Possible Role of Electron Donor–Acceptor Complexes in Chemical Reactions: Kinetic and Spectroscopic Studies

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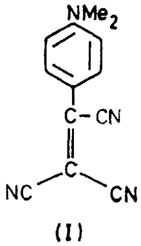
Kinetics and energetics of electron-transfer reactions of a few electron acceptors with *NNN'N'*-tetramethyl-*p*-phenylenediamine and other donors are reported. The kinetics are markedly affected by the solvent polarity and the acceptor strength. Solvent effects on the kinetics of the reaction between *NN*-dimethylaniline and tetracyanoethylene have been investigated in detail: the rate of formation of the tetracyanoethane derivative (which is the reaction intermediate), as well as of its subsequent reaction to yield *NN*-dimethyl-4-tricyanovinylaniline, are found to be equally solvent-sensitive. Reactions of a few substituted anilines with chloranil have been studied and the rate data are markedly dependent on the donor strength. Solvent effects on the reaction of aniline with chloranil are found to be appreciable.

SOME effort has been directed to elucidating reactions of electron donor–acceptor complexes. Various types of reactions of such complexes have been reported and the subject has been reviewed by Mulliken and Person,[1] Kosower,[2,3] Foster,[4] and Rao and his co-authors.[5,6] In most of the reactions reported hitherto, it has not been possible to establish unequivocally that the reactions go through the intermediate electron donor–acceptor complexes. We have investigated the kinetics and mechanisms of a few reactions which are likely to proceed through such complexes, namely (i) thermal electron-transfer reactions between electron donors and acceptors giving rise to radical ions,[2,5,6] (ii) reaction of *NN*-dimethylaniline with tetracyanoethylene giving *NN*-dimethyl-4-tricyanovinylaniline (I),[2,7] and (iii) reaction of aniline and substituted anilines with chloranil to yield nucleophilic substitution products.[8]



(I)

Under (i), we have studied the interaction of *NNN'N'*-tetramethyl-*p*-phenylenediamine with electron acceptors of different strengths in solvents of varying polarity. In addition, we have examined the interaction of a few anions with electron acceptors. Reaction (ii) is probably one of the few systems where some detailed mechanistic studies have been carried out.[7,9-12] The present study is mainly concerned with solvent effects on the rate constants for the formation of the tetracyanoethane intermediate (which was earlier considered to be a σ-complex) as well as of the product in some detail. We have also examined the interaction of *NN*-dimethyl-*p*-toluidine with tetracyanoethylene. Under (iii), we have studied the effect of solvents as well as of substituents on the nucleophilic substitution reaction of chloranil with aniline which is supposed to proceed through the formation of the outer π- and inner σ-complexes. These studies were intended to establish more definitively that the reaction really proceeds through the electron donor–acceptor complex.

RESULTS AND DISCUSSION

Electron-transfer Reactions.—Interaction of tetramethyl-*p*-phenylenediamine with tetracyanoethylene or chloranil in relatively polar solvents like acetonitrile readily produces radical ions exhibiting characteristic optical and e.s.r. spectra.[13-18] Interaction between tetramethyl-*p*-phenylenediamine and chloranil in non-polar solvents, however, gives rise to the charge-transfer band due to the donor–acceptor complex.[14,15] Similarly, the interaction of tetramethyl-*p*-phenylenediamine with *sym*-trinitrobenzene is reported to yield radical ions in methanol medium, but only the electron donor–acceptor complex in acetonitrile.[14]

In the systems of tetramethyl-*p*-phenylenediamine with both tetracyanoethylene and chloranil the energies of activation, E_a, for the electron-transfer reactions are relatively small and the entropies of activation, $\Delta S^\ddagger$, are large and negative as expected in such electron-

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transfer reactions.[19] In the tetramethyl-*p*-phenylene diamine–chloranil system, the rate constant increases and E_a decreases with increase in solvent polarity (as measured by the dielectric constant, ε, or Kosower's Z-parameter [20] of the solvents).

In the tetramethyl-*p*-phenylenediamine–trinitrobenzene system, electron-transfer kinetics could only be studied by employing the tetramethyl-*p*-phenylenediamine monocation band in both ethanol and methanol solvents. In less polar solvents like propan-2-ol or acetonitrile, only the charge-transfer band (due to the electron donor–acceptor complex) was observed. The rate is much faster and E_a much lower in methanol than ethanol (Table 1); $\Delta S^\ddagger$ is large and negative, the magnitude being higher in MeOH.

TABLE 1

Kinetic data on the reaction of tetramethylphenylenediamine with electron acceptors

Acceptor	Solvent	ε	Z [a]	$10^4k(298\ K)/s^{-1}$	E_a/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
Tetracyanoethylene	CH_2Cl_2	9·1	64	7·8 [c]	38	−180
Chloranil	CH_2Cl_2 [b]	9·1	64	3·1 [d]	60	−117
				2·9 [e]	63	−105
	MeCN–CCl_4 (1 : 1)	19·8	66	6·6 [d]	29	−209
				6·3 [e]	33	−201
Trinitrobenzene [f]	EtOH [g]	24·3	80	17 [e]	54	−117
	MeOH	32·6	84	29 [e]	42	−151

[a] Kosower's Z-values of solvent mixtures were estimated by us. [b] Electron-transfer rate was too fast to measure in MeCN–ether (2 : 1) mixture ($Z = 67$) and in MeCN ($Z = 71$). There was no measurable autoxidation of the diamine in CH_2Cl_2 solution. [c] Measured at the charge-transfer band maximum (960 nm). The development of tetracyanoethylene radical anion bands are clearly seen, but tetracyanoethylene radical anion appears to be unstable in solution. [d] Measured at the charge-transfer band maximum (950 nm). [e] Measured at the tetramethyl-*p*-phenylenediamine monocation band maxima (570 and 620 nm): same rates were found with both the wavelengths. [f] Tetramethyl-*p*-phenylenediamine undergoes autoxidation (by oxygen in air) to give the tetramethyl-*p*-phenylenediamine monocation in MeOH and EtOH solvents. E_a for the autoxidation in MeOH and EtOH solvents was *ca.* 17 kJ mol^{-1} ($\Delta S^\ddagger$ −251 J K^{-1} mol^{-1} at 298 K). [g] In Pr^{i}OH ($Z = 76$) or MeCN ($Z = 71$) medium, only the charge-transfer band is observed ($\lambda_{max.}$ *ca.* 585 nm).

Some features of the kinetic data on the reactions of tetramethyl-*p*-phenylenediamine with tetracyanoethylene, chloranil, and trinitrobenzene are relevant to understanding the mechanism of electron-transfer: (*a*) The rate constants determined by employing the charge-transfer band and the radical cation bands are similar; (*b*) the formation of radical ions is easier with strong acceptors (*e.g.*, compare tetracyanoethylene or chloranil with trinitrobenzene); (*c*) the rate is enhanced (and E_a lowered) by increase in solvent polarity; (*d*) the large negative entropy of activation is consistent with a transition state which is more polar than the initial state (which is likely to be the 'neutral' electron donor–acceptor complex). All these observations, particularly (*d*), seem to suggest the electron-transfer reactions of tetramethyl-*p*-phenylenediamine may proceed through donor–acceptor complexes. The reaction products of the electron-transfer reactions can be either in the form of intimate ion pairs or solvent-separated pairs [6] depending upon the solvent polarity. Kinetic studies do not, however, differentiate the nature of the products since these affect ΔH° of the reaction more markedly than E_a.

Interaction of some anions with strong acceptors like chloranil and tetracyanoethylene is known to produce radical anions of the acceptor.[21] We considered the possibility of studying the kinetics of electron-transfer reactions between halide ions and chloranil, tetracyanoethylene, or 7,7,8,8-tetracyanoquinodimethane employing a solvent of appropriate polarity. With the last as acceptor, I$^-$, Br$^-$, and Cl$^-$ readily gave the tetracyanoquinodimethane radical anion ($\lambda_{max.}$ 850, 770, 750, 685, 670, 435, and 420 nm) [22] even in CCl_4 and CH_2Cl_2 solvents. Similarly, I$^-$ instantaneously interacts with tetracyanoethylene or chloranil to give the radical anion (tetracyanoethylene radical anion, polybanded spectrum in the region 370—470 nm; chloranil radical anion, $\lambda_{max.}$ 425 and 450 nm) [14,18,21] in CCl_4 and CH_2Cl_2 solvents. However, interaction of Br$^-$ and Cl$^-$ with chloranil only gave the characteristic charge-transfer bands with equilibrium constants of 1 and 4 l. mol^{-1} respectively in CCl_4 medium; the enthalpies of formation were close to zero, indicating that these systems are contact-pairs.[1,5,23] Similar equilibrium constants and near-zero ΔH° values have been reported for the interaction of I$^-$, Br$^-$, and Cl$^-$ with trinitrobenzene and other acceptors.[24] Keeping of solutions of Br$^-$ and chloranil, Cl$^-$ + chloranil, I$^-$ + trinitrobenzene, or Br$^-$ + trinitrobenzene for long periods in highly polar solvents like MeCN or MeOH did not show evidence for the formation of radical anions.

Br$^-$ and Cl$^-$ gave rise to charge-transfer bands with tetracyanoethylene, but there was evidence for subsequent reactions giving rise to the pentacyanopropenide anion ($\lambda_{max.}$ 400 and 415 nm) [18,21] and other products. We carried out some preliminary kinetic studies of the reaction of Br$^-$ with tetracyanoethylene by measuring the time-dependence of the charge-transfer band ($\lambda_{CT} = 460$ nm) in MeCN solvent. We found the first-order rate constant to be $2{\cdot}2 \times 10^{-6}\ s^{-1}$ (at 298 K) with

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E_a 37 kJ mol^{-1}. This rate constant is much smaller than the constants found by us in the tetramethyl-*p*-phenylenediamine–acceptor systems and is unlikely to be due to an electron-transfer reaction.

Among the various anions examined by us, SCN$^-$ seemed to be ideal for the study of electron-transfer kinetics with tetracyanoethylene, since we could clearly see a charge-transfer band ($\lambda_{max.}$ 500 nm) which decreased in intensity with time. The first-order rate constant and E_a in MeCN solution were $7{\cdot}4 \times 10^{-4}$ s^{-1} (at 298 K) and 90 kJ mol^{-1} respectively. The magnitude of this rate constant is comparable with that found in the tetramethyl-*p*-phenylenediamine–acceptor systems. The tetracyanoethylene radical ion is quite unstable in solution and undergoes further transformations; the bands due to it do not appear to be suitable for kinetic measurements.

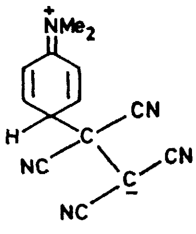
TABLE 2

Kinetic data on the reaction of *NN*-dimethylaniline with tetracyanoethylene [a]

			π-Complex ⟶ Intermediate (IV)			Intermediate (IV) ⟶ Product		
Solvent	ε	Z	10^3k_1 [b] (298 K)/s^{-1}	E_a/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}	10^5k_2 [c] (298 K)/s^{-1}	E_a/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}
$CHCl_3$	4·8	63	1·06	25	−208	2·4	50	−155
MeCN–CCl_4 (1 : 2)	14	63·8	3·2	17	−225	4·6	63	−107
CH_2Cl_2	9	64	3·2	13	−247	5·6	46	−161
MeCN–ether (1 : 1)	21	65	5·7	13	−241	15	75 [d]	−55
MeCN	37·5	71	Too fast to measure			187	79 [d]	−20

[a] Pseudo first-order rate constants; $\Delta S^\ddagger$ are calculated based on second-order rate constants. [b] Measured at the charge-transfer band maximum (675 nm). [c] Measured at the $\lambda_{max.}$ of the reaction product (515 nm). [d] These are higher than expected; the reason for this is not clear.

Reaction of NN-*Dimethylaniline with Tetracyanoethylene.*—Interaction of dimethylaniline with tetracyanoethylene in $CHCl_3$ solution first gives a charge-transfer band (675 nm) due to the π-complex which further decomposes to a colourless reaction intermediate (or the so-called σ-complex) ($\lambda_{max.}$ 279 nm). The second step involves the further reaction of the intermediate with dimethylaniline to give the final product (I). Rappoport[7] suggested the structure of the intermediate to be (II) and observed that the rate constants for the formation of the intermediate (k_1) and for the subsequent reaction of the intermediate (k_2) were both solvent-sensitive. When the solvent was changed from 80% CCl_4–20% $CHCl_3$ to 80% $C_2H_4Cl_2$–20% $CHCl_3$, k_1 increased by a factor of *ca.* 150 and k_2 by a factor of *ca.* 50. This large solvent-sensitivity of k_1 was taken to imply that the transition state differed greatly in polarity from the initial state. Accordingly, the large variation of k_1 in the limited range of solvent polarity was taken to be consistent with structure (II) for the intermediate. Kosower,[2] however, suggested that k_1 was associated with the slow step involving electron-transfer and that the σ-complex itself could be the bicyclo[4,2,0]octane derivative (III).

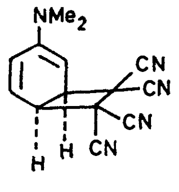


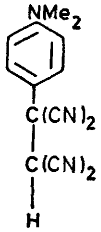
(II)

Rappoport and his co-workers[9] and Farrell and his co-workers[10-12] showed that the structure of the intermediate (IV); further, k_2 for the reaction of (independently prepared) (IV) with dimethylaniline was twice as fast as that of the second step in the reaction of dimethylaniline with tetracyanoethylene. We have investigated the solvent effects on k_1 and k_2 in greater detail (Table 2).

Table 2 shows that k_1 increases in the order MeCN > MeCN–ether (1 : 1) > CH_2Cl_2 ≈ MeCN–CCl_4 (1 : 2) > $CHCl_3$, the rate being too fast to measure in MeCN–ether (2 : 1) and MeCN; E_a decreases with increasing solvent polarity. The increase in k_1 is six-fold for a ΔZ of *ca.* 2. The $\Delta S^\ddagger$ values are large and negative indicating a polar transition state. It is interesting that the k_1 values found by us are comparable with those of the electron-transfer reactions of tetramethyl-*p*-phenylenediamine with trinitrobenzene in alcohol solvents or with tetracyanoethylene or chloranil in CH_2Cl_2.

(III)

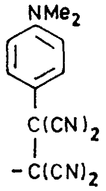




(IV)

The rate constant, k_2, corresponding to the transformation of the intermediate (III or IV) to the product (I) is generally smaller than k_1; k_2 also increases by a factor of *ca.* 6 for a ΔZ of *ca.* 2 just like k_1. The $\Delta S^\ddagger$ values are negative (though not as large as in the transformation of the π-complex to the intermediate) indicating that the transition state in the second step also differs in polarity from the initial state (intermediate). These solvent effects seem to be consistent with structure (IV) for the intermediate; structure (IV) will then give rise to (I) possibly through (V). We note that the solvent-dependence of k_1 and k_2 observed by us is far less than that reported by Rappoport.[7] It is possible that Rappoport's measurements in mixed solvents are in error.

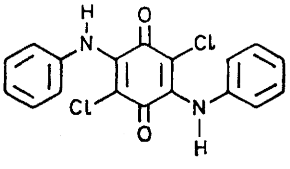
Since the reaction of dimethylaniline with tetracyanoethylene giving rise to (I) would require a free hydrogen



(V)

in the 4-position of dimethylaniline, we thought it worth while to study the reaction of tetracyanoethylene with *NN*-dimethyl-*p*-toluidine. This system only showed the electron-transfer reaction yielding the tetracyanoethylene radical anion with the characteristic polybanded electronic spectrum in the 370—470 nm region. The first-order rate constants for the reaction in CH_2Cl_2 and MeCN solvents were *ca.* $3{\cdot}3 \times 10^{-4}$ and *ca.* $24{\cdot}5 \times 10^{-4}$ s^{-1} at 298 K (with E_a values of 21 and 17 kJ mol^{-1}) respectively. These kinetic data are similar to those reported in Table 1 for the reaction of tetramethyl-*p*-phenylenediamine with electron acceptors.

Reaction of Anilines with Chloranil.—Interaction of aniline with chloranil gives rise to an outer π-complex which eventually transforms into 2,5-dichloro-3,6-dianilino-*p*-benzoquinone (VI) through inner σ-complex intermediates. We have studied the kinetics of the reaction of a few *para*-substituted anilines with chloranil and also solvent effects on the reaction between aniline and chloranil.



(VI)

Nagakura and his co-workers [8] showed that the transformation of the π-complex into (VI) involves a rather complex rate expression. The time-dependence of the intensity of the product absorption band can, however, be used to study some aspects of the mechanism. The rate curves thus obtained for the reaction of aniline, *p*-chloroaniline, and *p*-toluidine with chloranil are shown in Figure 1. The results clearly show that the donor strength markedly affects the rate of the reaction, the rates varying in the order, *p*-toluidine > aniline > *p*-chloroaniline. This order of donor strength is consistent with the electron-donating abilities of the *para*-substituents. This observation supports the assumption that the reaction of aniline with chloranil proceeds through an electron donor–acceptor complex. A similar dependence of donor strength on electrical properties of substituents has been noticed in the transformation of outer complexes into inner complexes.[25]

Since the transformation of the π-complex to the final product involves the formation of intermediate inner σ-complexes where there may be some charge separation, we would expect the kinetics of the reaction of aniline with chloranil to be affected markedly by solvents. We do indeed find that the rate of reaction varies in the following order of solvent polarity: propan-2-ol > MeCN > MeCN–ether (1 : 1) > ether; in ether (as also in CH_2Cl_2) the reaction is extremely slow (see Figure 2).

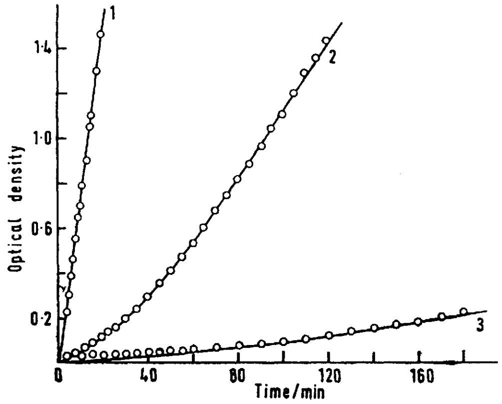


FIGURE 1 Time-dependence of optical densities of the reaction products of anilines ($1{\cdot}8 \times 10^{-2}$M) with chloranil (9×10^{-4}M) at 280 K in diethyl ether–isopropyl alcohol (3 : 1) medium: Curve 1, *p*-toluidine; 2, aniline; 3, *p*-chloroaniline

We have studied the reaction of *N*-methylaniline with chloranil and found that the product similar to (VI) with $\lambda_{max.}$ at 540, 285, and 250 nm is produced. The reaction is slower than with aniline. Interaction of dimethylaniline with chloranil in CH_2Cl_2 first gives rise to the charge-transfer band (650 nm) which decreases in intensity fairly rapidly giving place to the characteristic bands of the radical anion of chloranil ($\lambda_{max.}$ 425 and 450 nm); this is then followed by a slow reaction finally yielding the crystal violet cation ($\lambda_{max.}$ 590 nm; pseudo-first-order rate constant *ca.* 10^{-5} s^{-1} at 298 K with E_a

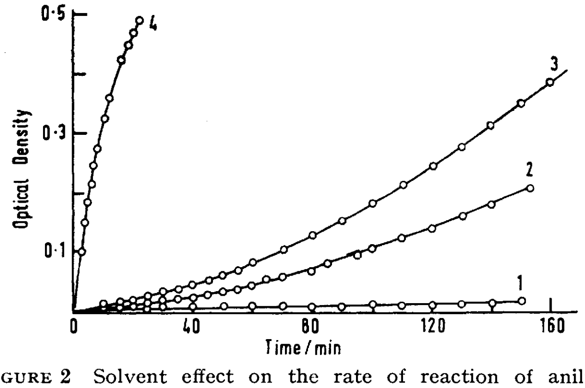


FIGURE 2 Solvent effect on the rate of reaction of aniline ($2{\cdot}466 \times 10^{-2}$M) with chloranil ($1{\cdot}045 \times 10^{-3}$M) at 280 K: Curve 1, diethyl ether or CH_2Cl_2; 2, MeCN–diethyl ether (1 : 1); 3, MeCN. Curve 4 is for the reaction of aniline ($2{\cdot}335 \times 10^{-2}$M) with chloranil ($9{\cdot}6 \times 10^{-5}$M) in propan-2-ol

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[25] S. N. Bhat and C. N. R. Rao, *J. Amer. Chem. Soc.*, 1966, **88**, 3216.

ca. 25 kJ mol^{-1}). In MeCN solvent, dimethylaniline readily gives the radical anion of chloranil and the crystal violet cation. These observations regarding the interaction of dimethylaniline with chloranil are in general agreement with literature reports.[2,17,26] The mechanism of crystal violet cation formation *via* the electron donor–acceptor complex and the chloranil radical anion has been discussed by Kosower.[2]

EXPERIMENTAL

All solvents and compounds were fractionated before use by standard procedures. Tetramethyl-*p*-phenylenediamine was liberated from its dihydrochloride (Eastman Organic Chemicals Co.) by aqueous NaOH, extracted into ether, and dried (Na_2SO_4). Distillation in a vacuum gave a white solid (m.p. 50 °C). Freshly distilled tetramethyl-*p*-phenylenediamine was used for all the measurements. *NN*-Dimethyl-*p*-toluidine was prepared by the method described by Hodgson and Kershaw.[27] Chloranil was recrystallized four times from benzene to give yellow platelets (sealed tube, m.p. 289 °C). *sym*-Trinitrobenzene was recrystallized four times from benzene–methanol and had m.p. 123 °C. Tetracyanoethylene was sublimed at 125—135 °C (1—2 mmHg) (m.p. 198 °C); it was stored at 0 °C to prevent decomposition. Tetracyanoquinodimethane was recrystallized from purified MeCN three times and dried in a vacuum over P_2O_5 at 80 °C.

Electronic absorption spectra were recorded on a Cary-14R recording spectrophotometer or a Beckman DU spectrophotometer fitted with variable-temperature cell compartments.

Pseudo-first-order rate constants (in presence of a large excess of donor) based on the measurements of the charge-transfer band intensity were evaluated by employing equation (1) where D_0 is the optical density at zero time and

$$t = \frac{2{\cdot}303}{k} \log \frac{D_0}{D_t} \qquad (1)$$

D_t is the optical density at time t. Pseudo-first-order rate constants based on the measurements of the intensity of the radical ion band (or the product band) were obtained from equation (2), where D_∞ is the optical density of the solution

$$t = \frac{2{\cdot}303}{k} \log \frac{D_\infty - D_0}{D_\infty - D_t} \qquad (2)$$

at the end of the reaction. The rate constants for the formation of the radical ions obtained from the decrease in the charge-transfer band intensity and the increase in the radical ion band intensity we quite similar in the case of the tetramethyl-*p*-phenylenediamine–chloranil system (Table 1). In all the kinetic studies, we recorded the rate data for the first *ca.* 30 min (with the exception of the tetramethyl-*p*-phenylenediamine–chloranil system where we have used data on the monocation band up to 1 h). Activation energies were calculated from the rate constants at different temperatures in the range 278—315 K.

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