N-Tricyanovinylation: the Reaction of Aniline with Tetracyanoethylene

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The kinetics of the aniline–tetracyanoethylene reaction in methylene chloride are reported. The results imply that the reaction proceeds *via* a 1 :1 π-complex formed between the reagents and that the overall reaction involves two additional molecules of aniline. Possible reaction mechanisms are discussed within a scheme encompassing both *C*- and *N*-tricyanovinylation of aromatic amines.

STUDIES of the interaction of tetracyanoethylene (TCNE) with aromatic amines have shown that initial charge-transfer (π-)complex formation occurs, followed by substitution by the aromatic function to form tricyanovinyl or tetracyanoethane derivatives.[1-3] The π-complexes formed in a number of amine–tetracyanoethylene systems have been studied spectroscopically and association constants for complex formation have been determined.[4] For some examples of *C*-tricyanovinylation the kinetics of the reactions of these π-complexes have been examined,[5-8] but we are unable to find any reports of similar detailed studies of the reactions of primary anilines with tetracyanoethylene, from which *N*-tricyanovinyl products are obtained. It is mechanistically important to know whether these π-complexes are, or are not, necessary intermediates in these substitutions.

For the *para*-tricyanovinylation of both *N*-methylaniline [6] and *NN*-dimethylaniline [5] the kinetics have been determined (in chloroform as solvent) and a detailed reaction mechanism suggested. This mechanism implies that the π-complex *is* an essential intermediate in the substitution and that a bimolecular exchange between a free amine molecule and the π-complex also occurs on the reaction pathway. An 'activated π-complex' may arise from this exchange process and this was suggested as the necessary intermediate in the *NN*-dimethylaniline reaction. A simple exchange pro-

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[2] Z. Rappoport and E. Shohamy, *J. Chem. Soc.* (*B*), 1969, 77.

[3] P. G. Farrell and R. K. Wojtowski, *J. Chem. Soc.* (*C*), 1970, 1390.

[4] N. S. Isaacs, *J. Chem. Soc.* (*B*), 1966, 1053.

[5] Z. Rappoport, *J. Chem. Soc.*, 1963, 4498.

[6] Z. Rappoport and A. Horowitz, *J. Chem. Soc.*, 1964, 1348.

[7] R. Foster and P. Hanson, *Tetrahedron*, 1965, **21**, 255.

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cess involving no 'activated π-complex' was invoked for the *N*-methylaniline system. Although both *C*- and *N*-tricyanovinyl products may be obtained from the reaction of tetracyanoethylene with certain anilines, *e.g.* *o*-toluidine, only *N*-tricyanovinylaniline is reported from the reaction with aniline itself.[1] We therefore have examined the reaction to determine whether an overall mechanism similar to that described for the methylated derivatives is operative. The greater nucleophilicity of nitrogen results in considerably faster reaction rates for the *N*-tricyanovinylation of aniline, as expected, and we report here our results, together with a discussion of possible reaction mechanisms.

RESULTS

The reaction of aniline with tetracyanoethylene in chloroform solution is extremely rapid and reproducible results could not be obtained. Dichloromethane was found to be a suitable solvent and the reaction was studied spectrophotometrically at four temperatures in this solvent. On mixing the reactants an immediate deep blue colour develops and this is attributed to 1 : 1 π-complex formation. The blue colour decreases in intensity with time, being replaced by the yellow colour of the product. The study of the overall reaction thus consists of three parts: the determination of the association constant for π-complex formation, the measurement of the rate of disappearance of the π-complex, and the measurement of the rate of appearance of the product (*N*-tricyanovinylaniline).

Association Constant K for π-Complex Formation.—The association constant K for π-complex formation is defined by equation (1) where $[\pi]$ is the 1 : 1 charge transfer

$$K = [\pi]/[\mathrm{T}]_f[\mathrm{A}]\ \mathrm{l\ mol^{-1}} \qquad (1)$$

complex concentration, and $[\mathrm{T}]_f$ and $[\mathrm{A}]$ are respectively the concentrations of free tetracyanoethylene and free aniline.

Values of K may be determined spectroscopically, but their determination in this system was rendered difficult by the rapid rate of disappearance of the π-complex. In an attempt to eliminate some of the inherent errors in the optical determination of K, both equimolar concentrations and a large excess of aniline were used.[9]

To calculate K from the experimental data simplifying assumptions are normally made. In the presence of a large excess of donor, the concentration of π-complex is assumed to be negligible when compared to donor concentration, so that equation (2) applies where $[\mathrm{A}]_0$ is the

$$[\mathrm{A}] = [\mathrm{A}]_0 - [\pi] \simeq [\mathrm{A}]_0 \qquad (2)$$

initial donor concentration.

At a wavelength where only the complex absorbs, the optical density (O.D.) is given by equation (3), ε and l

$$\mathrm{O.D.} = \varepsilon[\pi]l \qquad (3)$$

being respectively the extinction coefficient of the π-complex at the wavelength of measurement and the cell path length in cm.

Combination of equations (1)—(3) gives the Benesi-Hildebrand equation[10] for a 1 cm path-length of solution.

$$[\mathrm{T}]_0/\mathrm{O.D.} = 1/K\varepsilon[\mathrm{A}]_0 + 1/\varepsilon \qquad (4)$$

Equation (4) may be rewritten to give the Scott equation,[11]

$$[\mathrm{A}]_0[\mathrm{T}]_0/\mathrm{O.D.} = 1/K\varepsilon + [\mathrm{A}]_0/\varepsilon \qquad (5)$$

and further rearrangement gives equation (6)[12] where the

$$\mathrm{O.D.}/[\mathrm{A}]_0[\mathrm{T}]_0 = -\mathrm{O.D.}K/[\mathrm{T}]_0 + K\varepsilon \qquad (6)$$

gradient of the plot of $\mathrm{O.D.}/[\mathrm{A}]_0[\mathrm{T}]_0$ *versus* $\mathrm{O.D.}/[\mathrm{T}]_0$ gives directly $-K$.

Equations (5) and (6) were used for the evaluation of K and ε under the conditions of large excess of donor $[\mathrm{A}]_0$.

For comparable concentrations, the concentration of the donor may be expressed in terms of the acceptor, *i.e.* $[\mathrm{A}]_0 = n[\mathrm{T}]_0$ whereupon K is expressed by equation (7)[13] for a 1 cm path-length of solution.

$$[\pi]_0/\mathrm{O.D.} = (n + 1)/n\varepsilon + 1/nK\varepsilon[\mathrm{T}]_0 \qquad (7)$$

The long wavelength absorption maxima in dichloromethane of the starting materials, π-complex, and product are: aniline 287, tetracyanoethylene 265, π-complex 600, and *N*-tricyanovinylaniline 350 nm.

To determine K and ε for the π-complex under the experimental condition of large excess of donor, measurements of the variation of the optical density at 600 nm with time were made and the linear plots of $\log_{10}(\mathrm{O.D.})$ against time were extrapolated to zero time. (The decay of π-complex was found to follow first-order kinetics when the donor was in excess.)

When comparable concentrations of donor and acceptor were used, the decay of the complex no longer followed first-order kinetics and the O.D. of the π-complex at zero time was obtained by extrapolation of the O.D. *versus* time plot. The decay of the π-complex is very slow under these conditions so that extrapolated values of O.D. are reliable.

From the data obtained the product $K\varepsilon$ may be precisely calculated but the separation of the values may result in considerable errors.[14] We have computed the individual values using both ordinary graphical methods and a 'hill-climbing' optimization method,[15] and the results are shown in Table 1. A temperature independent value of ε_{600} (=2650) was obtained, and from the variation of K with temperature the thermodynamic parameters were calculated.

TABLE 1

Variation of association constant K with temperature for the aniline–TCNE complex in dichloromethane

	K/l mol^{-1} [a]	
Temp. (°C)	$[\mathrm{A}]_0 \approx [\mathrm{T}]_0$	$[\mathrm{A}]_0 \gg [\mathrm{T}]_0$
25·4	2·27	2·20
20·7	2·41	2·40
16·8		2·69
15·0		2·81

$\Delta H^\circ -15{\cdot}9\ \mathrm{kJ\ mol^{-1}}$. $\Delta S^\circ -54{\cdot}0\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

[a] $\pm 0{\cdot}03\ \mathrm{l\ mol^{-1}}$.

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[9] B. Dodson and R. Foster, *Chem. Comm.*, 1970, 1516.

[10] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

[11] R. L. Scott, *Rec. Trav. chim.*, 1956, **75**, 787.

[12] R. Foster, 'Organic Charge-Transfer Complexes,' Academic Press, London, 1969, p. 131.

[13] R. Foster and I. C. B. Matheson, *Spectrochim. Acta*, 1967, **23A**, 2037.

[14] W. B. Person, *J. Amer. Chem. Soc.*, 1965, **87**, 167.

[15] H. H. Rosenbrock, *Computer J.*, 1960, **3**, 175.

All analyses of the data * implied that only 1 : 1 complex formation occurs in this system.

Disappearance of the π-Complex.—The variation with time of the optical density at 600 nm was followed at each temperature, aniline being in large excess (100—400 fold), and found to be first-order in the π-complex {equation (8)

$$-\mathrm{d}[\pi]/\mathrm{d}t = k_{\mathrm{CT}}[\pi] \qquad (8)$$

where [π] = concentration of π-complex and k_{CT} is the pseudo-first-order rate coefficient}. Values of k_{CT} and of k_{exp} (=$k_{\mathrm{CT}}/[\mathrm{A}]_0$ where $[\mathrm{A}]_0$ = initial aniline concentration), the corresponding pseudo-second-order rate coefficient, are shown in Table 2.

Appearance of N-*Tricyanovinylaniline*.—The variation with time of the optical density at 350 nm was followed, aniline being in large excess. At this wavelength only the product absorbs (ε 14,000). Assuming that the rate of appearance of product P is directly proportional to the π-complex concentration [π] as shown in equation (9), then a plot of [P] against $(1 - e^{-k_{\mathrm{CT}}t})$ should be linear [equation (10)]. Linear plots were obtained for both

$$\mathrm{d}[\mathrm{P}]/\mathrm{d}t = c'[\pi] \equiv c'[\pi]_0 e^{-k_{\mathrm{CT}}t} \qquad (9)$$

$$[\mathrm{P}] = c'[\pi]_0(1 - e^{-k_{\mathrm{CT}}t})/k_{\mathrm{CT}} \qquad (10)$$

protiated and deuteriated aniline (Table 4; Figure 1).

TABLE 2

Typical pseudo-first-order rate coefficients k_{CT} and the corresponding pseudo-second-order coefficients k_{exp} for the disappearance of the aniline–TCNE π-complex in dichloromethane

Temp. (°C)	25·4	20·7	16·8	15·0	25·4	20·7	16·8	15·0
$10^4[\mathrm{T}]_0$/M	1·44	6·70	5·76	5·06	1·44	6·70	5·76	5·06
$10[\mathrm{A}]_0$/M	$10^3k_{\mathrm{CT}}/\mathrm{s}^{-1}$				$10^2k_{\mathrm{exp}}/\mathrm{l\ mol^{-1}\ s^{-1}}$			
2·10	6·40	4·75	3·43	2·31	3·05	2·26	1·63	1·10
1·80	4·47	2·77	2·24	1·50	2·48	1·54	1·24	0·833
1·50	2·33	1·82	1·28	0·942	1·55	1·21	0·853	0·628
1·20	1·37	0·883	0·835	0·558	1·14	0·736	0·696	0·465
0·90	0·906	0·456	0·370	0·332	1·01	0·507	0·411	0·369
0·60	0·285	0·198	0·142	0·169	0·475	0·330	0·237	0·282

TABLE 3

A comparison of k_1k_3'/k_{-1} values for the reactions of aniline and [*NN*-^{2}H$_2$]aniline with TCNE at 25·4° to illustrate the absence of any kinetic hydrogen isotope effect. The association constant $K = 2{\cdot}23$ l mol^{-1} for both complexes

	$[\mathrm{A}]_0$ /M†	$10^4[\mathrm{T}]_0$/M	$10k_1k_3'/k_{-1}$	Average
Aniline	$5{\cdot}00 \times 10^{-2}$—$2{\cdot}10 \times 10^{-1}$	4·876	4·09	$4{\cdot}34 \times 10^{-1} \pm 0{\cdot}020$
	$6{\cdot}00 \times 10^{-2}$—$2{\cdot}10 \times 10^{-1}$	1·440	4·34	
	$6{\cdot}00 \times 10^{-2}$—$1{\cdot}80 \times 10^{-1}$	1·083	4·58	
[*NN*-^{2}H$_2$]Aniline	$4{\cdot}51 \times 10^{-2}$—$1{\cdot}84 \times 10^{-1}$	4·696	4·16	$4{\cdot}39 \times 10^{-1} \pm 0{\cdot}023$
	$7{\cdot}10 \times 10^{-2}$—$1{\cdot}95 \times 10^{-1}$	4·696	4·62	

† Within each range at least six separate concentrations were used.

It is seen that the pseudo-second-order rate coefficient k_{exp} increases with increasing aniline concentration, thus implying an order greater than unity with respect to aniline.

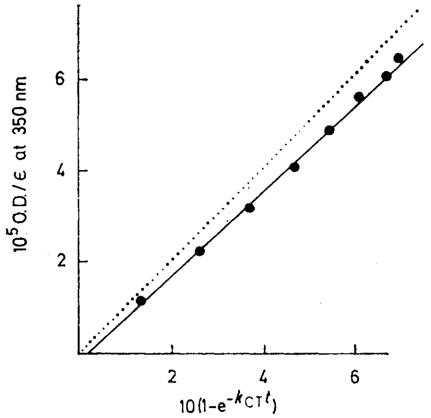

FIGURE 1 The variation of the product concentration with $(1 - e^{-k_{\mathrm{CT}}t})$ [equation (10)]. —— Experimental: · · · · theory

Examination of the reaction for a kinetic isotope effect using [*NN*-^{2}H$_2$]aniline (>94% deuteriated) at 25 °C showed no rate difference between protiated and deuteriated material (Table 3).

p-*Substituted Anilines*.—The disappearance of the π-complex for the *p*-chloroaniline, *p*-toluidine, and *p*-anisidine reactions was also studied and found to be first order in the π-complex but of higher order in aniline. A negative value of the Hammett ρ is obtained from these results.

TABLE 4

Typical values for the linear variation of product concentration with a function of time $(1 - e^{-k_{\mathrm{CT}}t})$ at 25·4° [equation (10)], $\lambda_{\mathrm{max.}}$ 350 nm (ε 14,000)

$10[\mathrm{A}]_0$/M	10^{-4} Slope of equation (10)	Average
	[*NN*-^{2}H$_2$]Aniline	
	$[\mathrm{T}]_0 = 1{\cdot}678 \times 10^{-4}$ mol l^{-1}	
1·79	1·53	$1{\cdot}79 \times 10^{-4}$
1·11	1·56	
0·890	2·19	
0·714	1·90	
	Aniline	
	$[\mathrm{T}]_0 = 1{\cdot}055 \times 10^{-4}$ mol l^{-1}	
0·600	1·40	$1{\cdot}07 \times 10^{-4}$
0·900	0·975	
1·20	1·07	
1·80	0·875	
2·10	0·795	

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* Full details of all methods used in the data analysis will be published elsewhere.

DISCUSSION

An examination of Table 2 shows that the order of the π-complex decay with respect to aniline is greater than unity. Similar results were found for both the indole[7] and *N*-methylaniline[6] reactions with tetracyanoethylene and this increase in the pseudo-second-order rate coefficient with increasing amine concentration was discussed at length by Rappoport.[6] He attributed such behaviour to either a bimolecular reaction of the π-complex with the amine or two bimolecular reactions of the amine with the complexed and uncomplexed tetracyanoethylene.

In a TCNE–amine system in which the amine is in large excess, equations (11)—(13) hold where $[\mathrm{T}]_{\mathrm{total}}$ is

$$[\mathrm{T}]_{\mathrm{total}} = [\mathrm{T}]_{\mathrm{f}} + [\mathrm{T}]_{\pi} \qquad (11)$$

$$[\mathrm{T}]_{\mathrm{f}} = [\pi]/K[\mathrm{A}]_0 \qquad (12)$$

$$[\mathrm{T}]_{\pi} = [\pi] \qquad (13)$$

the total concentration of TCNE, complexed or uncomplexed, $[\mathrm{T}]_{\mathrm{f}}$ is the concentration of free TCNE, and $[\mathrm{T}]_{\pi}$ is the concentration of complexed TCNE.

Combining equations (11)—(13) gives (14). If the

$$[\mathrm{T}]_{\mathrm{total}} = [\pi](1 + K[\mathrm{A}]_0)/K[\mathrm{A}]_0 \qquad (14)$$

π-complexed TCNE reacts with a second molecule of amine equation (15) is obtained which, from (14), gives

$$-\mathrm{d}[\mathrm{T}]_{\mathrm{total}}/\mathrm{d}t = k_1[\pi][\mathrm{A}]_0 \qquad (15)$$

(16). The experimentally determined pseudo-first-order

$$-\mathrm{d}[\pi]/\mathrm{d}t = k_1[\pi]K[\mathrm{A}]_0^2/(1 + K[\mathrm{A}]_0) \qquad (16)$$

rate constant k_{CT} and pseudo-second-order rate constant k_{exp} would then correspond to the expressions (17)

$$k_{\mathrm{CT}} = k_1K[\mathrm{A}]_0^2/(1 + K[\mathrm{A}]_0) \qquad (17)$$

$$k_{\mathrm{exp}} = k_{\mathrm{CT}}/[\mathrm{A}]_0 = k_1K[\mathrm{A}]_0/(1 + K[\mathrm{A}]_0) \qquad (18)$$

and (18). If both the π-complexed and the uncomplexed TCNE each react with a molecule of amine, with different rate coefficients, equation (19) applies.

$$-\mathrm{d}[\mathrm{T}]_{\mathrm{total}}/\mathrm{d}t = k_1[\pi][\mathrm{A}]_0 + k_2[\mathrm{T}]_{\mathrm{f}}[\mathrm{A}]_0 \qquad (19)$$

Expressing $[\mathrm{T}]_{\mathrm{total}}$ and $[\mathrm{T}]_{\mathrm{f}}$ in terms of $[\pi]$ and $[\mathrm{A}]_0$ gives equation (20) whence (21) and (22) are derived.

$$-\mathrm{d}[\pi]/\mathrm{d}t = [\pi][\mathrm{A}]_0(k_1K[\mathrm{A}]_0 + k_2)/(1 + K[\mathrm{A}]_0) \qquad (20)$$

$$k_{\mathrm{CT}} = [\mathrm{A}]_0(k_1K[\mathrm{A}]_0 + k_2)/(1 + K[\mathrm{A}]_0) \qquad (21)$$

$$k_{\mathrm{exp}} = (k_1K[\mathrm{A}]_0 + k_2)/(1 + K[\mathrm{A}]_0) \qquad (22)$$

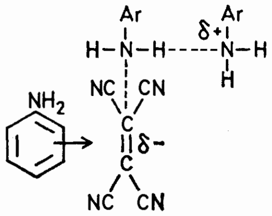
For both the indole and *N*-methylaniline reactions linear plots of $k_{\mathrm{exp}}(1 + K[\mathrm{A}]_0)$ *versus* $[\mathrm{A}]_0$ were obtained, as required by the above analysis. However, in the present study a plot of these data is non-linear, whereas when $k_{\mathrm{exp}}(1 + K[\mathrm{A}]_0)$ is plotted against $[\mathrm{A}]_0^2$ a linear relationship is observed, implying a higher order in amine in this reaction.

The intercepts with the ordinate are all very small (either positive or negative) and irreproducible and we believe that these arise through experimental errors, *i.e.* the curve passes through the origin. Similar plots were obtained for the *p*-substituted anilines. The pseudo-second-order rate coefficient may therefore be expressed as equation (23).

$$k_{\mathrm{exp}} = kK[\mathrm{A}]_0^2/(1 + K[\mathrm{A}]_0) \qquad (23)$$

From the linear plots of $k_{\mathrm{exp}}(1 + K[\mathrm{A}]_0)$ *versus* $[\mathrm{A}]_0^2$ the lack of a finite positive intercept implies that any contribution from the direct attack of TCNE upon a molecule of aniline (k_2) is negligibly small. Hence the reaction appears to proceed predominantly *via* the π-complex and we have omitted k_2 from our subsequent kinetic analysis.

This higher order in amine may arise from the attack of two amine molecules upon the π-complex in a concerted reaction, the second molecule of amine facilitating the proton transfer [*e.g.* (I)]. This type of mechanism



(I)

was proposed to account for the addition of amines to methyl vinyl ketone and *p*-tolyl vinyl sulphone.[16] The attack by aniline dimers in the addition of aniline to double-bond systems has been likened to general-base catalysis, involving hydrogen bonding in the transition state (I).

The equilibrium constant for aniline dimerization in cyclohexane is *ca.* 0·4 l mol^{-1} at 20° and in the more polar methylene chloride will be less than this.[17] The dimer concentration, although small relative to that of monomer, would thus be comparable to the π-complex concentration, but it is difficult to understand why only the dimeric species would react with the π-complex.

This order in amine may also be explained by the attack of a free aniline molecule on a 2 : 1 donor–acceptor complex. The presence of termolecular complexes in equilibrium with bimolecular complexes has been suggested by various workers[18-21] to account for anomalies in association constant determinations, and a recent quantitative determination of K and ε for such 2 : 1 complexes has been reported.[9] However, no

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[16] S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc.* (*B*), **1967**, 343; P. J. Lillford and D. P. N. Satchell, *ibid.*, p. 360; Y. Ogata, A. Kawasaki, and I. Kishi, *ibid.*, **1968**, 703.

[17] J. H. Lady and K. B. Whetsel, *J. Phys. Chem.*, 1964, **68**, 1001.

[18] G. D. Johnson and R. E. Bowen, *J. Amer. Chem. Soc.*, 1965, **87**, 1655.

[19] S. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.*, 1957, **79**, 76.

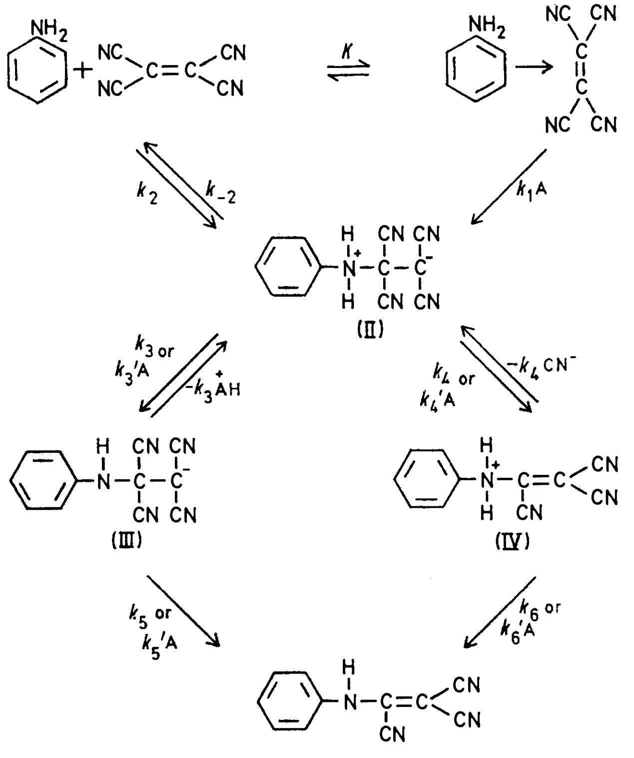
[20] M. J. S. Dewar and C. C. Thompson, *Tetrahedron*, 1966, Supp. 7, p. 97.

[21] S. Carter, *J. Chem. Soc.* (*A*), **1968**, 404.

evidence for 2 : 1 complexes was reported for *N*-methylaniline– or *NN*-dimethylaniline–tetracyanoethylene systems and we have obtained identical K and ε values, assuming only 1 : 1 complexes, under both equimolar and excess of donor conditions. It would also seem improbable that *only* 2 : 1 complexes should react to form products.

The self-dissociation of aniline to give an aniline anion which attacks the π-complex in the slow step may be excluded on the basis of the negative ρ value.

An alternative to the concerted mechanisms described above is the two-step mechanism suggested by Rappoport and Ta-Shma in their study of the reaction of anilines with 1,1-dicyano-2-*p*-dimethylaminophenyl-2-halogenoethylenes.[22] In this mechanism the initial attack of amine upon the π-complex gives a zwitterionic intermediate from which a proton is lost in a slow base-catalysed step. Fast elimination of cyanide ion from the resulting carbanion gives the product (see Scheme). The zwitterionic adduct (II) may also revert to aniline plus tetracyanoethylene (see Appendix) or lose cyanide ion in base-catalysed or uncatalysed reactions. Proton loss from (IV) would again give *N*-tricyanovinylaniline. Attempts to regenerate the π-complex from the zwitterionic intermediate observed in the *C*-tricyanovinylation of *NN*-dimethylaniline were unsuccessful[5] and we were also unable to reverse the first step by addition of stronger bases. While our kinetic results do not eliminate a concerted mechanism, increasing pseudo-second-order rate constants with aniline concentration, the observation of base catalysis by pyridine, and the similarity of this reaction to other amine–polycyanoethylene reactions lead us to prefer to interpret our data in terms of a two-step mechanism.



Scheme

The first step of this mechanism is analogous to the 'exchange' suggested for the *N*-methylaniline–tetracyanoethylene reaction and (II) thus corresponds to the σ-complex of that reaction.[6] The proximity of the quaternary nitrogen to the dicyanomethylene group will make (II) very unstable relative to the σ-complexes of the *C*-tricyanovinylation reactions. In accord with this, product formation is observed immediately after mixing the solutions in the aniline reaction, whereas most of the π-complex absorption had disappeared before any product could be detected in the *N*-methylated aniline reactions.[5,6]

The termolecular reaction between two aniline and one tetracyanoethylene molecule is unlikely to compete with the bimolecular reactions shown and other workers have found that the π-complex–(II) step in reactions involving similar zwitterionic intermediates is not reversible. The addition of cyanide ion to (IV) would be unlikely to compete with the extremely rapid loss of a proton from (IV) and these reactions have been ignored. Support for the rapid proton loss from (IV) comes from the observation that 4-tricyanovinyl-*NN*-dimethylaniline is not protonated by perchloric acid. Similarly, the proton concentration in this medium will be negligibly small and the protonation of (III) to give (II), either by free proton or by anilinium ion, is unlikely to compete with cyanide ion loss from this intermediate. Although the carbanion (III) may pick up a proton to yield the neutral tautomer of (II), the relative acidities of the ionizing groups[23] imply that the cyanocarbon acid is the stronger and the zwitterionic structure would predominate. The steady-state approximation applied to (II)—(IV) then gives their concentrations by equations (24)—(26). $[\mathrm{T}]_{\mathrm{total}}$ in

$$[(\mathrm{II})] \simeq k_1[\mathrm{A}]_0[\pi]/\{k_{-2} + k_3 + k_4 + (k_3' + k_4')[\mathrm{A}]_0\} \quad (24)$$

$$[(\mathrm{III})] = [(\mathrm{II})](k_3 + k_3'[\mathrm{A}]_0)/(k_5 + k_5'[\mathrm{A}]_0) \quad (25)$$

$$[(\mathrm{IV})] = [(\mathrm{II})](k_4 + k_4'[\mathrm{A}]_0)/(k_6 + k_6'[\mathrm{A}]_0) \quad (26)$$

this scheme will be given by (27) but the last three

$$[\mathrm{T}]_{\mathrm{total}} = [\mathrm{T}]_f + [\mathrm{T}]_\pi + [\mathrm{T}]_{(\mathrm{II})} + [\mathrm{T}]_{(\mathrm{III})} + [\mathrm{T}]_{(\mathrm{IV})} \quad (27)$$

terms on the right hand side may be neglected because species (II)—(IV) are in very small steady state concentrations. [Equations (11)—(14) still hold.]

The rate of disappearance of total tetracyanoethylene is equal to the rate of appearance of the product [equation (28)]. Combining equations (24)—(26) and (28) gives

$$\mathrm{d}[\mathrm{P}]/\mathrm{d}t = -\mathrm{d}[\mathrm{T}]_{\mathrm{total}}/\mathrm{d}t = (k_5 + k_5'[\mathrm{A}]_0)[(\mathrm{III})] + (k_6 + k_6'[\mathrm{A}]_0)[(\mathrm{IV})] \quad (28)$$

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[22] Z. Rappoport and R. Ta-Shma, *J. Chem. Soc.* (*B*), 1971, 871; Z. Rappoport and N. Ronen, *J.C.S. Perkin II*, 1972, 955.

[23] A. G. Rehiem, personal communication.

(29). Expressing $[\mathrm{T}]_{\mathrm{total}}$ in terms of $[\pi]$ as in equation

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = \frac{-\mathrm{d[T]_{total}}}{\mathrm{d}t} = \frac{k_1\{k_3 + k_4 + (k_3' + k_4')[\mathrm{A}]_0\}}{k_{-2} + k_3 + k_4 + (k_3' + k_4')[\mathrm{A}]_0} \times [\pi][\mathrm{A}]_0 \quad (29)$$

(14) gives (30) whence (31) is obtained. The observed

$$\frac{-\mathrm{d}[\pi]}{\mathrm{d}t} = \frac{K[\mathrm{A}]_0^2[\pi]}{1 + K[\mathrm{A}]_0} \cdot \frac{\{k_3 + k_4 + (k_3' + k_4')[\mathrm{A}]_0\}k_1}{k_{-2} + k_3 + k_4 + (k_3' + k_4')[\mathrm{A}]_0} \quad (30)$$

$$k_{\mathrm{exp}} = \frac{K[\mathrm{A}]_0}{1 + K[\mathrm{A}]_0} \cdot \frac{k_1\{k_3 + k_4 + (k_3' + k_4')[\mathrm{A}]_0\}}{k_{-2} + k_3 + k_4 + (k_3' + k_4')[\mathrm{A}]_0} \quad (31)$$

linear relationship between $k_{\mathrm{exp}}(1 + K[A]_0)$ and $[\mathrm{A}]_0^2$ will be obtained when the relationship (32) is satisfied, *i.e.* when equation (33) holds.

$$k_{-2} \gg (k_3' + k_4')[\mathrm{A}]_0 \gg k_3 + k_4 \quad (32)$$

$$k_{\mathrm{exp}} = K[\mathrm{A}]_0^2 \cdot k_1(k_3' + k_4')/k_{-2}(1 + K[\mathrm{A}]_0) \quad (33)$$

Thus the base-catalysed abstraction of either a proton or cyanide ion from (II) is favoured over the uncatalysed reaction, as would be anticipated for proton removal, and reversal to uncomplexed starting materials occurs (see Appendix). The base-catalysed cyanide ion elimination is probably slower than the proton abstraction and therefore the slope of Figure 1 may be approximated by (k_1k_3'/k_{-2}).

Although only four anilines were studied the results indicate a negative Hammett ρ value of the order of −3·7. From the kinetic analysis it can be seen that the observed rate coefficient is a composite one and the ρ value therefore a sum of the separate values. If the transition states for decomposition of (II) are similar and resemble the least stable species of reactants or products,[24] *i.e.* (II), then the corresponding ρ values (ρ_{-2} and ρ_3') should have similar values. The observed value may then approximate that for the formation of (II) from the π-complex and is in agreement with the development of a positive charge on nitrogen.[25]

The lack of any significant kinetic hydrogen isotope effect (Table 3) is not surprising. In the formation of (II) or its dissociation to yield starting materials only rehybridization of the N–H bonds occurs and any effect should be very small. The greater inductive electron release from deuterium[26] should lead to an inverse effect ($k_{\mathrm{H}}/k_{\mathrm{D}} < 1$) in the attacking step, as was observed in the benzoylation of aniline,[27] but the base catalysis would effectively minimize any zero-point energy differences in the transition states and this may result in no observable isotope effect.

The rate of formation of the product P may be expressed as shown in equation (29).

Assuming that the inequalities of equation (32) are valid, the product concentration at any time will be given by equation (34). (The π-complex concentration

$$[\mathrm{P}] = [\pi]_0[\mathrm{A}]_0^2(1 - e^{-k_{\mathrm{CT}}t})k_1k_3'/k_{-2} \quad (34)$$

is expressed as $[\pi] = [\pi]_0e^{-k_{\mathrm{CT}}t}$). Thus the variation of the product concentration with $(1 - e^{-k_{\mathrm{CT}}t})$ should be linear, the slope being given by equation (34). Substitution in (34) for $[\pi]_0$ and k_{CT} results in a predicted slope equal to the initial tetracyanoethylene concentration, as is approximately observed (Figure 2).

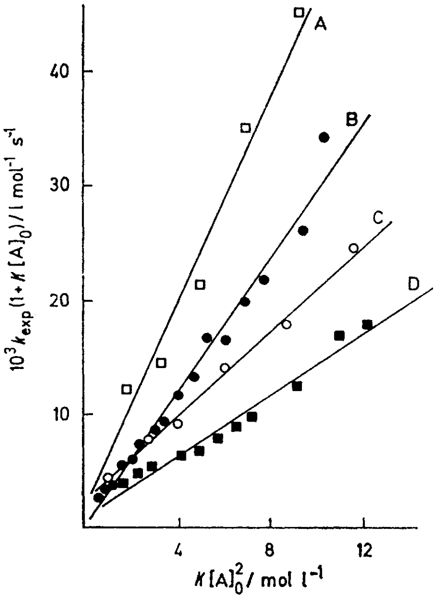

FIGURE 2 The variation of k_{exp}, the pseudo-second-order rate coefficient, as a function of initial aniline concentration [equation (33)]: A, 25·4; B, 20·7; C, 16·8; and D, 15·0 °C

Our results are therefore in accord with the π-complex being an initial intermediate on the reaction pathway followed by the formation of a zwitterionic intermediate (II). The formation of (II) requires an ' exchange ' mechanism in which a further molecule of aniline takes part, as was suggested for the *NN*-dimethylaniline reaction, and the zwitterion is less stable than the corresponding *C*-tricyanovinylation intermediate. The reaction scheme shown here would therefore accommodate both *C*- and *N*-tricyanovinylation of aromatic amines, the relative rates of the individual steps determining the observed kinetics, order with respect to amine, *etc.* The kinetic data indicate that the π-complex of this reaction is less stable than those of *N*-alkylated anilines in contrast to the report by Isaacs.[4] The dependence of the rate of disappearance of the π-complex upon donor concentration was also observed by Rappoport[5] in the reactions of dienes with tetracyanoethylene.

The participation of a π-complex in the iodination of alkylbenzenes in non-polar solvents was proposed

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[25] K. B. Wiberg, ' Physical Organic Chemistry,' Wiley, New York, 1964, p. 405.

[26] C. Bernasconi, W. Koch, and H. Zollinger, *Helv. Chim. Acta*, 1963, **46**, 1184.

[27] J. J. Elliott and S. F. Mason, *Chem. and Ind.*, 1959, 488.

by Andrews and Keefer,[28] who interpreted the third-order dependence upon iodine monochloride by postulating attack of halogen dimer upon the π-complex in the rate-determining step. In polar solvents the order in halogen decreased due to solvent assistance in the interhalogen bond breakage. Attempts to obtain more compelling evidence for π-complexes as reaction intermediates have been made in recent studies of inner and outer complexes,[29] electron transfer reactions,[30] solvent effects upon complex formation, *etc.*,[31] but these have achieved only limited success.

EXPERIMENTAL

Materials.—The amines and tetracyanoethylene were purified commercial products, aniline being stored under nitrogen in a desiccator at 0 °C after fractional distillation. Dichloromethane (Fisher spectrograde) was dried for 1 day ($CaCl_2$) and distilled, b.p. 39·8°, immediately before use into Polythene bottles.

[*NN*-$^2H_2$]Aniline was prepared by reacting a solution of aniline in anhydrous ether with a four-fold excess of n-butyl-lithium, followed by hydrolysis of the product with excess of deuterium oxide, and had b.p. 184°. The n.m.r. spectrum of this compound showed $>94\%$ deuterium incorporation. No deuterium exchange between [*NN*-$^2H_2$]-aniline and dichloromethane could be detected by n.m.r. spectrometry.

Kinetic Procedure.—Stock solutions of the reactants were prepared daily at the reaction temperature. Aliquot portions of these solutions were rapidly mixed in stoppered silica absorption cells (40, 10, or 1 mm path length) contained in the constant-temperature cell housing of a Beckman DB spectrophotometer, the time of half-addition being taken as $t = 0$, and the variation of the absorbance at a constant wavelength was recorded. The temperature inside the reaction cell was measured by means of a copper–constantan thermocouple to $\pm 0{\cdot}1°$. A series of runs at constant $[T]_0$ and varying $[A]_0$ was followed at each temperature. The disappearance of the π-complex was usually followed to $>90\%$ reaction but the appearance of the product was followed to only 50—60% reaction in most cases because of the higher extinction coefficient.

Products.—*N*-Tricyanovinylaniline was prepared according to the method of McKusick *et al.*[1] and had m.p. 168° (decomp.), $\lambda_{max.}$ (CH_2Cl_2) 350 nm (ε 14,000).

A solution of aniline (10 parts) and tetracyanoethylene (1 part) in dichloromethane was allowed to react at 25° for several hours, after which the solvent and excess of aniline were removed. Analysis of the solid product by t.l.c. indicated five products; *N*-tricyanovinylaniline (70%), 1,1-dianilino-2,2-dicyanoethylene (15%), and three unidentified minor products (none of these products corresponded to *p*-tricyanovinylaniline.)

1,1-*Dianilino*-2,2-*dicyanoethylene* was isolated by fractional crystallization of the solid product described above from dichloromethane, was recrystallized as platelets from the same solvent, and had m.p. 264° (Found: M^+, 260·101650. $C_{16}H_{12}N_4$ requires M, 260·106191). Reaction of *N*-tricyanovinylaniline with excess of aniline in dichloromethane results in the same mixture of products in approximately the same ratios, implying that *N*-tricyanovinylaniline is the precursor of the other products. The reactions to form these products are slow and do not interfere with the kinetic study.

APPENDIX

Assuming that (II) reverts to π-complex in a base catalysed step (see Scheme), then application of the steady state approximation as before leads, after substitution, *etc.*, to expression (35) for k_{exp}. Agreement with the experimental observations requires the conflicting inequalities (36) and (37).

$$k_{exp} = \frac{K[A]_0}{1 + K[A]_0} \cdot \frac{k_1(k_3 + k_4 + (k_3' + k_4')[A]_0)}{k_3 + k_4 + (k_{-1} + k_3' + k_4')[A]_0} \qquad (35)$$

$$k_3 + k_4 \ll (k_3' + k_4')[A]_0 \qquad (36)$$

$$k_3 + k_4 \gg (k_{-1} + k_3' + k_4')[A]_0 \qquad (37)$$

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.).

[2/1525 *Received*, 30*th June*, 1972]

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