 1.5×10^{-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).

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 the reciprocal absolute temperature gave a straight line above 2.5°, the melting point. Below −30°, the function could be approximated by a straight line, but the slope was many times greater than the slope above 2.5°. If one assumes that the slope is proportional to 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° was $^1/_{20}$ that of the liquid at 2.5°. 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.**—A typical time dependence of e.s.r. is illustrated in Fig. 5c. Eleven measurements of the reaction kinetics by e.s.r. showed the kinetics to be irreproducible. The reaction proceeded to completion in a few hours if the dimethylaniline was exposed to air for several months before chloranil was added. Vacuum distilled dimethylaniline took several days to react with chloranil.

The concentration of free radicals observed always decreased when the solution was exposed to air at any time during the course of the reaction. This may be due to the oxidation of the semiquinone by air to regenerate quinone.

The *g*-value of the intermediate radical was measured, $g = 2.0056 \pm 0.0002$. This agrees with the value $g = 2.0058$ of the familiar chloranil semiquinone.[26] Below is given additional evidence which shows that the semiquinone is the intermediate radical.

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 unchanged particles left in solution would be 200 mμ.

5. **Simultaneous Measurements.**—The reaction of dimethylaniline and chloranil was followed simultaneously by three physical measurements. The results are reproduced in Fig. 5. The charge-transfer absorption by the dimethylaniline-chloranil complex decreases (Fig. 5a). The ionic product is observed by its conductivity to increase (Fig. 5b), after a slow initial period. The intermediate radical (Fig. 5c) and an optically observed species at 410 mμ (Fig. 5d) follow similar kinetics. Source of the absorption at 410 mμ is not known.

Figure 6 shows the results of another experiment with simultaneous measurement of the optical and the e.s.r. absorptions, this time in the presence of air. The reaction mixture consisted of 7 mmoles of chloranil dissolved in 50 ml. of dimethylaniline. It was kept at 55° for 24 hr. in an open bottle. The disappearance of the dimethylaniline-chloranil complex (determined by the change in absorption at 780 mμ) appears linear with time. The e.s.r. signal amplitude reaches its maximum when about half of the complex has disappeared. The curve for the formation of crystal violet was determined by the difference between the measured absorption at 610 mμ and the calculated absorption of the dimethylaniline-chloranil complex at this wave length. After about 8 hr. the crystal violet started to precipitate from the solution. In 24 hr. 200 mg. of crystal violet had been formed. This corresponds to 14% of the chloranil. After the reaction mixture had been kept at room temperature for 6 days more, the yield had increased to 30%.

Interpretation of the Results

Because there is insufficient information about the partially oxidized intermediates, it is impossible to suggest a definite mechanism for the oxidation, but some general characteristics of the reaction may be discussed.

1. **Optical Absorption.**—In the solvent dimethylaniline, essentially all the chloranil is complexed with dimethylaniline initially.

2. **Conductivity.**—In the introduction to this report we have shown how radical-ions are formed

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[25] J. C. Turgeon and V. K. La Mer, *J. Am. Chem. Soc.*, **74**, 5989 (1952), and references cited therein.

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

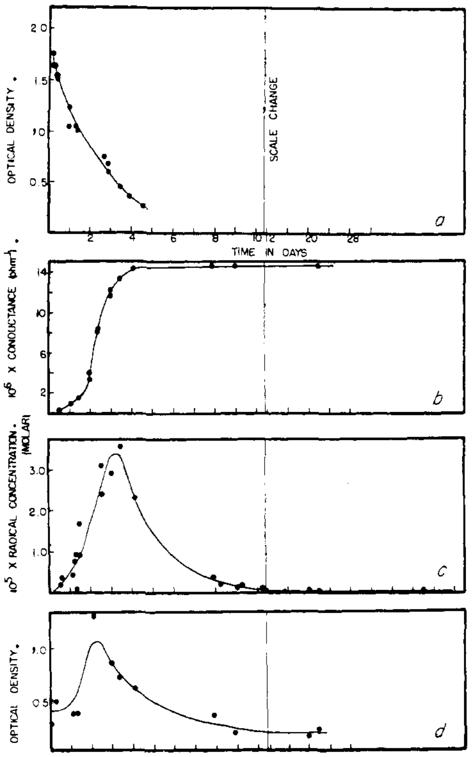

Fig. 5.—The reaction in a nitrogen atmosphere of 0.14 *M* chloranil in dimethylaniline: (a) charge-transfer absorption at 650 mμ (using a 0.005 cm. optical cell), (b) conductivity (cell constant $\sim 10^{-1}$ cm.$^{-1}$), (c) radical concentration by e.s.r., (d) intermediate absorption at 410 mμ. The abcissas are all time in days; because of the scale in Fig. 5b, the initial rapid rise in conductivity does not appear.

by the transfer of electrons from TMPD to chloranil. In the reaction of dimethylaniline with chloranil, the rapid initial rise in conductivity may be caused by ions which also are products of electron transfer. If one assumes an equivalent conductance of $\Lambda = 100 \frac{\text{cm.}^2}{\text{eq. ohm}}$, for the hypothetical organic radical-ions produced, the ionization constant $K = \frac{[D^+][A^-]}{[A]} \sim 10^{-13}$ mole/l. may be estimated from a measurement of the conductivity. If this ionization does occur, the concentration of radicals would be barely detectable by e.s.r., and we have not observed any. Only 10^{-7} *M* ions are necessary to produce the rapid initial increase in conductivity. If the ions are impurities in the chloranil, only 10^{-6} mole ions per mole of chloranil are necessary to cause this increase. Thus the initial increase of conductivity could be attributed to ionic impurities in the chloranil. The constant $K \sim 10^{-13}$ mole/l., may thus be taken as an upper limit of ionization if we assume that electron transfer does occur.

After the initial increase in conductivity, it remains fairly constant until crystal violet salt formation begins and semiquinone accumulates. During the initial intermediate steps, no large concentration of ions is formed. An increase in conductivity occurs during the final oxidation periods, after which the solid salt is precipitated.

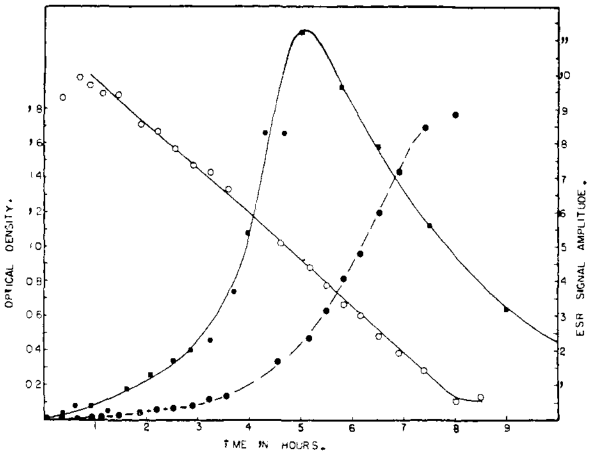

Fig. 6.—The reaction in air at 55° of 7 mmoles chloranil in 50 ml. of dimethylaniline: ——— (open circles), absorption at 780 mμ; – – – –, measured absorption at 610 mμ minus absorption due to the dimethylaniline–chloranil complex calculated on the basis of its absorption at 780 mμ; ——— (squares), e.s.r. signal amplitude.

The optical density (assuming ϵ = 87,000 (mole/l.)$^{-1}$ cm.$^{-1}$) and conductivity (assuming $\Lambda = \left(\frac{50 \text{ cm.}^2}{\text{eq. ohm}}\right)$ have been used to estimate a solubility product approximately $K \sim 10^{-6}$ (mole/l.)^2.

3. Electron Spin Resonance.—Throughout the course of this work we have assumed that the observed semiquinone radicals are intermediates in the reaction which produces crystal violet. When quinones are used as oxidizing agents, the reaction generally proceeds by way of semiquinone radicals.

A general characteristic of the e.s.r. absorption behavior is that the maximum rate of radical formation does not occur at the beginning of the reaction when the initial reactants are at their highest concentrations. There are at least four ways to explain this characteristic of the e.s.r. absorption. First of all, if quinones were reduced at three stages in the reaction, the rate of semiquinone formation would be the sum of three rates. The sum would reach a maximum at some intermediate time in the course of the reaction rather than at the beginning. Secondly, though it seems unlikely, an inhibitor may be present which reduces the initial rate. Thirdly, delayed increase in the rate of radical formation may be a result of autocatalysis. Finally, there may be some unknown reaction which precedes the build-up of an observable semiquinone concentration.

The oxidation reaction may proceed by electron transfer or by hydrogen atom transfer. The dielectric constant and the ionization potential of dimethylaniline may be unfavorable to the transfer of electrons, as was discussed in the introduction. To arrive at the crystal violet cation, the central carbon atom must be formed, presumably from a methyl group of the dimethylaniline. Several hydrogen atoms must be moved during the reaction. Transfers of hydrogen atoms may provide a mechanism by which the oxidation can proceed in fewer steps than are needed in an ionic mechanism.

At present there are many ways to qualitatively account for the kinetics of the changes of optical absorption, e.s.r. absorption and conductivity, and more investigation is necessary in order to obtain reproducible data from which a mechanism can be substantiated.

TABLE I

FREQUENCY OF MAXIMUM CHARGE-TRANSFER ABSORPTION BY QUINONES DISSOLVED IN DIMETHYLANILINE

Quinone	Frequency × 10^{-3} (cm.$^{-1}$)
Fluoranil	15.55
Chloranil	15.6
Bromanil	15.1
o-Chloranil	15.9
o-Bromanil	15.7

Another accountable fact is that only semiquinone radicals were observed and no other radicals. If arylamine radicals are present, their steady-state concentrations must be very low. On the other hand, it is possible that the arylamine radicals are present but that they have very short spin lifetimes. If the spin lifetimes are short enough, say less than 10^{-11} sec., e.s.r. absorption by these radicals may be too broad to be observed. Because dimethylaniline is the solvent in the reaction and it is present in extremely high concentration, rapid electron transfer may occur throughout the solvent so that the mean lifetime of each radical is short enough to broaden its e.s.r. absorption. In such a case, one may expect the charge carriers in the solution to be electrons rather than ions. However, we have no other evidence on this most interesting possibility.

TABLE II

COMPARISON OF *g*-VALUES

Method of preparation

Semiquinones of the quinone	This work[a] Quinone + dimethylaniline in dimethylaniline	Quinone + sodium iodide in acetonitrile	Other work Air oxidation of hydroquinone in ethanolic KOH	Quinone + sodium iodide precipitate[b] [29]
Fluoranil	2.0054		2.0048 ± 0.0006[30]	
Chloranil	2.0056	2.0055	2.0058[26]	2.0044 ± 0.0008
			2.00568 ± .00002[31]	
Bromanil	2.0085	2.0085	2.00875 ± .00002[31]	2.0068 ± .0010
o-Chloranil	2.0058			
o-Bromanil	2.0094			2.0077 ± .0008

[a] Usual average deviation of individual measurements from recorded value is ±0.0002. [b] We have obtained for the solid salt of chloranil, $g = 2.0057$, demonstrating a systematic error in these measurements; add 0.0015 to numbers in this column.

Reaction of Other Quinones Dissolved in Dimethylaniline. 1. Charge-transfer Frequencies.—We have observed the reaction of dimethylaniline with fluoranil, bromanil, *o*-chloranil (3,4,5,6-tetrachloro-1,2-benzoquinone) and *o*-bromanil (3,4,5,6-tetrabromo-1,2-benzoquinone). In each case, a blue complex was formed immediately when the quinone was dissolved in dimethylaniline. The frequencies of maximum charge-transfer absorption by these complexes are recorded in Table I. They are all nearly the same.

For a given donor and a series of acceptors, it is sometimes assumed that $\nu_{CT} = C - E_a$, where C is a constant, E_a is the electron affinity of the acceptor, and ν_{CT} is the frequency of maximum charge-transfer absorption.[27] If this simple approximation applies to the case where dimethylaniline is the solvent and donor and where quinones are the acceptors, then the electron affinities of paraquinones and orthoquinones are the same within 600 cm.$^{-1}$. However, in chloroform the frequency of maximum charge-transfer absorption by a perylene-*p*-quinone complex is greater by 1400 cm.$^{-1}$ than the frequency of absorption by the corresponding perylene–*o*-quinone complex.[23] Obviously the approximation does not hold quantitatively in all cases, since it is extremely unlikely that the entire list of quinones in Table I has the same electron affinity. The electron affinities of the quinones may differ even though the observed frequencies of maximum charge-transfer absorption by the dimethylaniline–quinone complexes are the same. The approximation neglects the polarizability of the components, and it is based upon the assumption that only one kind of complex contributes to the observed optical absorption.

2. **Rates of Reaction.**—The over-all reactions of *ortho*-quinones with dimethylaniline occurred over one hundred times faster than the reactions of *para*-quinones with dimethylaniline. If the reaction proceeds *via* an initial electron transfer from dimethylaniline to quinone, the difference in rate may be due to a difference in the initial equilibrium concentration of radical-ions. The concentration of radical-ions may be greater when *ortho*-quinones are used than when *para*-quinones are used if the electron affinities of the *ortho*-quinones are greater than the electron affinities of the *para*-quinones.

If hydrogen atom transfers occur in the rate determining steps rather than electron transfers, the *ortho*-quinones may react more quickly than the *para*-quinones for several reasons. First of all, in protonic solvents like water, the reduction potentials of the *ortho*-quinones are greater than the reduction potentials of the *para*-quinones. This is because *ortho*-semiquinones form a stabilizing hydrogen bond.[28] On the other hand, the mechanisms of the rate determining reactions may involve steric factors so that the *ortho*-quinones react faster than *para*-quinones.

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(27) R. Foster, *Tetrahedron*, **10**, 96 (1960).

(28) G. E. K. Branch and M. Calvin, "Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 309.

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3. **g-Values.**[32]—The g-values of radical intermediates observed in the dimethylaniline–quinone reactions may be compared with the g-values of semiquinones prepared by other methods (Table II). The radicals which we observed in dimethylaniline have g-values which are identical to the independently determined g-values of the corresponding semiquinones. In fact, it is this comparison which shows that the radical intermediates are indeed semiquinones.

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

Summary.—Chloranil reacts with N,N-dimethylaniline in N,N-dimethylaniline as solvent to yield a crystal violet salt. Diamagnetic donor-acceptor complexes and paramagnetic semiquinones are two observed intermediates. Four other tetrahalogenated quinones react similarly with dimethylaniline.

Preliminary kinetic data have been obtained from measurements of optical absorption, conductivity and e.s.r. absorption and the mechanism of the oxidation has been discussed. If the transfer of an electron from dimethylaniline to chloranil occurs, the steady-state concentration of ions produced by the electron transfer is very small.

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Effect of Urea on Hydrogen Bonding in Some Dicarboxylic Acids[1]

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The effect of urea on proteins has been attributed to hydrogen bond "breaking." In the course of testing this hypothesis we have developed a method of calculating the free energies of hydrogen bonding between carboxyl groups in a dicarboxylic acid as well as between carboxyl and carboxylate groups in its mono-anion. This involves comparison of titration constants between hydrogen bonded forms (*e.g.*, maleic acid) and comparable non-bonded compounds (*e.g.* fumaric acid). Titration constants of these acids and of malonic, dimethylmalonic, diethylmalonic and ethylisopropylmalonic aids are recorded in aqueous media containing 0-7 M urea and at 7, 25 and 37°. From these data it does not appear that urea has any great effect on the hydrogen bonds. Thus in maleic acid the free energy of the carboxyl–carboxylate bond is about −2300 calories in water and about −2200 calories in 7 M urea at 25°.

Proteins are "denatured" in aqueous solutions which contain large concentrations of urea. This result was ascribed by Mirsky and Pauling[2] to an ability of urea to "break" hydrogen bonds and this postulate has been widely accepted. No direct evidence of such an action of urea in aqueous solution has been adduced, unless its action on proteins and certain polymers of amino acid is considered evidence. Kauzman[3] has emphasized intramolecular hydrophobic bonds as stabilizing influences in the specific molecular conformations of proteins and assumes that urea affects these. Klotz and Stryker[4] suggest "solvent-(macromolecular) solute interaction" as a stabilizing influence and further suggest that a perturbation of this interaction by urea results in denaturation. In this hypothesis the action of urea could be more directly with the water than with the protein.[5] It is in connection with the problems of the effect of urea on proteins that one of us began a study of the influence of urea on acid-base behavior.[6] The present paper concerns dicarboxylic acids which contain intramolecular hydrogen bonds in aqueous solutions and the effect of urea upon these bonds.

The existence of hydrogen bonded structures in mono-anions of certain dicarboxylic acids was assumed by Jones and Soper[7] (more recently by Hunter[8] and by McDaniel and Brown[9]) to account for the large ratio K_1/K_2 in such acids. This qualitative idea was formulated in terms of equilibria by Westheimer and Benfey[10] and applied to maleic acid in water. The formulation leads to a hydrogen bonding constant which seemed reasonable. Some uncertainty (a factor of 2) in the theory results from the nature of the models used to estimate the dissociation constants unperturbed by hydrogen bonding. We will use the same formulation of equilibrium but different final equations and models. We believe the formulation below takes maximum advantage of the Westheimer and Benfey equilibrium scheme.

Formulation.—Let MH_2 represent a dicarboxylic acid. Reactions 1 and 2 show its successive ionizations. The lower case letters represent con-

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