Ebulliometric and Spectroscopic Kinetic Studies on the Reaction between Tetracyanoethylene and *NN*-Dimethylaniline

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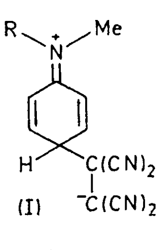
The equilibrium constant for the 1:1 charge-transfer complex between *NN*-dimethylaniline (DMN) and tetracyanoethylene (TCNE) in dichloromethane has been determined by Benesi–Hildebrand and equimolar methods. The second-order rate constants, k_2, for the DMN–TCNE reaction increase with increasing amine concentration. This suggests that the charge-transfer complex is an intermediate in the reaction sequence and the rate constant, k_c, corrected on the basis of this mechanism does not vary with concentration. The Arrhenius plot, using the k_c values obtained from the three experimental methods, is a good straight line. Evidence is also presented for the reversibility of the charge-transfer complex ⟶ σ-complex step.

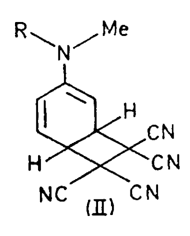
It has been shown[1] that *N*-alkylanilines react with tetracyanoethylene (TCNE) to give *para*-substituted tricyanovinyl compounds. The kinetics of the reaction between TCNE and both *NN*-dimethylaniline (DMN)[2] and *N*-methylaniline[3] have been studied and the results indicate that the reaction sequence is as follows:

$$\mathrm{TCNE} + \mathrm{Amine} \rightleftharpoons \text{Charge-transfer complex } (1:1) \longrightarrow \qquad (1)$$

$$\text{Intermediate} \xrightarrow{-\mathrm{HCN}} p\text{-Tricyanovinyl amine}$$

The nature of the intermediate has been the subject of considerable discussion[3-6] and the structures (I)—(III) have all been postulated (R = H or Me). Recent work[6,7] has indicated that the linear adduct (III) is the intermediate in the reaction and may be formed by the rapid rearrangement of the σ-complex (I). It has been shown[2,3] that the formation of the intermediate is much faster than the formation of the final tricyanovinyl


(I)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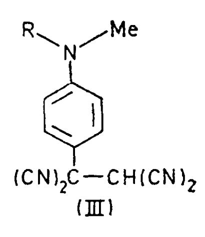
(III)

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

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

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

[4] P. G. Farrell, J. Newton, and R. F. M. White, *J. Chem. Soc.* (*B*), 1967, 637.

[5] E. M. Kosower, *Progr. Phys. Org. Chem.*, 1965, **3**, 81.

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

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

product and the two reactions may be followed independently.

The disappearance of the charge-transfer complex was followed spectrophotometrically[3] in chloroform using large excesses of amine at various temperatures. For the *N*-methylaniline–TCNE system the calculated value of the second-order rate constant, k_2, increased as the concentration of *N*-methylaniline was increased. Because of the high value of the equilibrium constant for the formation of the charge-transfer complex similar work[2] using DMN did not show this trend and the high amine concentrations used resulted in the value of k_2 being approximately equal to the true second-order rate constant, k_c.

The present work concerns the DMN–TCNE system and reports a kinetic study of the disappearance of the charge-transfer complex studied in dichloromethane by visible spectroscopy using an excess of DMN and by kinetic ebulliometry and ultraviolet spectroscopy using equimolar concentrations of reactants.

RESULTS

Formation of the Charge-transfer Complex.—An intense blue colour ($\lambda_{max.}$ 675 nm) is formed on mixing solutions of the two reactants in dichloromethane.

Benesi–Hildebrand Method.[8]—The value for the equilibrium constant, K, for the formation of the complex was determined using large excesses of DMN and the values obtained at three temperatures (Table 1) were compared with those obtained using equimolar concentrations of DMN and TCNE.

TABLE 1

Values of equilibrium constant for the DMN–TCNE complex

Temp. (°C)	24·7	32·6	36·5
K (l mol^{-1})	26·8	22·7	20·9

Equimolar Method.—If A = acceptor, D = donor, and AD* = donor–acceptor (1 : 1) complex, then for the system

$$A + D \rightleftharpoons AD^* \tag{2}$$

$$K = [AD^*]/[A][D] \tag{3}$$

If $[A]_0 = [D]_0$ = total concentration (mol l^{-1}) of donor (free and complexed)
then for a 1-cm cell

$$K = \frac{d}{\varepsilon([A]_0 - d/\varepsilon)^2} \tag{4}$$

where d is the absorbance (optical density) and ε is the molar extinction coefficient for the complex.

Hence $$\frac{[A]_0}{\sqrt{d}} = \frac{\sqrt{d}}{\varepsilon} + \frac{1}{\sqrt{K\varepsilon}} \tag{5}$$

and a plot of $[A]_0/\sqrt{d}$ against $\sqrt{d}$ should give a straight line of slope $1/\varepsilon$ and intercept $1/\sqrt{K\varepsilon}$.

This method was first checked using the hexamethylbenzene–TCNE system in dichloromethane and measuring absorbance values at 530 nm. The values of K(16·4 l mol^{-1}) and ε_{530}(2080 l mol^{-1} cm^{-1}) at 22·2 °C agree with the literature.[9]

For the DMN–TCNE system, values of initial optical density, d_0, were obtained by extrapolating the time *vs. d* curves to zero time. The value obtained for K at 25·8 °C by this method was 26·3 l mol^{-1}. A plot of ln K against $1/T$ for the results obtained by the Benesi–Hildebrand method gave a value of 26·1 l mol^{-1} for K at 25·8 °C by interpolation. The two values were considered to be sufficiently close to justify the use of the values obtained by the Benesi–Hildebrand method. The enthalpy ($\Delta H = -3{\cdot}8 \pm 0{\cdot}2$ kcal mol^{-1}) and entropy ($\Delta S = -19 \pm 2$ e.u.) for the equilibrium were calculated from the above plot.

The Kinetics of the Formation of the Intermediate

By Visible Spectroscopy.—The reaction was followed by measuring the decrease in absorbance of the charge-transfer complex at 675 nm using amine concentrations 60—240 times greater than those of TCNE. The reaction was found to be first-order with respect to the complex and hence to the TCNE, and the values of the first-order rate constants, k_1, are given in Table 2, where $[D]_0$ = concentration (mol l^{-1}) of DMN and $[A]_0$ = concentration (mol l^{-1}) of TCNE. The second-order rate constant, $k_2 = k_1/[D]_0$.

TABLE 2

Values of k_1 (s^{-1}), k_2 (l mol^{-1} s^{-1}) and corrected second-order rate constants, k_c (l mol^{-1} s^{-1}), for the disappearance of the charge-transfer complex

λ = 675 nm, $[A]_0$ = 0·668 mM

$[D]_0$ (M)	0·0395	0·0593	0·0790	0·1185	0·158	at 24·7 °C
$k_1 \times 10^3$	0·399	0·731	1·09	1·86	2·71	
$k_2 \times 10^2$	1·01	1·24	1·38	1·57	1·72	
$k_c \times 10^2$	2·0	2·0	2·0	2·1	2·1	
$k_1 \times 10^3$	0·516	0·985	1·38	2·30	3·49	at 32·6 °C
$k_2 \times 10^2$	1·31	1·66	1·75	1·94	2·21	
$k_c \times 10^2$	2·8	2·9	2·7	2·7	2·8	
$k_1 \times 10^3$	0·576	1·13	1·69	2·82	4·11	at 36·5 °C
$k_2 \times 10^2$	1·46	1·90	2·14	2·38	2·60	
$k_c \times 10^2$	3·2	3·6	3·4	3·3	3·4	

The order of reaction, with respect to the amine, was found to be greater than unity as shown by the increase of the second-order rate constant with increasing amine concentration. Of six possible reaction mechanisms, an increase in k_2 with increasing amine concentration has been shown to be consistent[3] only with one of the reaction Schemes 1 and 2 where AD is the first reaction product (intermediate).

$$A + D \rightleftharpoons AD^* \qquad \text{Scheme 1}$$
$$AD^* + D = AD + D$$

$$\begin{tikzcd} A + D \rightleftharpoons AD^* \arrow[d] \\ AD \end{tikzcd} \qquad \text{Scheme 2}$$
$$AD^* + D = AD + D$$

By Ebulliometry.—The reaction kinetics were followed by studying the change in boiling point of an equimolar solution of DMN and TCNE. Second-order rate constants were calculated (Table 3) and these showed an increase with increasing reactant concentration.

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

[9] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.

TABLE 3

Ebulliometrically determined second-order rate constants, k_2 (l mol^{-1} s^{-1}), and corrected values, k_c (l mol^{-1} s^{-1}) for the formation of the first reaction product

$[D]_0 = [A]_0$ (M)	0·0498	0·0705	0·0801	0·0896
$k_2 \times 10^3$	8·25	9·5	9·8	10·4
$k_c \times 10^2$	4·1	4·1	4·1	4·2

Corrected Second-order Rate Constants.—The suggested reaction path for the *N*-alkylaniline–TCNE system [3] was Scheme 1. In this case the true second-order rate constant, k_c, for the reaction where the amine is in large excess, is given by the expression

$$k_c = k_2(1 + K[D]_0)/K[D]_0 \qquad (6)$$

The values of k_2 were corrected on this basis and the values obtained for k_c are given (Table 2).

A similar procedure was used to correct the ebulliometric results. If the initial total concentrations of A and D are each a, and if at time t the concentration of AD* and AD are x and y respectively, then [A] and [D] are each $(a - x - y)$.

Then $$K = x/(a - x - y)^2 \qquad (7)$$

and the rate of reaction = dy/dt.

$$= k_c[AD^*][D] = k_c(x)(a - x - y) = k_c\, x^{\frac{3}{2}}/\sqrt{K} \qquad (8)$$

Hence by substitution for dy in (8) it can be shown that

$$t = \frac{\sqrt{K}}{k_c}\left[\frac{2}{\sqrt{x}} + \frac{1}{2x\sqrt{K}}\right] + \text{constant} \qquad (9)$$

Hence a plot of the variable function on the right-hand side of (9) *versus* t should give a straight line with slope $\sqrt{K}/k_c$.

From a plot of ln K against $1/T$(K) a value of 19·4 l mol^{-1} was obtained for K at the boiling point of dichloromethane (40·1 °C), and values of x were obtained at various times using this value and the ebulliometric data. Graphs of t (s) *vs.* $\left[\frac{2}{\sqrt{x}} + \frac{1}{2x\sqrt{K}}\right]$ were plotted for each set of ebulliometric data and values of k_c calculated from the slopes of the straight lines obtained (Table 3).

Ultraviolet Spectroscopy.—The reaction was followed by measuring the change in absorbance due to tetracyanoethylene at 260 nm. The solutions used were equimolar with respect to DMN and TCNE and the values of k_c were calculated directly from the experimental results, using equation (9), in the same way as for the ebulliometric results (Table 4).

TABLE 4

Corrected second-order rate constants, k_c (l mol^{-1} s^{-1}) for the disappearance of TCNE; λ = 260 nm

$[DMN]_0 = [TCNE]_0 = 0{\cdot}079$M

Temp. (°C)	30·9	34·9
$k_c \times 10^2$	2·6	3·1

DISCUSSION

The agreement between the values of K and ε obtained by the Benesi–Hildebrand and equimolar methods indicates that the charge-transfer complex has primarily a 1 : 1 stoicheiometry.

The increase in k_2 with increasing amine concentration is consistent with Schemes 1 and 2. The values of k_c and k_2 for the two mechanisms are related by expressions (10) and (11) when the amine is in large excess. It

Scheme 1 $$k_2 = \frac{k_c K[D]_0}{1 + K[D]_0} \qquad (10)$$

Scheme 2 $$k_2 = \frac{(k_c K[D]_0 + k_c')}{1 + K[D]_0} \qquad (11)$$

can be seen from these equations that a plot of $k_2(1 + K[D]_0)$ against $K[D]_0$ should be linear in both cases. For Scheme 1 the line should pass through the origin but for Scheme 2 the line should have an intercept with the ordinate axis of k_c', the rate constant for the reaction between D and A which directly forms the adduct, AD. Of the three sets of results obtained [3] for the *N*-methylaniline–TCNE system all gave good straight lines and that at the highest temperature passed through the origin, the other two lines gave negative intercepts with the ordinate axis. On this basis it was concluded that the reaction path was that illustrated in Scheme 1, and the negative intercepts were attributed to curvature of the lines at low amine concentrations. Such a scheme would also apply to the results obtained for the DMN–TCNE system [2] which gave apparently constant values of k_2. Since the value of K for the DMN–TCNE complex is large (Table 1), then at high amine concentrations such as those used by Rappoport, from equations (10) and (11) $K[D]_0/(1 + K[D]_0) \sim 1$ and hence $k_2 \sim k_c$. This could also be explained by Scheme 2 if $k_c \gg k_c'$ when equation (11) approximates to equation (10).

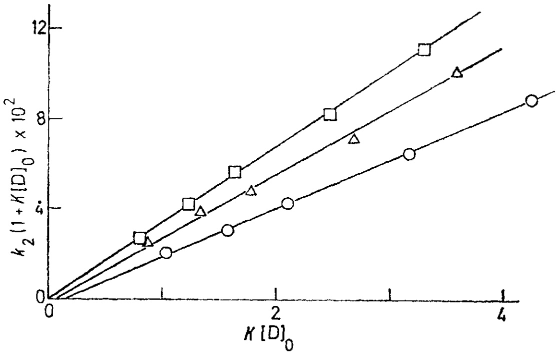


FIGURE 1 Plot of $k_2(1 + K[D]_0) \times 10^2$ against $K[D]_0$ for the DMN–TCNE reaction. —○— = 24·7 °C; —△— = 32·6 °C; —□— = 36·5 °C

In the present investigation the concentrations of DMN were less than those used by Rappoport and there is a pronounced increase in k_2 with increasing DMN concentration (Tables 2 and 3). Graphs of $k_2(1 + K[D]_0)$ against $K[D]_0$ were plotted for each set of results (Figure 1) and small negative intercepts, tending to zero as the temperature was increased, were obtained. The negative intercepts obtained indicate that, although Scheme 1 provides a close approximation, neither Scheme 1 nor 2 completely fits the kinetics. It can be seen from Figure 1 that if k_2 were slightly larger the lines would pass through the origin, hence, if Scheme 1 provides the major route to adduct formation then there must be some secondary effect which tends to decrease the observed k_2 and also must increase the charge-transfer complex concentration. A possible explanation is that the initial formation

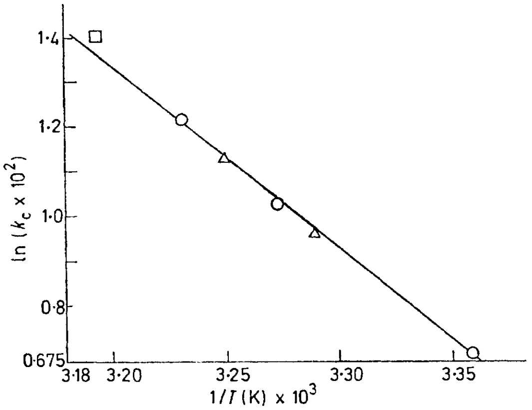
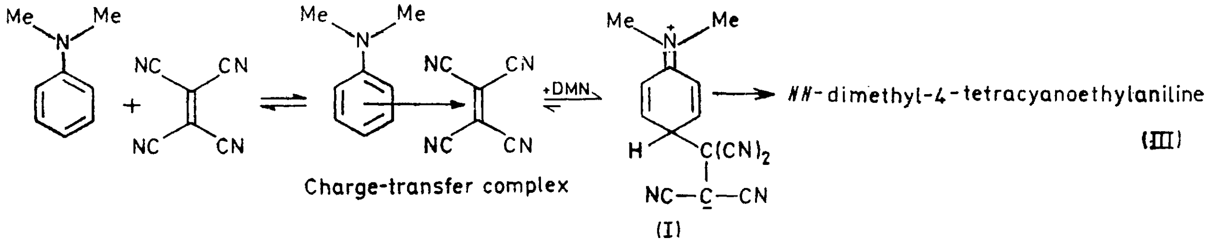


FIGURE 2 Arrhenius plot of the kinetic data for the DMN–TCNE reaction in dichloromethane: —○— = visible spectroscopy; —□— = ebulliometry; —△— = ultraviolet spectroscopy

of the σ-complex (I) is reversible although the bulk of this complex will give rise to the linear adduct (III) by an irreversible reaction. At the higher temperatures the adduct (III) formation becomes so fast that the reversal cannot be detected hence the small negative intercept disappears; Kosower [5] has suggested that the σ-complex should show reversible decomposition to the charge-transfer complex.



SCHEME 3

Further evidence that Scheme 1 is correct is provided by ebulliometric and ultraviolet spectroscopic results which, when corrected on the basis of this mechanism, give constant values of k_c at each temperature. An Arrhenius plot was drawn from the kinetic data obtained by the three different methods using the values of k_c calculated on the basis of Scheme 1 (Figure 2). From the slope a value of 8·2 ± 0·2 kcal mol^{-1} was obtained for the energy of activation for the reaction with an entropy of activation of −38 ± 3 e.u. indicating a highly ordered transition state. The overall reaction for the formation of the linear adduct is probably that illustrated in Scheme 3.

EXPERIMENTAL

Purification of Reagents.—Tetracyanoethylene was recrystallised from chlorobenzene followed by vacuum sublimation and had a m.p. 198 °C. *NN*-Dimethylaniline was distilled (15 mm) with a nitrogen bleed; dichloromethane was dried through a column of molecular sieve (type 4A) and fractionally distilled, b.p. 40—41 °C.

Spectroscopy.—Visible and ultraviolet spectroscopy measurements were carried out using a Unicam SP 500 spectrophotometer fitted with a thermostatted cell housing.

Ebulliometry.—Measurements were made using a pair of Heitler ebulliometers [10–13] fitted with matched thermistors. One ebulliometric flask contained dichloromethane only and the second the reaction solution. The thermistors formed adjacent arms of a Wheatstone Bridge and the change in resistance between the thermistors, and hence the change in boiling point of the reaction solution, was measured as an out of balance voltage on a potentiometric recorder.

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[10] C. Heitler, *Analyst*, 1958, **83**, 223.

[11] C. Heitler, *Talanta*, 1964, **11**, 1471.

[12] C. Heitler, *Talanta*, 1964, **11**, 1081.

[13] C. Heitler, *J. Chem. Soc.*, 1963, 4885.