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INTERACTION OF ELECTRON ACCEPTORS WITH BASES—XIII

THE INTERACTION OF INDOLE WITH TETRACYANOETHYLENE IN DICHLOROMETHANE

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Abstract—Visible absorption studies of the system indole–tetracyanoethylene in dichloromethane show that an intermolecular charge-transfer complex is initially formed. This decomposes to yield a second product, presumed to be a σ-complex, which finally yields 3-tricyanovinylindole.

RECENTLY[1] evidence has been adduced for the formation of intermolecular charge-transfer complexes[2] from indole and methylated indoles with various electron acceptor molecules. The system indole–tetracyanoethylene in dichloromethane has now been studied in detail. When a 1M solution of indole is mixed with a 5×10^{-4}M solution of tetracyanoethylene a royal blue colouration ($\lambda_{max} = 560$ mμ) is immediately obtained. This appears to be the result of the very fast formation of a 1:1 intermolecular charge-transfer complex between the molecules of the two solute species. At room temperature the blue slowly fades to give a near-colourless solution after 4 hr. On standing for several days the solution becomes yellow due to the formation of 3-tricyanovinylindole.[3]

RESULTS

Stability constants of indole-tetracyanoethylene charge-transfer complex in dichloromethane at various temperatures

The equilibrium constant (K) is defined as:

$$K = [AD_{CT}]/[A][D] \text{ l . mole}^{-1}$$

where AD_{CT} is the 1:1 intermolecular charge-transfer complex between the electron acceptor tetracyanoethylene (A) and the electron donor (D), in this case indole K has been obtained by an application of the method of Benesi and Hildebrand.[4] This requires measurements of optical density (d) for a series of solutions in which $[A_0] \ll [D_0]$; where $[A_0]$ and $[D_0]$ are the *total* concentrations (free and complexed) of the acceptor and donor respectively. The plots of $[A_0]\, d^{-1}$ versus $[D_0]^{-1}$ (Fig. 1) have gradients $K^{-1}\epsilon^{-1}$ and an intercept with the ordinate ϵ^{-1}, where ϵ is the molar extinction coefficient of the complex, and the optical density (d) corresponds to the absorption of the species AD_{CT} alone. The linearity of the plots in Fig. 1 confirms

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[1] R. Foster and P. Hanson, *Trans. Faraday Soc.* (in the press).

[2] R. S. Mulliken, *J. Amer. Chem. Soc.* **72**, 605 (1950); **74**, 811 (1952); *J. Phys. Chem.* **56**, 801 (1952).

[3] G. N. Sausen, V. A. Engelhardt and W. J. Middleton, *J. Amer. Chem. Soc.* **80**, 2815 (1958).

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

that the ratio of the component molecules in the complex is 1 : 1. Values for a typical plot are given in Table 1. The values of K and ϵ at various temperatures evaluated from least square determinations of the plots in Fig. 1 are given in Table 2. From van't Hoff's equation, $\Delta H = -3{\cdot}0_8$ kcal.mole^{-1} and $\Delta S = -8{\cdot}3_2$ e.u. for the formation of the complex.

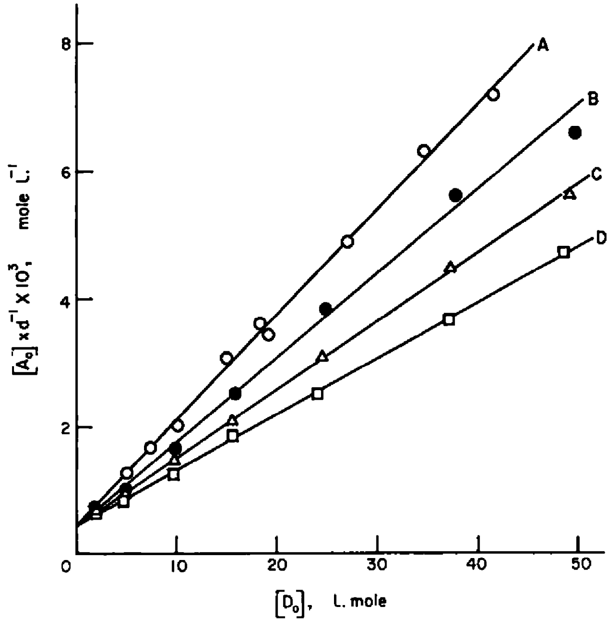

FIG. 1. Benesi–Hildebrand plots for the complex indole–tetracyanoethylene in dichloromethane: (A) at 25·0° ○; (B) at 15·0° ●; (C) at 4·75° △; (D) at −2·25° □.

Decomposition of the charge-transfer complex

The decay of the absorption at 560 mμ, characteristic of the charge-transfer complex was followed spectrophotometrically for a series of solutions at 25·0° and 4·75°. In every case there was a large excess of indole. Plots of log d against time gave good straight lines, thus the reaction is first order with respect to the charge-transfer complex. These pseudo first order rate constants are dependent on the indole concentration (Table 3).

Formation of 3-tricyanovinylindole

From determinations in the previous section it is estimated that for a mixture M with respect to indole and 5×10^{-4}M with respect to tetracyanoethylene the charge-transfer complex should have decomposed to an extent >95% after 4 hr at 25°. The optical densities of three such solutions were measured after 14 hr at intervals over a period of 5 hr. The optical density at 460 mμ remained constant, while that at 456 mμ (corresponding to 3-tricyanovinylindole) increased. From the constancy of the optical density at 560 mμ it was inferred that the decomposition of the charge-transfer complex was complete so that the initial concentration of the second complex could

TABLE 1. DATA FOR THE DETERMINATION OF K FOR INDOLE–TETRACYANOETHYLENE IN DICHLOROMETHANE AT 25·0°

$[D_0] \times 10^2$ (M)	$[A_0]$ (M)	d (560 mμ)	$[A_0] + 10^3/d$	$[D_0]^{-1}$ (M)
2·406	$2{\cdot}161 \times 10^{-4}$	0·030	7·202	41·54
2·889	$2{\cdot}161 \times 10^{-4}$	0·034	6·355	34·61
3·720	$2{\cdot}161 \times 10^{-4}$	0·044	4·910	26·88
5·219	$2{\cdot}161 \times 10^{-4}$	0·063	3·430	19·15
9·887	$2{\cdot}161 \times 10^{-4}$	0·107	2·020	10·11
20·088	$2{\cdot}161 \times 10^{-4}$	0·172	1·256	4·97
50·091	$2{\cdot}161 \times 10^{-4}$	0·280	0·772	1·99
6·642	$1{\cdot}953 \times 10^{-3}$	0·636	3·070	15·05
13·514	$1{\cdot}953 \times 10^{-3}$	1·151	1·697	7·40
5·448	$1{\cdot}953 \times 10^{-4}$	0·054	3·633	18·36

TABLE 2. VALUES OF THE EQUILIBRIUM CONSTANT (K), EXTINCTION COEFFICIENT AT 560 mμ (ε) ENTHALPY (ΔH) AND ENTROPY (ΔS) OF FORMATION OF THE INDOLE–TETRACYANOETHYLENE COMPLEX IN DICHLOROMETHANE

Temp (°C)	K (l.mole⁻¹)	ε	ΔH (kcal.mole⁻¹)	ΔS (e.u.)
−2·25	$4{\cdot}6_2$	2420	$-3{\cdot}0_8$	$-8{\cdot}3_2$
4·75	$4{\cdot}2_0$	2230		
15·0	$3{\cdot}3_4$	2330		
25·0	$2{\cdot}7_8$	2170		

TABLE 3. PSEUDO FIRST-ORDER RATE COEFFICIENTS (k) AND SECOND-ORDER COEFFICIENTS (k_{exp}) FOR THE DECOMPOSITION OF THE INDOLE–TETRACYANOETHYLENE COMPLEX IN DICHLOROMETHANE

Temp °C	$[D_0]$ (M)	$[A_0] \times 10^4$ (M)	$k \times 10^4$ (sec⁻¹)	$k_{exp} \times 10^4 = k[D_0]^{-1} \times 10^4$ (l.mole⁻¹sec⁻¹)
25·0	0·474	4·57	0·67	1·41
25·0	0·655	7·67	1·19	1·82
25·0	0·703	4·57	1·31	1·86
25·0	0·923	4·57	2·10	2·27
4·75	0·510	5·03	0·57	1·13
4·75	0·681	2·52	1·10	1·61
4·75	0·766	5·03	1·31	1·71
4·75	1·021	2·52	2·29	2·24

be taken as equivalent to that of the initially weighed out quantity of tetracyanoethylene. From a knowledge of the extinction coefficient of 3-tricyanovinylindole in dichloromethane (separately determined $\epsilon_{456} = 20{,}640$) the percentage reaction over the period of measurement was determined. Plots of d (at 456 mμ) versus time were linear. From these observations, a second order rate constant of $2{\cdot}9 \times 10^{-7}$ l.mole⁻¹ sec⁻¹ for the reaction at 25·0° was obtained (Table 4).

DISCUSSION

The interaction of indole with tetracyanoethylene in dichloromethane has many features in common with the interaction of N-alkylanilines with tetracyanoethylene which has recently been studied by Rappoport *et al.*[5,6] He suggested that for such systems there is a three step reaction (a) the rapid formation of the charge-transfer complex; (b) the formation of a σ-complex (c) the final formation of N-alkyl-4-tricyanovinylaniline.

In the reaction with indole, previous and present work strongly supports the initial rapid formation of a charge-transfer complex with tetracyanoethylene. The thermodynamic formation constants and the position and intensity of the intermolecular optical transition are typical of such complexes.[7]

TABLE 4. SECOND ORDER RATE COEFFICIENTS (k_2) FOR THE REACTION $\sigma \rightarrow$ 3-TRICYANOVINYLINDOLE, AT 25·0°

$[D_0]$ (M)	$[A_0] = [\sigma]$ (M)	$\Delta d/\Delta t = x$ sec^{-1}	k_2 $(= x[\sigma]^{-1}[D_0]^{-1}\epsilon^{-1})$ (l.mole^{-1}sec^{-1})	% reaction
0·930	$4{\cdot}628 \times 10^{-4}$	$2{\cdot}67 \times 10^{-6}$	$3{\cdot}00 \times 10^{-7}$	1·64 – 1·89
1·00	$5{\cdot}377 \times 10^{-4}$	$3{\cdot}22 \times 10^{-6}$	$2{\cdot}90 \times 10^{-7}$	1·36 – 1·70
1·00	$5{\cdot}052 \times 10^{-4}$	$2{\cdot}96 \times 10^{-6}$	$2{\cdot}84 \times 10^{-7}$	1·31 – 1·64

The decomposition of this charge-transfer complex gives rise to no immediate new visible absorption. The high concentration of indole which had to be used made it practically impossible to distinguish any new transition in the near UV which might correspond to the transition at 279 mμ claimed by Rappoport to be due to the σ-complex of tetracyanoethylene with dimethylaniline.[5] Rate determinations for the decomposition of the indole charge-transfer complex indicate that the kinetics do not depend on some simple function of the indole concentration. In particular the reaction is not first order in respect to [D], this latter relationship was observed by Rappoport for the reaction of N,N-dimethylaniline with tetracyanoethylene in chloroform and chloroform—dichloromethane mixtures.[5] The second order rate coefficients (k_{exp}) (first order coefficients divided by indole concentration) increased with increasing indole concentration (Table 3). This is similar to the observation of Rappoport for the corresponding N-methylaniline system.[6] Of six alternative reactions for the formation of the σ-complex from tetracyanoethylene and N-methylaniline Rappoport showed that only two are commensurate with the above observation, namely either: (i) a bimolecular reaction of the charge-transfer complex with a second molecule of N-methylaniline whence:

$$k_{exp} = k'K[D_0]/(1 + K[D_0]$$

where k′ is the rate constant for the bimolecular reaction of the charge-transfer complex with the base to give the σ-complex. (ii) the above reaction concurrent with the bimolecular reaction of uncomplexed tetracyanoethylene with base to yield the σ-complex. In this case

$$k_{exp} = (k'K[D_0] + k'')/(1 + K[D_0]) \qquad (2)$$

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

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

[7] E.g., G. Briegleb, *Donator-Acceptor-Complexe.* Springer-Verlag, Berlin (1961).

where k″ is the rate coefficient for the bimolecular reaction of uncomplexed tetracyanoethylene with base. The kinetics for both the reactions of N,N-dimethylaniline and of N-methylaniline with tetracyanoethylene could be interpreted in terms of the former reaction. The appearance of the overall kinetics is different in the two cases because of the magnitude of the term $K[D_0]$ compared with unity in the denominator of the right hand side of the equation (1). For the dimethylaniline reaction $K(D_0)$ is large and effectively $k_{exp} = k'$. In the present system the term $K[D_0]$ varies from 1·3 to 4·8, a circumstance similar to that for N-methylaniline–tetracyanoethylene in chloroform studied by Rappoport.[6] For either equation (1) or (2) a plot of $k_{exp}(1 + K[D_0])$ should be linear, in the former case the line should pass through the origin in the latter the intercept with the ordinate should be equal to k″. Such plots are given in Fig. 2.

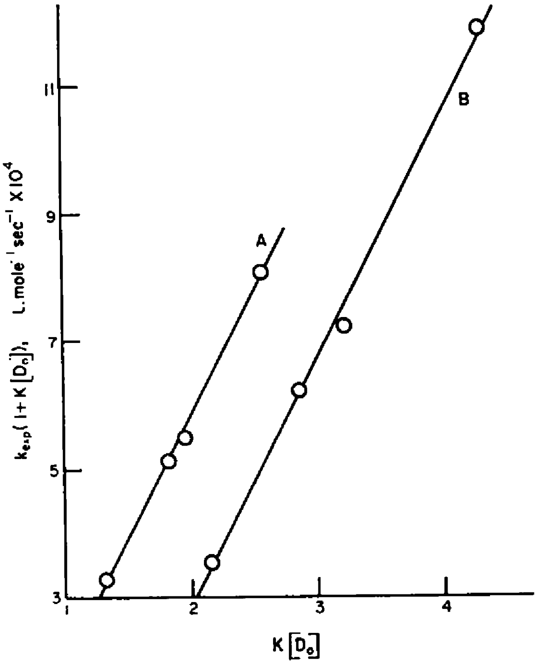


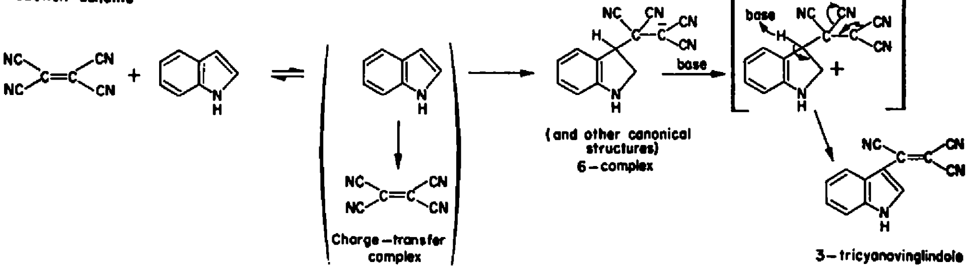
FIG. 2. Plots of $k_{exp}(1 + K[D_0])$ against $K[D_0]$ for the decay of the indole–tetracyanoethylene charge-transfer complex in dichloromethane: (A) at 25·0°; (B) at 4·75°.

Although apparently linear, a linear extrapolation yields a negative intercept with the ordinate. Rappoport noted a similar though much smaller effect and suggested that a curvature may exist at low amine concentrations.

The kinetics of formation of the final product at 25° show that the rate is first order in σ-complex and in indole (Table 4). The slow rate of reaction did not permit of further determinations at lower temperatures. The high volatility of the solvent (b.p. 40·1°) makes determinations at elevated temperatures impracticable. That this reaction is the slow proton removal from the σ-complex by indole is confirmed by the observation that the reaction is accelerated by the addition of the more effective base N,N-diethylaniline. If this amine is added after the charge-transfer complex has decomposed to the σ-complex, only the absorption band at 456 mμ, corresponding to 3-tricyanovinylindole is observed. The absence of a band at 530 mμ due, to N,N-diethyl-4-tricyanovinylaniline, indicates the proton abstraction rôle of the excess base and incidentally demonstrates the lack of reversibility of the formation of the σ-complex in the preceding step.

All the observations made on the present system are consistent with the scheme:

Reaction scheme



which corresponds exactly with Rappoport's mechanism for the interaction of N-alkylanilines with tetracyanoethylene.[5,6]

EXPERIMENTAL

Materials. Indole, tetracyanoethylene and dichloromethane were purified as described previously.[1]

3-Tricyanovinylindole was prepared by the method of Sausen *et al.*,[3] m.p. 273–275°. The IR spectrum was identical with that obtained from week-old solutions of indole–tetracyanoethylene in dichloromethane which showed a visible absorption with a maximum at 456 mμ.

Analytical. Each solution was contained in a 1 cm cuvette, the same cuvette being used with light passed through in the same direction in all determinations. A Unicam SP600 spectrophotometer with a water jacketed cuvette-holder was used for the optical density measurements. The cell compartment was purged with N_2. Comparisons were made against a blank compartment to avoid problems of mis-matched cuvettes; an arithmetical correction was subsequently made for absorption by the solvent and cuvette. In the case of equilibrium determinations, solutions were measured as soon as possible after mixing. For solutions containing a high concentration of indole where fading was significant, the variation of optical density with time was measured and values obtained by extrapolation to the time of mixing were used.

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