Radical-ion Formation in Aromatic Amine–Tetracyanoethylene Systems

By **Patrick G. Farrell** * and **Phi Nga Ngô**, Department of Chemistry, McGill University, P.O. Box 6070, Montreal 101, Canada

The kinetics of the formation and decay of the tetracyanoethylene radical anion from aromatic amine–tetracyanoethylene systems in dichloromethane have been studied. A mechanistic scheme to account for the observed reaction products and kinetic order is proposed and reaction with an excess of donor is suggested to be the major pathway within this mechanism.

THE theory proposed by Mulliken [1] to account for the properties of charge-transfer complexes assigns to the ground state of the complex an essentially non-bonded character with only minor contributions from a singlet dative state. In accord with this theory many charge-transfer complexes are diamagnetic, but there are also a number which give rise to e.s.r. absorptions, either in the solid or in solution. These paramagnetic species generally arise from the interaction of ' strong ' donor and acceptor molecules, under conditions suitable for some stabilization of the radical ions, and have been identified in many cases as either the donor or the acceptor radical ion.

The importance of the solvent stabilization of these radical ions has been shown by several workers by either

---

[1] R. S. Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 610, 4493; 1952, **74**, 811; *J. Chem. Phys.*, 1951, **19**, 514; *J. Phys. Chem.*, 1952, **56**, 801.

optical or e.s.r. studies.[2-7] Thus the tetramethyl-*p*-phenylenediamine–chloranil system shows optical absorption attributed to the charge-transfer complex in carbon tetrachloride but in acetonitrile has absorption attributed to the radical ions.[8] Furthermore, the addition of the non-polar to the polar solvent in this system led to the appearance of absorption bonds due to both species, radical ions and charge-transfer complex, implying that these exist in equilibrium under these conditions. The possibility of reaction in such systems *via* the charge-transfer complex is thus self-evident. Although this possibility has been investigated in some cases, very few kinetic or comparative studies have been reported for radical ions derived from charge-transfer complexes. As part of our study of the role of charge-transfer complexes as reaction intermediates, and specifically of the reactions of aromatic amines with tetracyanoethylene (TCNE), we compare here the extent of radical-ion formation in various systems. We have also followed the variation of e.s.r. signal intensity with time for the *NN*-diethylaniline–TCNE system to elucidate a possible reaction course.

RESULTS

E.s.r. absorptions obtained from the interactions of TCNE with pyridine, indole, aniline, *N*-methylaniline, *p*-methylaniline, and *p*-methoxyaniline were of extremely low intensity and the signals were unresolved. With *NN*-dimethylaniline a nine line resolved signal attributed to the TCNE radical ion was observed and with *NN*-diethylaniline at least 17 lines were obtained. The hyperfine splitting constant due to nitrogen was 1·54 ± 0·03 G. No signal arising from the radical cation was detected. All signals gave a *g* value of 2·0029 ± 0·0003.

Radical Concentration.—Owing to the variation of the signal intensity with time, *etc.*, the estimates of radical concentrations are only approximate (±25%), but of sufficient accuracy for the present purpose. Values for the extent of radical formation in various systems are shown in Table 1.

Variation with Time.—In all cases where significant radical concentrations were observed the e.s.r. absorption increased to a maximum and then decreased (Figure 1 *). The time required to attain the maximum depended both upon the nature of the donor and the relative donor–acceptor concentrations. We have assumed that the radical concentration is directly proportional to the signal peak height as symmetrical absorptions were obtained in all cases. In the absence of oxygen the maximum signal amplitude was reached after a longer period of time and the decay of the absorption was slower.

The variation of the e.s.r. signal intensity with time was followed for a series of runs with constant TCNE concentration and a varying excess of *NN*-diethylaniline concentration, and also for a series with varying TCNE concentration in the presence of a constant excess of this donor. An excess of donor was used so that the results could be compared with spectroscopic data for the complexes. The final product of the reaction was mainly pentacyanopropenide ion as shown by visible absorption spectroscopy. The decay of the signal in all cases followed first-order rather than second-order kinetics, as shown in Figure 2, and typical results are shown in Table 2. Attempts to correlate the decay of the optical absorption, due to the initially formed charge-transfer complex, with the variation in radical concentration were unsuccessful (Figure 3).

TABLE 1

Percentage TCNE radical-ion formation, donor ionization potentials (I_D), and equilibrium constants (K_{CT}) of charge-transfer complexes for various donor–TCNE systems. Radical-ion percentages refer to dichloromethane as solvent and the donor : acceptor ratio was 10 : 1; [Donor] $\simeq 10^{-1}$M

Donor	Radical ion	I_D/eV	K_{CT}/l mol^{-1}
NN-Diethylaniline	100	6·99 [a]	
NN-Dimethylaniline	1	7·44 [b]	15·0 [e] (CHCl$_3$, 32·5°)
Pyridine	~0·1	9·3 [a]	
p-Toluidine	~0·05	7·57 [c]	4·85 [f] (CH$_2$Cl$_2$, 25·3°)
Indole	~0·03	8·01 [d]	2·7 [g] (CH$_2$Cl$_2$, 25°)
N-Methylaniline	~0·02	7·58 [b]	8·2 [h] (CHCl$_3$, 32·5°)
Aniline	~0·01	7·76 [b]	2·22 [f] (CH$_2$Cl$_2$, 25·3°)

[a] Ref. 23. [b] P. G. Farrell and J. Newton, *J. Phys. Chem.*, 1965, **69**, 3506. [c] P. G. Farrell and J. Newton, *Tetrahedron Letters*, 1966, 5517. [d] A. R. Cooper, C. W. P. Crowne, and P. G. Farrell, *Trans. Faraday Soc.*, 1966, **62**, 2725. [e] Z. Rappoport, *J. Chem. Soc.*, 1963, 4498. [f] P. G. Farrell and P. N. Ngô, *J. Phys. Chem.*, 1973, **77**, 2545. [g] R. Foster and P. Hanson, *Tetrahedron*, 1965, **21**, 255. [h] Z. Rappoport and A. Horowitz, *J. Chem. Soc.*, 1964, 1348.

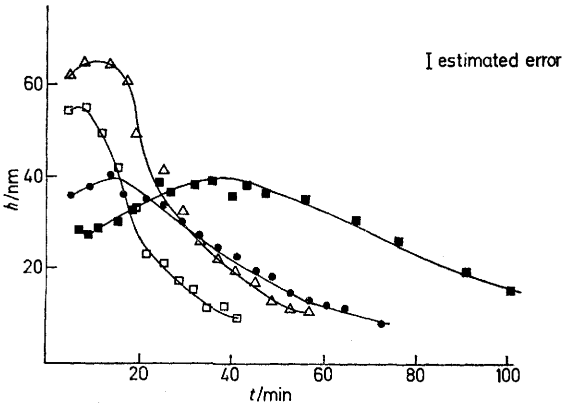


FIGURE 1 Variation of the e.s.r. signal intensity (TCNE$^{\overline{\cdot}}$) (h = height of central peak) in dichloromethane with time showing the effect of *NN*-diethylaniline concentration: [TCNE]$_0$ 1·02 × 10^{-3}; [*NN*-Diethylaniline]$_0$, ■, 1·27 × 10^{-2}M, ●, 2·06 × 10^{-2}M, △, 4·67 × 10^{-2}M, □, 6·56 × 10^{-2}M

---

* Excellent linear first-order plots were obtained from the data in Figure 1.

[2] R. E. Miller and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 1959, 2375; 1961, 4886.

[3] H. Kainer and A. Uberle, *Chem. Ber.*, 1955, **88**, 1147.

[4] J. W. Eastman, G. Engelsma, and M. Calvin, *J. Amer. Chem. Soc.*, 1962, **84**, 1339.

[5] H. M. Buck, J. H. Lupinski, and L. J. Oosterhof, *Mol. Phys.*, 1958, **1**, 196.

[6] I. Isenberg and S. L. Baird, *J. Amer. Chem. Soc.*, 1962, **84**, 3803.

[7] R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, 1962, **58**, 860.

[8] R. Foster and J. W. Morris, *Rec. Trav. chim.*, 1970, **89**, 636.

DISCUSSION

Comparison of the e.s.r. signals observed with those of the TCNE radical anion, produced from sodium iodide–TCNE in tetrahydrofuran, indicated the presence of this radical in all cases. No evidence of hyperfine splitting by the ethylenic carbon atoms was found[9] but ^{13}C splitting due to the nitrile carbon atoms was observed, having a value of $6a_{CN}{}^{14N}$ (= 9·24 G) as found by previous workers.[9,10] The exchange of the positive ' hole ' between the large excess of neutral donor molecules, resulting in band broadening, is presumably responsible for the lack of any signal attributable to the radical cation. The radical concentrations correlate approximately with the equilibrium constants of the corresponding charge-transfer complexes or the donor ionization potentials, except for pyridine and indole (Table 1). As anticipated from the high ionization potentials for these latter compounds, the extent of radical formation in these systems is very low. With a constant excess of donor and increasing acceptor concentration the absolute radical concentration increases as expected, but there is no apparent correlation between radical concentration and donor–acceptor ratios. From the very small radical concentration observed in the aniline–TCNE system, it may be concluded that the major reaction mechanism is ionic (99%) as suggested from kinetic studies.[11]

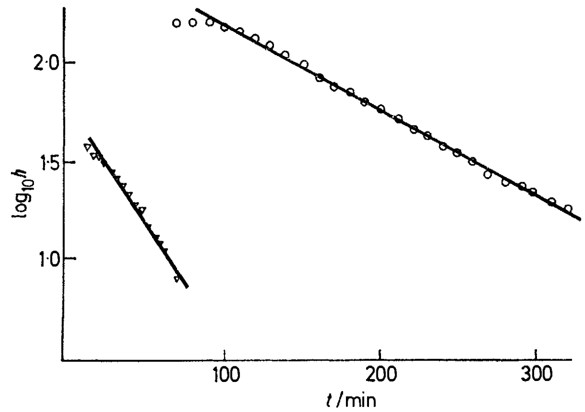


FIGURE 2 Variation of the e.s.r. intensity of TCNE$^{\overline{\cdot}}$ with time, plotted as a first-order reaction: ▽, under air, $[TCNE]_0$ = 1·02 × 10^{-3}M; $[NN\text{-Diethylaniline}]_0$ = 2·06 × 10^{-2}M; ○, under nitrogen, $[TCNE]_0$ = 1·04 × 10^{-3}M, $[NN\text{-Diethylaniline}]_0$ = 1·00 × 10^{-2}M

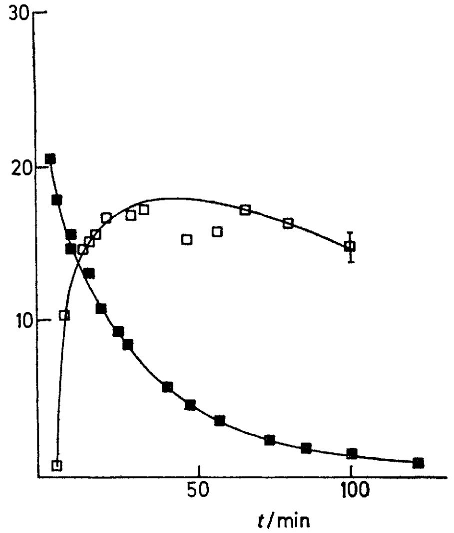


FIGURE 3 Decay of the charge-transfer complex (■), and variation of the e.s.r. signal intensity (□), with time for the *NN*-diethylaniline–TCNE system in dioxan: $[TCNE]_0$ = 1·36 × 10^{-2}M, $[NN\text{-Diethylaniline}]_0$ = 7·0 × 10^{-1}M. The ordinate is calibrated in ' arbitrary units.' The error bar indicates the limits of error for the e.s.r. measurements. The errors of the optical density readings are well within the squares used

TABLE 2

Pseudo-first-order rate coefficents, k_1, for the decay of the TCNE radical anion in solutions of *NN*-diethylaniline (DEA) and TCNE in dichloromethane at 25°

10 [DEA]/M	10^3[TCNE]/M	10^3k_1/s^{-1}
	Under air	
0·127	1·02	8·4
0·206	1·02	12·7
0·467	1·02	18·5
0·656	1·02	24·4
1·03	1·23	38·0
1·03	2·46	40·0
1·03	3·69	31·0
	Under nitrogen	
0·10	1·04	4·4
1·00	1·04	8·6

For reactions of charge-transfer complexes in solution, the majority of results are accommodated by Mulliken's concept of ' inner ' and ' outer ' complexes.[12] He suggested that only a small transfer of charge occurred in the outer complex, but that large charge transfer occurred in the inner complex. Under suitable conditions of donor ionization potential, acceptor electron affinity, and solvent dielectric constant the inner complex may dissociate into solvated radical ions which give rise to the observed signals. Kosower [13] proposed that the electron transfer was a thermal process occurring after complex formation, but these two theories are in essential agreement as to the origin of the radical species. Other workers [14,15] have been more specific as to the nature of the species immediately preceding the free radicals, $D^{\cdot+}$ and $A^{\cdot-}$. They proposed that a donor–acceptor interaction to form ground-state singlet complexes, followed by thermal excitation to the triplet state, preceded the formation of radical ions. Irradiation in the charge-transfer band of a solution of TCNE in tetrahydrofuran produces the TCNE radical anion, in

---

[9] P. Rieger, I. Bernal, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1961, **83**, 3918.

[10] W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.*, 1960, **33**, 626.

[11] P. G. Farrell and P. N. Ngô, *J.C.S. Perkin II*, 1973, 974.

[12] See R. S. Mulliken and W. B. Person, ' Molecular Complexes,' Wiley, New York, 1969.

[13] E. M. Kosower, *Progr. Phys. Org. Chem.*, 1965, **3**, 118.

[14] D. F. Ilten and M. Calvin, *J. Chem. Phys.*, 1965, **42**, 3760.

[15] F. E. Stewart, M. Eisner, and W. R. Carper, *J. Chem. Phys.*, 1966, **44**, 2866.

support of this proposal.[14] Further, weak complexes can be made to exhibit paramagnetism by photoinduction, implying that electron transfer may be initiated by prior excitation of one of the components or of the complex itself.[16] However, these results do not *necessarily* mean that the triplet state charge-transfer complex is on the pathway leading to radical formation in systems involving strong donor–acceptor pairs. In the amine–TCNE systems studied here the maximum in the e.s.r. signal intensity occurs some minutes or hours after mixing, whereas in systems where the triplet state gives rise to the radical ions the rise times are of the order of milliseconds. Longer rise times, such as observed in the *NN*-dimethylaniline–chloranil system, are more probably due to conventional ' chemical ' processes.[4]

With the exception of the detailed study of the *NN*-dimethylaniline–chloranil reaction,[4,13] few kinetic studies of the formation and/or decay of radical ions in donor–acceptor systems have been reported. The kinetics of the dimethyl sulphoxide–TCNE system in carbon tetrachloride were studied by Stewart *et al.* who reported that the decay of the e.s.r. signal followed second-order kinetics.[15] A first-order decay was found for the chloranil–dioxan system and for various solvent–TCNE systems,[17] and complex decays for the *p*-chloranil–tetrahydrofuran and the *o*-chloranil–thiophen systems.[18]

Our results are consistent with the Scheme, although they do *not* provide unambiguous evidence for all the steps as written.

$$\mathrm{A} + \mathrm{D} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AD} \tag{1}$$

$$\mathrm{AD} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\mathrm{A}^{\cdot-}\,.\,\mathrm{D}^{\cdot+}) \tag{2}$$

$$\mathrm{S} + (\mathrm{A}^{\cdot-}\,.\,\mathrm{D}^{\cdot+}) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{AS}^{\cdot-} + \mathrm{DS}^{\cdot+} \tag{3}$$

$$\mathrm{AS}^{\cdot-} + \mathrm{DS}^{\cdot+} \xrightarrow{k_4} \mathrm{AD} \text{ or } \mathrm{A} + \mathrm{D} \text{ or } \mathrm{X} \xrightarrow{k_4'} \text{products} \tag{4}$$

$$\mathrm{AS}^{\cdot-} + \mathrm{AS}^{\cdot-} \xrightarrow{k_5} \mathrm{A}\,.\,\mathrm{A}^{2-} \xrightarrow{k_5'} \text{products} \tag{5}$$

$$\mathrm{AD} + \mathrm{D} \xrightarrow{k_6} \text{products} \tag{6}$$

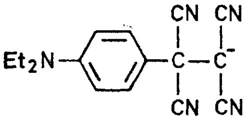
$$\mathrm{AS}^{\cdot-} + \mathrm{D} \xrightarrow{k_7} \text{products} \tag{7}$$

SCHEME A = Acceptor; D = donor; S = solvent; X = new species

The first equilibrium is attained spontaneously, as found in the majority of donor–acceptor systems, as the energy barrier to outer complex formation is small (4—8 kJ mol^{-1}) and arises mainly through solvation changes.[19] The k_1 value for the hexamethylbenzene–TCNE complex in 1-chlorobutane at $-83°$ has been estimated to be $1{\cdot}45 \times 10^8$ l mol^{-1} s^{-1}, only one order of magnitude less than the calculated diffusion controlled rate ($1{\cdot}7 \times 10^9$ l mol^{-1} s^{-1}).[19] The k_2 value should be relatively low as this step involves both complete electron transfer and solvent reorganization; the inner complex resembles an ion-pair. From u.v. measurements at the charge-transfer band maximum, Rao [20] has estimated an activation energy of 42 kJ mol^{-1} for the electron transfer from *NNN'N'*-tetramethyl-*p*-phenylenediamine to TCNE in dichloromethane and this may be approximated to the outer–inner complex activation barrier, assuming a similar activation energy in our system. Solvent assistance may then allow separation of the radical ions as in equation (3). Reactions (1)—(3) may also explain the induction period reported for the *NN*-dimethylaniline–chloranil reaction.[4]

The decay of the signal results from the reactions shown in equations (4)—(7). Radical recombination [equation (4)] would be expected to be rapid in solution, although relatively high energy barriers to radical-ion recombination have been reported. Stewart and Eisner [21] estimated a value of 77·8 kJ mol^{-1} for the TCNE–acetone system in acetone and 63·6 kJ mol^{-1} for the TCNE–tetrahydrofuran system in tetrahydrofuran, values which seem extremely high. These recombination reactions result in regeneration of reactants, or possibly the formation of some new species which reacts rapidly to form products. No evidence of any dimerization products has been found (*e.g.* salts of the *sym*-octacyanobutane dianion). The dimerization of the 1,1-diphenylethylene radical ion in cyclohexane has a $\Delta H^{\ddagger}$ value of 24·7 kJ mol^{-1} at 31° [22] and a similar value may be required for the TCNE radical ion. Furthermore, equations (4) and (5) predict second-order decays of the signal.

Reaction of the radical anion with neutral *NN*-diethylaniline molecules to yield a *para*-substituted intermediate (I) would account for both the observed products and the observed kinetics. The rate coefficients are thus pseudo-first order and increase with donor concentration, the derived second-order rate coefficient being *ca.* 38×10^{-2} l mol^{-1} s^{-1}. Intermediate (I) may react rapidly with another molecule of TCNE to eventually yield the pentacyanopropenide ion. Reduction of the TCNE molecule in a mechanism similar to that proposed by Kosower [13] for the *NN*-dimethylaniline–chloranil system is unlikely as no product corresponding



(I)

---

[16] N. S. Isaacs and J. Paxton, *Photochem. Photobiol.*, 1970, **11**, 137.

[17] R. M. Haines, A. Pryce, and L. Shields, *J. Chem. Soc.* (*B*), 1970, 820.

[18] D. F. Ilten, M. E. Kronenberg, and M. Calvin, *Photochem. Photobiol.*, 1968, **7**, 331.

[19] E. F. Caldin, D. O'Donnell, D. Smith, and J. E. Crooks, *Chem. Comm.*, 1971, 1358.

[20] P. C. Dwivedi and C. N. Rao, *J.C.S. Perkin II*, 1972, 238.

[21] F. E. Stewart and M. Eisner, *Mol. Phys.*, 1967, **12**, 173.

[22] A. G. Evans and J. C. Evans, *Trans. Faraday Soc.*, 1965, **61**, 1202.

to the Crystal Violet cation has been reported from TCNE–amine systems. The electron exchange process proposed by Shields and his co-workers to account for the first-order decay of the TCNE radical anion in various solvent systems is accommodated by our Scheme as annihilation of the anion arises here from reaction, rather than from regeneration of the original charge-transfer complex.[17]

The effect of oxygen is to decrease both the signal intensity and the rate of decay, but it does not affect the reaction order. In order to extend the conclusions from this work to other results,[11] oxygen was not, in general, excluded. If the (ground-state) oxygen is present in a minimal amount within the solution, and is regenerated after interaction with the radical anion, then a pseudo-first-order kinetic process will occur. Taking the solubility of oxygen in dichloromethane as equal to that in water (at 25°) [23] the second-order rate coefficient for the reaction of oxygen with the TCNE radical anion may be estimated to be *ca.* 1.* Close examination of the results of Stewart and Eisner [21] on the decay of the photoinduced TCNE anion radical in dimethyl sulphoxide, at high acceptor concentrations, suggests that this did not obey second-order kinetics, as these authors suggested, but rather first-order kinetics. This probably also arises from reaction with the donor solvent.

EXPERIMENTAL

E.s.r. measurements were carried out at constant microwave power on a Varian V-4502 X band spectrometer fitted with a Varian V-4532 dual sample cavity, but used as a single cavity. The signal to noise ratio was estimated to be 17 : 1 and the operating temperature was 25 ± 1°. All compounds, solvents, *etc.* were commercially obtained (best available grade) and purified by standard literature methods. The solvent used was dichloromethane.

Procedure.—Solutions of each compound were prepared in separate 10 ml volumetric flasks. Equal volumes of donor and acceptor were abstracted with calibrated syringes and mixed together, and *ca.* 1 ml of the mixture transferred to an e.s.r. tube, which was then sealed. All tubes were identical (3 mm i.d. quartz) having 4 mm external diameter. Measurements commenced *ca.* 4 min after mixing. Exclusion of oxygen was achieved by working under nitrogen, care being taken to flush all solutions thoroughly with oxygen-free nitrogen.

Instrument Calibration, etc.—Field sweep calibration was performed using Fremy's salt in saturated sodium carbonate solution. Modulation amplitude calibration was carried out using the Varian standard pitch on KBr (*ca.* 3×10^{15} spins cm^{-1}).

The *g* value for the TCNE radical ion was determined using a solution of diphenylpicrylhydrazyl in benzene as standard (g 2·0036 ± 0·003).

Radical concentrations were determined using the numerical integration method of Wyard [24] on the first derivative of the absorption. The TCNE radical-ion multiplet was approximated to a single curve passing through the peaks of the multiplet and integration performed upon this composite curve. Areas were normalized to standard spectrometer readings.

Products.—The reaction of TCNE with aromatic amines in general results in either *N*- or *C*-substitution, to yield the corresponding tricyanovinyl derivative.[25] In some cases (*e.g.* *NN*-dimethylaniline) the 1,1,2,2-tetracyanoethane derivative has been isolated, while in others salt formation occurs, normally as the pentacyanopropenide, *e.g.* pyridine. The reaction with *NN*-diethylaniline may also give bis-(*p*-*NN*-diethylanilinium)malononitrile bis-1,1,2,3,3-pentacyanopropenide.[26]

We are grateful to the National Research Council of Canada for financial support and to McGill University for the award of a McConnell Fellowship (to P. N. N.).

[3/2099 *Received*, 15*th October*, 1973]

---

* Although this is most unlikely, a gross estimate of the maximum second-order rate coefficient is thus obtained.

[23] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, The Chemical Rubber Co., Cleveland, 1970.

[24] S. J. Wyard, *J. Sci. Instruments*, 1965, **42**, 769.

[25] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Amer. Chem. Soc.*, 1958, **80**, 2806.

[26] P. G. Farrell and R. K. Wojtowski, *J. Chem. Soc. (C)*, 1970, 1394.