860. *Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part V. The Reaction of Dimethylaniline with Tetracyanoethylene: π- and σ-Complexes in Electrophilic Aromatic and Nucleophilic Vinylic Substitutions.*[1]

By Zvi Rappoport.

The formation of *NN*-dimethyl-4-tricyanovinylaniline by the reaction of tetracyanoethylene and dimethylaniline in chloroform was studied kinetically by a spectrophotometric method and found to be a three-step reaction: (*a*) rapid formation of a 1 : 1 π-complex, (*b*) formation of a second, presumably σ-complex, and (*c*) formation of *NN*-dimethyl-4-tricyanovinylaniline and hydrogen cyanide. The equilibrium constant and the heat of formation of the π-complex were determined. Step (*b*) was of first order in both the π-complex and the dimethylaniline. " Exchange " reaction between free and π-complexed dimethylaniline during the formation of the σ-complex is suggested, and the process has a low activation energy (5·7 kcal. mole^{-1}). A zwitterionic structure is suggested for the σ-complex. Step (*c*) was of first order in both the σ-complex and the dimethylaniline and was very slow compared with step (*b*); it had an activation energy of 12·4 kcal. mole^{-1}. Steps (*b*) and (*c*) were both accelerated by increasing the dielectric constant of the medium. A detailed reaction mechanism is suggested.

Although π-complexes of aromatic compounds are well known, their role in electrophilic aromatic substitution is not yet clear. Some reactions have been formulated as occurring through π-complex formation in the rate-determining step,[2,3] and others through σ-complexes (" Wheland intermediates ")[4,5] leading to the final substitution products. Whether π-complexes are formed in independent side-reactions or whether they are essential intermediates is still a matter of controversy.[6] The same question arises in some cases of nucleophilic aromatic substitution, *e.g.*, the reaction of 1-chloro-2,4-dinitrobenzene with aniline, in which the occurrence of a π-complex has been proved, but where the kinetic results cannot distinguish between the possibilities that this complex is an essential intermediate and that it is a concurrently and competitively formed species.[7] In nucleophilic vinylic substitution of the " addition–elimination " type, it is usually accepted[8,9] that a carbanion intermediate with some stability is formed, but very little is known about its half-life which seems to be very short. π-Complexes in nucleophilic vinylic substitutions are as yet unknown.

Recently, reactions of tetracyanoethylene were studied comprehensively,[10] but not mechanistically. This compound is an unusually strong π-acid and is also attacked very rapidly by nucleophilic reagents in vinylic substitutions; it is, therefore, convenient for the study of the above-mentioned reactions. The objects of the present work are to show that, in the formation of *NN*-dimethyl-4-tricyanovinylaniline in the system

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[1] Part IV, *J.*, 1962, 396.

[2] Dewar, " Electronic Theory of Organic Chemistry," Oxford University Press, New York, 1949, p. 163.

[3] Olah, Kuhn, and Flood, *J. Amer. Chem. Soc.*, 1961, **83**, 4571; 1962, **84**, 1688.

[4] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

[5] Melander, " Isotope Effects on Reaction Rates," Roland Press Co., New York, 1960, p. 107.

[6] Streitwieser, " Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, 1961, p. 313.

[7] Ross and Kurtz, *J. Amer. Chem. Soc.*, 1954, **76**, 3000; Rheinlander, *J.*, 1923, 3099; Singh and Peacock, *J.*, 1935, 1410, 1411; *J. Phys. Chem.*, 1936, **40**, 669.

[8] Eliel, " Stereochemistry of Carbon Compounds," McGraw-Hill, New York, 1962, p. 369.

[9] Jones and Vernon, *Nature*, 1955, **176**, 791; Jones, Morris, Vernon, and White, *J.*, 1960, 2349.

[10] Cairns, Carboni, Coffman, Engelhardt, Heckert, Little, McGeer, McKusick, Middleton, Scribner, Theobald, and Winberg, *J. Amer. Chem. Soc.*, 1958, **80**, 2775, and following papers in the series " Cyanocarbon Chemistry."

tetracyanoethylene–dimethylaniline,[11] both π- and σ-complexes are essential to study their stability and behaviour.

The reaction is formulated as follows:

$$(NC)_2C{:}C(CN)_2 + p\text{-}Me_2N{\cdot}C_6H_5 \rightleftharpoons \pi\text{-Complex} \longrightarrow \sigma\text{-Complex} \longrightarrow p\text{-}Me_2N{\cdot}C_6H_4{\cdot}C(CN){:}C(CN)_2 + HCN$$

RESULTS

The reaction was studied spectrophotometrically in chloroform solution at 32·5°, 40°, and 48°. Initial attempts were made to follow the rate in dimethylformamide which was used before in synthesis.[11] However, the rates were very different for aged and for fresh stock solutions of tetracyanoethylene in this solvent. The initial bright yellow colour of this stock solution faded after one hour to 5% of its original intensity. The rate of disappearance was of first order in tetracyanoethylene, and an approximate rate coefficient of $1{\cdot}03 \times 10^{-3}$ sec.$^{-1}$ was calculated from the half-life of the reaction. In accordance with the behaviour of tetracyanoethylene described below, the yellow colour is attributed to a π-complex of the tetracyanoethylene with dimethylformamide, which disappears *via* tricyanovinylation of the latter. Similar behaviour was also found in ethanol solution, but these reactions were not investigated. A stock solution in chloroform was stable for several days and reproducible results ($\pm$1—2% in the rate coefficients) were obtained by using chloroform and dimethylaniline distilled immediately before use and conducting the reaction in Polythene vessels.

Mixing the reactants in chloroform at the reaction temperature or even at very low temperatures (—60°) gave instantaneously a blue colour ($\lambda_{\text{max.}}$ 675 mμ) which changed rapidly to pink and then to red. The blue colour was shown to be a 1 : 1 complex of the reactants by Keefer and Andrews's method [12] as applied recently also for the π-complexes of tetracyanoethylene with aromatic compounds.[13] The equilibrium constant for the 1 : 1 π-complex formed in the reaction, (TCE) + (DMA) $\rightleftharpoons$ (π-complex) is given by eqn. (1), where [TCE], [DMA], and [π] are the concentrations of tetracyanoethylene,

$$K = [\pi]/[\text{TCE-}\pi][\text{DMA}] \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

dimethylaniline, and the π-complex, respectively (where dimethylaniline is in such excess that its concentration remains practically constant). Now from the relation $D = \varepsilon[\pi]l$, where D is the optical density, ε the molar extinction coefficient of the π-complex, and l the cell length, eqn. (2) is obtained.

$$y \equiv [\text{TCE}]l/D = (1/K\varepsilon[\text{DMA}]) + 1/\varepsilon \quad . \ . \ . \ . \ . \quad (2)$$

At low dimethylaniline concentrations the optical density was measured directly, and at higher concentrations, where decomposition rates of the π-complex were appreciable, the D values were obtained by extrapolation to zero time of the optical density against time curves of the kinetic runs. Plotting y against 1/[DMA] gave straight lines (Fig. 1) with a nearly identical intercept ($1/\varepsilon$). From this, $\varepsilon = 3600$ at 48° for the complex, but this value is slightly temperature-dependent in the range studied ($\varepsilon = 3400$ at 32°). Values of the equilibrium constant, obtained from the reciprocal of the slopes, were 15·0, 11·1, and 8·5 l. mole^{-1} at 32·5°, 40°, and 48°, respectively (Table 1). The value for $-\Delta H°$, calculated from the equilibrium constants, gave 6·86 kcal. mole^{-1} as the heat of formation of the π-complex. The validity of this treatment is shown by the fact that when the base concentration was increased, in the range in which 80—90% of the tetracyanoethylene

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[11] (*a*) McKusick, Heckert, Cairns, Coffman, and Mower, *J. Amer. Chem. Soc.*, 1958, **80**, 2806; (*b*) McKusick and Melby, *Org. Synth.*, **39**, 68.

[12] Keefer and Andrews, *J. Amer. Chem. Soc.*, 1950, **72**, 4677; Andrews and Keefer, *J. Amer. Chem. Soc.*, 1951, **73**, 462.

[13] Merrifield and Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.

TABLE 1.

Equilibrium constants at 48° for the 1 : 1 π-complex of tetracyanoethylene (TCE) and dimethylaniline (DMA) from the absorption data at 675 mμ.

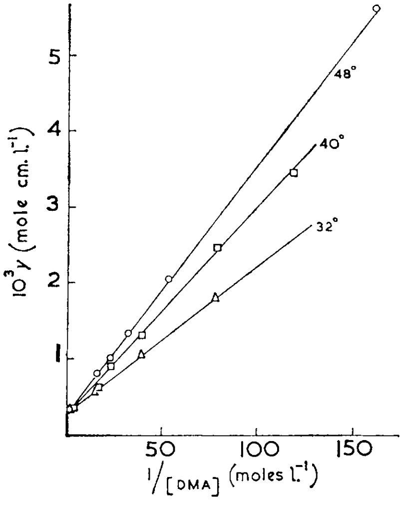
10^3[DMA] (moles l.$^{-1}$)	6·15	18·45	30·75	43·05	61·5	615
10^3D	35	96	145	200	250	615 [a]
$10^3[y]$ [b] (moles cm. l.$^{-1}$)	5·71	2·08	1·35	1·00	0·8	0·33
K (l. mole^{-1}) [c]	8·30	8·35	8·44	8·94	8·65	8·60

Average $K = 8{\cdot}54 \pm 0{\cdot}18$ l. mole^{-1}.

[a] Extrapolated from a kinetic run. [b] [TCE] = 2×10^{-4} mole l.$^{-1}$; $l = 1$ cm. [c] Calculated from eqn. (1) in the rearranged form, $K = 1/[\text{DMA}](\varepsilon y - 1)$; ε taken as 3600.

was calculated to be converted into the π-complex, the optical density was little affected and ε, calculated for 90% conversion, was the same as that calculated from the slopes.

The Disappearance of the π-complex (π-Complex $\longrightarrow$ σ-Complex Reaction).—This was followed by observing the disappearance of the absorption at 675 mμ for a 500—2000-fold excess of dimethylaniline, most of the initially introduced tetracyanoethylene (75—95%) was converted into the π-complex. The slight increase in the optical densities at 32·5°, with increasing dimethylaniline concentration, is shown in Table 2. Under these conditions the reaction was of first order in both the dimethylaniline and the π-complex (Table 2). The concentration of the latter at the beginning of the reaction was obtained from eqn. (3) which was obtained from rearrangement of eqn. (1). The reaction was



Dependence of the reciprocal of the dimethylaniline concentration on y (eqn. 2) for the 1 : 1 π-complex.

$$[\pi]_0 = K[\text{DMA}][\text{TCE}]/(1 + K[\text{DMA}]) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

usually followed up to 90—95% completion and the rate coefficients of each run remained constant to at least 75% reaction, showing the practically complete decomposition of the π-complex. Values of $\tau_{\frac{1}{2}}$ and $\tau_{\frac{3}{4}}$ for the disappearance of the π-complex at 32·5° (Table 2) show this behaviour. A sample run is given in Table 3.

Irreversibility of the Reaction.—Berson and Mueller observed formation of the blue colour in non-polar solvents and noted that it disappears with time but reappears on cooling.[14] We found that the decomposition of the π-complex is slowed by lowering the temperature, but the blue colour cannot be regenerated after a reaction in the presence of high concentrations of dimethylaniline even at temperatures down to the freezing point

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[14] Berson and Mueller, *J. Amer. Chem. Soc.*, 1961, **83**, 4940.

TABLE 2.

First-order (k_1) and second-order ($k_2 = k_1/[\mathrm{DMA}]$) rate coefficients for the disappearance of the π-complex (π) of dimethylaniline (DMA) and tetracyanoethylene (TCE) in chloroform at various temperatures.

At 32·5°.

10[DMA] (moles l.$^{-1}$)	1·57	3·14	6·28	9·42	3·14	3·14	3·14	3·14
10^4[TCE] (moles l.$^{-1}$)	3·24	3·24	3·24	3·24	0·81	1·62	4·86	6·48
$10^4[\pi]$ (moles l.$^{-1}$) [a]	2·27	2·67	2·93	3·03	0·66	1·34	4·01	5·34
10^3k_1 (sec.$^{-1}$)	0·62	1·34	2·33	3·47	1·21	1·24	1·36	1·33
10^3k_2 (l. mole^{-1} sec.$^{-1}$)	4·0	4·2	3·7	3·6	3·9	3·9	4·3	4·2
$10^3 \log (I/I_0)$	713	915	1030	1050	242	505	1520	1940
$\tau_{\frac{1}{2}}$ (sec.)	1170	568	315	210	600	557	513	521
$\tau_{\frac{3}{4}}$ (sec.)	2380	1170	638	417	1194	1100	1020	1040

Average $10^3k_2 = 4·0 \pm 0·2$ l. mole^{-1} sec.$^{-1}$.

	At 40°.			At 48°.				
10[DMA] (moles l.$^{-1}$)	3·10	6·20	9·30	3·07	6·14	9·21	3·07	3·56 [b]
10^4[TCE] (moles l.$^{-1}$)	2·67	2·75	2·75	2·75	3·32	2·75	2·58	6·35
$10^4[\pi]$ (moles l.$^{-1}$) [a]	2·07	2·40	2·51	1·98	2·63	2·44	1·87	4·81
10^3k_1 (sec.$^{-1}$)	1·54	3·43	4·96	2·10	3·66	5·93	1·96	2·27
10^3k_2 (l. mole^{-1} sec.$^{-1}$)	5·0	5·5	5·2	6·8	6·0	6·5	6·4	6·4.

Average $10^3k_2 = 5·2 \pm 0·2$ l. mole^{-1} sec.$^{-1}$. Average $10^3k_2 = 6·4 \pm 0·2$ l. mole^{-1} sec.$^{-1}$.

[a] From eqn. (3). [b] At 47·5°.

TABLE 3.

Sample run for the reaction, π-complex ⟶ σ-complex, in chloroform at 32·5° and 675 mμ.

([TCE] = $6·48 \times 10^{-4}$ mole l.$^{-1}$; [DMA] = 0·314 mole l.$^{-1}$; [π-complex] = $5·35 \times 10^{-4}$ mole l.$^{-1}$).

Time (sec.)	0	38	80	123	170	220	267	319	378	445	521	1040
$10^3 \log (I/I_0)$	1940 [a]	1843	1745	1649	1551	1454	1358	1260	1163	1066	970	458
Reaction (%)	0	5	10	15	20	25	30	35	40	45	50	75
10^3k_1 (sec.$^{-1}$)	—	1·34	1·32	1·34	1·31	1·30	1·34	1·35	1·34	1·34	1·34	1·33

Average $k_1 = 1·33 \times 10^{-3}$ sec.$^{-1}$; $k_2 = k_1/[\mathrm{DMA}] = 4·2 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$.

[a] Extrapolated value.

of chloroform. Thus, pink or colourless solutions containing only 1—2% of *NN*-dimethyl-4-tricyanovinylaniline and σ-complex, or σ-complex alone, did not give a blue colour on cooling, so that under these conditions the reaction is essentially irreversible. However, when the initial dimethylaniline concentration was the same as the initial tetracyanoethylene concentration (5×10^{-3} mole l.$^{-1}$) and the formation of the σ-complex was not complete even if the reaction mixture was colourless, cooling the solution to 0°, after the decomposition of most of the π-complex, restored the blue colour, but this re-formed colour disappeared much more rapidly than the original one (2 min. compared with 6 hr. at the concentration studied) when the solution was brought to room temperature. We believe that the π-complex is newly formed from unchanged reactants as a result of the equilibrium position at the low temperature (Fig. 1), and not as a result of the reversibility of the reaction.

Formation of the Final Product from the σ-Complex.—This reaction (followed at 515 mμ) was very slow compared with the decomposition of the π-complex, and measurements were usually begun only after 90—95% and finished after 93—97% of the decomposition. Calculations of the rate coefficients for the product formation were based on the concentration of σ-complex calculated from eqn. (6), obtained in the following manner:

At time t the equilibrium constant is given by eqn. (4):

$$K = [\pi]_t/([\mathrm{TCE}] - [\pi]_t - [\sigma]_t)[\mathrm{DMA}] \quad . \; . \; . \; . \; . \quad (4)$$

Dividing eqn. (4) by eqn. (3) and rearranging we obtain

$$[\sigma]_t = [\text{TCE}]_0 - ([\pi]_t/[\pi]_0)[\text{TCE}]_0 \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$\text{Defining } f \text{ by } f = [\pi]_t/[\pi]_0 \text{ we obtain } [\sigma]_t = (1 - f)[\text{TCE}]_0 \quad . \; . \quad (6)$$

where the values with the index zero and t refer to concentrations at the beginning of the reaction and at time t, respectively. The values of f (the fraction of π-complex remaining at time t) in the calculation of the σ-complex concentration were usually lower than 0·1, and the average of the f's at the beginning and the end of these measurements was used. An example of this procedure is given in Table 4, which also shows that the formation of the final product is very slow compared with the $\pi \longrightarrow \sigma$ reaction, so that complications did not arise in studying the disappearance of the π-complex.

TABLE 4.

Sample run for the reaction, σ-complex $\longrightarrow$ *NN*-dimethyl-4-tricyanovinylaniline, in chloroform at 32·5° and 515 mμ.

Time (sec.) ...	1680	1710	1740	1770	1800	1830	1860	1895	1920	1980	2040	2100	2160
$10^3 \log (I/I)_0$	1450	1483	1515	1555	1590	1622	1665	1705	1731	1795	1880	1940	1992

$$s = \Delta \log (I/I_0)/\Delta t = (1940 - 1590) \times 10^{-3}/300 = 1{\cdot}17 \times 10^{-3}.$$

Linearity at λ = 515 mμ was observed when $10^3 \log (I/I_0)$ (at 675 mμ) was 135 (f = 135/1940 = 0·07) and measurements were finished at $10^3 \log (I/I_0)$ = 78; (f = 78/1940 = 0·04). Average f = 0·055.

$$[\sigma] = (1 - f)[\text{TCE}]_0 = 0{\cdot}945 \times 6{\cdot}48 \times 10^{-4} = 6{\cdot}15 \times 10^{-4} \text{ mole l.}^{-1}.$$
$$k_1 = s/\varepsilon[\sigma] = 1{\cdot}17 \times 10^{-3}/484 \times 10^2 \times 5{\cdot}96 \times 10^{-4} = 4{\cdot}05 \times 10^{-5} \text{ sec.}^{-1}.$$
$$k_2 = k_1/[\text{DMA}] = 1{\cdot}29 \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}.$$

The rate coefficients were calculated by using the straight D against time lines obtained for 2—4% formation of *NN*-dimethyl-4-tricyanovinylaniline, by using the relation $[\text{Product}]\varepsilon_{\text{product}} = D$, and the rate equation $\Delta\text{Product}/\Delta t = k_2[\sigma][\text{DMA}]$, hence $k_2 = \Delta D/\Delta t)/[\sigma]\varepsilon[\text{DMA}]$. The constancy of the k_2 values in Table 5 shows that the reaction is of first-order in both the σ-complex and the dimethylaniline. Formation of the final product is proportional to the concentration of the σ-complex even in the first stages of the reaction. This can be seen from Table 6 which gives the percentage of the σ-complex (as f's) at various times, together with the appropriate rate coefficients for the formation of *NN*-dimethyl-4-tricyanovinylaniline, determined at the same times. In some preliminary experiments, for reasons unknown, chloroform aged in glass vessels gave

TABLE 5.

First-order (k_1) and second-order ($k_2 = k_1/[\text{DMA}]$) rate coefficients for the formation of *NN*-dimethyl-4-tricyanovinylaniline from the σ-complex (σ) of dimethylaniline (DMA) and tetracyanoethylene (TCE) in chloroform at various temperatures.

At 32·5°.

10[DMA] (moles l.$^{-1}$)	1·57	3·14	6·28	9·42	3·14	3·14	3·14	3·14
10^4[TCE] (moles l.$^{-1}$)	3·24	3·24	3·24	3·24	0·81	1·62	4·86	6·48
$10^4[\sigma]$ (moles l.$^{-1}$)	2·79	2·98	2·98	3·04	0·73	1·53	4·58	6·15
$10^5 k_1$ (sec.$^{-1}$)	1·73	3·84	7·46	10·8	3·32	3·72	3·83	3·92
$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$)	1·10	1·22	1·19	1·14	1·06	1·18	1·22	1·25

Average $10^4 k_2$ = 1·17 ± 0·05 l. mole^{-1} sec.$^{-1}$.

	At 40°.				At 48°.			
10[DMA] (moles l.$^{-1}$) ...	3·10	6·20	9·30	3·10	3·07	6·14	9·21	3·07
10^4[TCE] (moles l.$^{-1}$) ...	2·75	2·75	2·75	11·0	2·63	3·32	2·75	2·58
$10^4[\sigma]$ (moles l.$^{-1}$)	2·64	2·64	2·64	10·7	2·50	3·05	2·59	2·42
$10^5 k_1$ (sec.$^{-1}$)	5·81	11·65	16·7	5·78	9·95	19·1	29·2	9·00
$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$)	1·88	1·86	1·80	1·87	3·24	3·12	3·18	2·90

Average $10^4 k_2$ = 1·85 ± 0·03 l. mole^{-1} sec.$^{-1}$.

Average $10^4 k_2$ = 3·11 ± 0·11 l. mole^{-1} sec.$^{-1}$.

equilibrium concentrations of the π-complex after 50—80% decomposition. Even in these cases the formation of the final product was still proportional to the equilibrium value of the σ-complex.

TABLE 6.

Second-order rate coefficients (k_2) for the formation of *NN*-dimethyl-4-tricyanovinylaniline from the σ-complex, determined during formation of the latter by the decomposition of the π-complex at 32·5° in chloroform.[a, b]

Time (sec.)	0	33	69	110	162	216	270	330	396
$10^3 \log (I/I_0)$[c].........	227	228·3	230·7	234	239·3	245·5	256	269	284
f	0	0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40
$10^4[\sigma]$ (moles l.$^{-1}$) ...	0	0·155	0·310	0·465	0·620	0·775	0·930	1·085	1·240
$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$)	—	1·35	1·35	1·27	1·24	1·22	1·35	1·25	1·22

Time (sec.)	462	546	630	727	843	966	1166	1300	1572
$10^3 \log (I/I_0)$[c].........	304	329·5	358	394	440·5	496	562	654·5	804
f	0·45	0·50	0·55	0·60	0·65	0·70	0·75	0·80	0·85
$10^4[\sigma]$ (moles l.$^{-1}$) ...	1·395	1·550	1·705	1·860	2·015	2·170	2·325	2·480	2·635
$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$)	1·42	1·27	1·31	1·31	1·31	1·35	1·24	1·34	1·35

[a] [Tetracyanoethylene] = $3·1 \times 10^{-4}$ mole l.$^{-1}$; [Dimethylaniline] = 0·314 mole l.$^{-1}$. [b] The Table covers $0·86 \times 10^{-2}$—3·86% transformation of the tetracyanoethylene into the final product. [c] These values are due only to the absorption of the final product. They were obtained by using the optical-density values determined experimentally at 515 mμ and corrected for the decrease of absorption at this wavelength owing to the π-complex decomposition. In the correction, the value 0·29 for $\varepsilon_{515}/\varepsilon_{675}$ of the π-complex and the values of the optical densities at 675 mμ at the same time, determined by independent runs, are used.

Absence of Free Tetracyanoethylene after the Decomposition of the π-Complex.—After the decomposition of all the π-complex, and before appreciable formation of the final product, an excess of anthracene was added to the solution. The green colour of the anthracene–tetracyanoethylene complex is a sensitive indication of free tetracyanoethylene,[15] but its absence showed the quantitative formation of the σ-complex.

Effect of Solvents on the Reaction Rate.—Increasing the dielectric constant of the medium (for chloroform, 5·05 at 20°) [16] by the addition of ethylene dichloride (dielectric constant = 10·5 at 20°)[16] increased the rates of both reactions, π-complex $\longrightarrow$ σ-complex and σ-complex $\longrightarrow$ final product. The relative effects on the two reactions were similar, the first being slightly more sensitive to solvent effects (Table 7). On decrease of the dielectric constant by addition of carbon tetrachloride (dielectric constant = 2·24 at 20°) [16] the rate coefficients decreased, again slightly more in the reaction π-complex $\longrightarrow$ σ-complex

TABLE 7.

Second-order rate coefficients (k_2) for the formation of the σ-complex and for the formation of *NN*-dimethyl-4-tricyanovinylaniline (TCVDMA) in chloroform–ethylene dichloride mixtures [a] at 32·5° and 48°.

Ethylene dichloride (% v/v)	0	4	8	16	28	40	60	80
	π-Complex $\longrightarrow$ σ-complex reaction.							
$10^3 k_2$ (l. mole^{-1} sec.$^{-1}$) at 32·5° [b]	4·0	6·2	6·8	7·4	10·2	12·7	17·8	21
$10^3 k_2$ (l. mole^{-1} sec.$^{-1}$) at 48° [c]	6·4	8·3	8·6	11·1	13·2	14·6	20·7	26·6
	σ-Complex $\longrightarrow$ (TCVDMA) reaction.							
$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$) at 32·5° [d]	1·15	1·37	1·62	1·67	1·85	2·02	2·43	2·72
$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$) at 48° [e]	3·22	3·86	4·34	5·45	5·83	5·80	7·12	7·67

[a] The solution contains 4% (v/v) of dimethylaniline. [b] [TCE] = $2·74 \times 10^{-4}$ mole l.$^{-1}$; [DMA] = 0·314 mole l.$^{-1}$; initial [π-complex] = $2·48 \times 10^{-4}$ mole l.$^{-1}$. [c] [TCE] = $2·63 \times 10^{-4}$ mole l.$^{-1}$; [DMA] = 0·307 mole l.$^{-1}$; initial [π-complex] = $2·38 \times 10^{-4}$ mole l.$^{-1}$. [d] [σ-complex] = 2·52—$2·65 \times 10^{-4}$ mole l.$^{-1}$. [e] [σ-complex] = 2·34—$2·72 \times 10^{-4}$ mole l.$^{-1}$.

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[15] Middleton, Heckert, Little, and Krespan, *J. Amer. Chem. Soc.*, 1958, **80**, 2783.

[16] " Handbook of Chemistry and Physics," 37th edn., Chemical Rubber Publishing Co., 1955—1956, p. 2323.

(Table 8). The same effect was found also on addition of benzene (dielectric constant = 3·1 at 20°) [16] (Table 9).

TABLE 8.

Second-order rate coefficients (k_2) for the reactions π-complex ⟶ σ-complex and σ-complex ⟶ *NN*-dimethyl-4-tricyanovinylaniline (TCVDMA) in chloroform–carbon tetrachloride mixtures [a] at 32·5°.[b]

CCl_4 (% v/v)	0	4	8	12	28	40	60	80
	π-Complex ⟶ σ-complex reaction.[c]							
10^3k_2 (l. mole^{-1} sec.$^{-1}$)	4·27	3·80	3·12	2·43	1·40	1·02	0·62	0·13
	σ-Complex ⟶ (TCVDMA) reaction.[d]							
10^4k_2 (l. mole^{-1} sec.$^{-1}$)	1·27	1·10	1·07	0·79	0·53	0·32	0·26	0·05

[a] The solution contains 4% (v/v) of dimethylaniline. [b] [Dimethylaniline] = 0·314 mole l.$^{-1}$; [tetracyanoethylene] = 2·74 × 10^{-4} mole l.$^{-1}$. [c] [π-complex] = 2·26 × 10^{-4} mole l.$^{-1}$. [d] [σ-complex] = 2·44—2·52 × 10^{-4} mole l.$^{-1}$.

TABLE 9.

Second-order rate coefficients (k_2) for the reactions, π-complex ⟶ σ-complex and σ-complex ⟶ *NN*-dimethyl-4-tricyanovinylaniline (TCVDMA) in chloroform–benzene mixtures [a] at 32·5°.[b]

Benzene (% v/v)	0	4	8	12
	π-Complex ⟶ σ-complex reaction.[c]			
10^3k_2 (l. mole^{-1} sec.$^{-1}$)	4·26	4·01	3·76	3·00 [e]
	σ-Complex ⟶ (TCVDMA) reaction.[d]			
10^4k_2 (l. mole^{-1} sec.$^{-1}$)	1·25	1·14	1·12	0·92 [e]

[a] The solution contains 4% (v/v) of dimethylaniline. [b] [Dimethylaniline] = 0·314 mole l.$^{-1}$; [tetracyanoethylene] = 3·08—3·24 × 10^{-4} mole l.$^{-1}$. [c] [π-complex] = 2·54—2·67 × 10^{-4} mole l.$^{-1}$; [d] [σ-complex] = 0·92—1·25 × 10^{-4} mole l.$^{-1}$. [e] At 33°.

It should be noted that the extrapolated optical densities of the π-complex decreased steadily with increasing content of ethylene dichloride of the medium. This could be attributed to a shift in the equilibrium, affecting the π-complex concentration according to eqn. (3). However, as the optical density increased only slightly with increasing dimethylaniline concentration (with the same tetracyanoethylene concentration) in pure ethylene dichloride, formation of π-complex is probably nearly complete. The explanation may therefore be based on the fact that increasing the dielectric constant and the polarity of the medium is known to shift the $\lambda_{max.}$ of charge-transfer complexes to higher wavelengths. This is found for example with alkylpyridinium iodides and serves as the base of Kosower's *Z* values.[17] Thus, the absorption measurements at 675 mμ are conducted at a position which is increasingly shifted away from the maximum of the π-complex.

Complex Formation in Various Solvents.—In some qualitative experiments the formation of the blue colour on mixing of the reactants in various solvents was followed visually. In solvents with low dielectric constant, such as aromatic hydrocarbons, the initial colour was in some cases fainter than in chloroform, probably owing to competition with the solvent for the tetracyanoethylene, but the decomposition was very slow. Slow decomposition was found also in pure carbon tetrachloride, in light petroleum, and in cyclohexane. In these solvents the π-complex was stable for several days at 10^{-2}—10^{-3} mole l.$^{-1}$ concentrations of dimethylaniline. In solvents of higher dielectric constant such as acetonitrile, β-ethoxypropionitrile, formic acid, acetic acid, and ethanol, the blue colour disappeared very rapidly at room temperature but slowly at lower temperatures.

Reaction in the Presence of Amines.—No blue colour was formed in the presence of triethylamine, even if the triethylamine concentrations were much lower than those of the dimethylaniline. The yellow π-complex between triethylamine and tetracyanoethylene

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[17] Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253, 3261.

seems to be stable and unreactive towards dimethylaniline. With identical concentrations of triethylamine and dimethylaniline, no blue colour and no *NN*-dimethyl-4-tricyanovinylaniline were formed even after 24 hr. at 30°. The reaction with triethylamine showed the irreversibility of the $\pi \longrightarrow \sigma$ reaction: when a reaction mixture containing unchanged π-complex was treated with triethylamine, the blue colour of the π-complex disappeared rapidly and only the π-complex of triethylamine with tetracyanoethylene was found on the basis of spectrophotometric analysis. If, on the other hand, the triethylamine was added after the decomposition of the π-complex to the solution of the σ-complex no absorption corresponding to the triethylamine–tetracyanoethylene π-complex was found, and the formation of *NN*-dimethyl-4-tricyanovinylaniline was very rapid. Addition of triethylamine at intermediate stages of the $\pi \longrightarrow \sigma$ reaction gave mixtures of the final product and triethylamine–tetracyanoethylene π-complex, corresponding to the degree of completion of the $\pi \longrightarrow \sigma$ reaction at the time of the addition of triethylamine. The general base catalysis in the reaction, σ-complex $\longrightarrow$ final-product, is also shown by the greatly accelerated formation of the final product when a dilute solution of tri-n-butylamine or di-n-butylamine in chloroform is added to a solution of the σ-complex.

Attempts to Isolate the π- and σ-Complexes.—Attempts to isolate the π-complex by freezing reaction mixtures containing it were unsuccessful, although this complex is relatively stable at low temperatures. Decomposition to the σ-complex is one factor preventing the isolation of the π-complex; on filtration, the blue colour on the filter paper is immediately changed to the colourless σ-complex and then to the red final product. The same freezing procedure applied to the solution of the σ-complex did not give crystalline σ-complex.

The polar nature of the σ-complex can be demonstrated as follows. Extraction of a chloroform solution of tetracyanoethylene with water gave a yellow colour. Addition of an aqueous dimethylaniline solution obtained by water-extraction of a chloroform dimethylaniline solution (in order to retain identical reaction conditions) to the yellow solution gave no reaction even after 24 hr. However, water-extraction of a reaction mixture containing the σ-complex gave initially a colourless solution which rapidly gave the red final product in the water phase. These results cannot be due to a reaction of the two reagents in the water, and are explained by the solubility of the σ-complex in water.

Spectral Properties of the σ-Complex.—The fact that the decomposition of both the π- and the σ-complex is of first-order in dimethylaniline makes it possible to obtain relatively stable solutions of the two complexes by using low and equal concentrations of the two reactants. When the concentrations were approximately 5×10^{-3} mole $l.^{-1}$, the disappearance of the blue colour was complete after 6 hr. at 30° and a further 18 hr. at 0°, and only 0·1% of the final product was formed. The spectrum of this solution was determined after dilution with chloroform or carbon tetrachloride and was different from that of the two reactants, either alone or mixed. A new high absorption maximum at 279 mμ was attributed to the σ-complex (ε, calculated on the basis of complete transformation of the reactants to the σ-complex, is 34·300). Lower peaks (by ~20%) were found at the same wavelength in other cases and attributed to incomplete formation or slight decomposition of the σ-complex. Although no kinetic measurements on the formation of this complex at wavelength maximum were made because of experimental difficulties, it was found that during the decomposition of the π-complex the absorption of the solution decreased at 500—700 mμ, but increased simultaneously at wavelengths below and up to 350 mμ, in accordance with the formation of the σ-complex absorbing in this range. The absorption at 279 mμ of a solution of the σ-complex decreased slowly with time during the formation of the final product.

Reactions of Tetracyanoethylene with Dienes.—The first-order dependence of the reaction π-complex $\longrightarrow$ σ-complex on the dimethylaniline concentration may be due to the existence of basic nitrogen in the molecule or to the π-base character, due to the π-electrons, of the aromatic nucleus. To differentiate between the two possibilities, the disappearance of other π-complexes of tetracyanoethylene was studied with a second component having no basic heteroatom. The disappearance of the yellow colour of isoprene–tetracyanoethylene and of the green colour of 9-phenylanthracene–tetracyanoethylene π-complexes was too rapid to be followed kinetically in their reactions leading to Diels–Alder products. Qualitative observations showed that in these two reactions, even in cases where most of the tetracyanoethylene was converted into the π-complex, more concentrated diene solutions lost their colour more rapidly than the dilute ones, showing a dependency of the overall reaction order on the concentration of the diene in addition to the dependence on the concentration of the π-complex. An example is given in the Experimental section.

Activation Parameters.—Table 10 summarises the activation parameters for the two reactions in chloroform and chloroform–ethylene dichloride mixtures as obtained from the rate coefficients given in Tables 2, 5, and 7. The reaction π-complex $\longrightarrow$ σ-complex has an unusually low activation energy (E_a) and high negative entropy of activation ($-\Delta S^\ddagger$) in all solvent mixtures, while the process, σ-complex $\longrightarrow$ final product, has a usual energy of activation and again high negative values for the entropy of activation. It is seen that on increasing the polarity of the medium the activation energy remains practically constant for the reaction σ-complex $\longrightarrow$ final product, and slightly decreases in the reaction π-complex $\longrightarrow$ σ-complex. In the latter case the values of E_a are less accurate owing to the small differences in the rate coefficients. For similar reasons the differences in the entropy of activation are of such an order of magnitude that they may be due to the experimental inaccuracy.

TABLE 10.

Activation parameters for the π-complex $\longrightarrow$ σ-complex reaction and the σ-complex $\longrightarrow$ final-product reaction in chloroform–ethylene dichloride mixtures.

Ethylene dichloride (% (v/v)	0	4	8	12	28	40	60	80
π-Complex $\longrightarrow$ σ-complex reaction.								
E_a (kcal. mole^{-1})	5·7	3·6	2·9	5·0	4·6	4·9	2·0	2·9
$-\Delta S^\ddagger$ (e.u.)	52·3	58·3	60·5	53·4	54·2	53·1	61·5	58·2
σ-Complex $\longrightarrow$ final-product reaction.								
E_a (kcal. mole^{-1})	12·4	12·6	12·1	14·2	13·6	10·5	12·7	12·6
$-\Delta S^\ddagger$ (e.u.)	37·3	36·4	37·7	30·8	32·3	42·0	34·8	35·0

DISCUSSION

There is little doubt that the " blue complex " which is formed in the first step is a 1 : 1 π-complex derived from dimethylaniline and tetracyanoethylene. This assumption is in accord with its rapid formation, characteristic of other π-complexes,[18,19] and with the well-known ability of tetracyanoethylene to form π-complexes with aromatic hydrocarbons.[13,20] The equilibrium constants of many of these have been determined;[13] several were even obtained in crystalline form[21] and others are used in qualitative and quantitative analysis.[22] The position of $\lambda_{\text{max.}}$ in our π-complex is in accordance with the increase in $\lambda_{\text{max.}}$ with increasing electron-donating ability of the aromatic hydrocarbon,[13,20] and the equilibrium constants and the molar extinction coefficients fit well the values for other tetracyanoethylene–arene complexes. In the formulation (I) the arrow serves only as a symbol for the interaction of the whole molecular orbital of the planar dimethylaniline (including the aromatic sextet and the lone pair of the nitrogen atom) with the molecular orbital of the planar tetracyanoethylene. This is consistent with formulations

[18] Hammick and Yule, *J.*, 1940, 1593.

[19] Ross, Bassin, Finkelstein, and Leach, *J. Amer. Chem. Soc.*, 1954, **76**, 69.

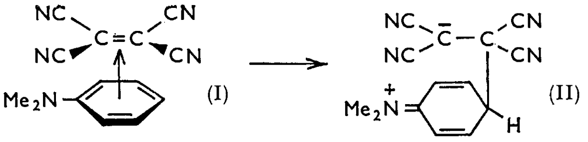
[20] Dewar and Rogers, *J. Amer. Chem. Soc.*, 1962, **84**, 395.

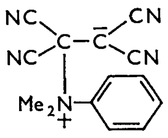
[21] Hafner and Moritz, *Angew. Chem.*, 1960, **72**, 918.

[22] Peurifov, Slaymaker, and Nager, *Analyt. Chem.*, 1959, **31**, 1740; Schenk and Ozolins, *Analyt. Chem.*, 1961, **33**, 1562.

for other similar tetracyanoethylene complexes, with the assumption of a " sandwich " structure in which the component molecules lie in parallel planes. Maximum overlap is obtained when the tetracyanoethylene is directed along the nitrogen and the *para*-position of the aromatic system.

The fast disappearance of the blue colour and the slow formation of the end-product (Tables 2 and 5) can be explained by assuming the formation of a second, relatively stable intermediate, the decomposition of which is rate-determining for the overall substitution. The low activation energy (Table 10) of the transition between the two intermediates





(III)

enables us to use " Hammond's postulate " [23] that there is little reorganization in the transition from the first " directed " (I) to the second (II) intermediate. This requires only the formation of a bond between two adjacent carbon atoms, in nearly bonding distance, with the transition state involving only slight distortion of the π-electron system. (II) is therefore a " Wheland intermediate " or σ-complex [24] of an electrophilic aromatic substitution. Moreover, it is also the " addition–elimination " intermediate of a vinylic nucleophilic substitution on the tetracyanoethylene. Recent work on the formation of cyclobutane derivatives from tetracyanoethylene and electron-rich double bonds gives some evidence for a similar zwitterionic intermediate.[25]

Isomeric structures such as (III) cannot be excluded *a priori* (aniline undergoes *N*-tricyanovinylation) but formation of the final product then requires nucleophilic attack of the carbanionic portion in (III) on the *para*-position of the anilinium ion, which is a very improbable process.*

As dimethylaniline was used in considerable excess and the equilibrium constant for the π-complex is high, it could be expected that the $\pi \longrightarrow \sigma$ reaction should depend only on the concentration of the π-complex. Lacking a better criterion to understand whether the dependence on the dimethylaniline concentration is a result of the basic character of the dimethylamino-nitrogen or of its π-base character, we compared our reaction with the Diels–Alder reaction. In the reaction of tetracyanoethylene with isoprene or 9-phenylanthracene the disappearance of the π-complexes was dependent on the concentration of the excess of diene, which is only a π-base in this case. By analogy, we assume that the dependence on the dimethylaniline concentration in our case is connected with its π-base properties.

This kinetic dependency may be explained by a bimolecular "exchange" reaction in which the dimethylaniline portion of the π-complex is exchanged for a second dimethylaniline molecule, leading to an activated π-complex. Only the latter has a sufficient

* It has been pointed out by one of the referees that the net composition of (II) could also be (*a*) TCE + DMA − H; (*b*) TCE + DMA − CN; (*c*) TCE + DMA − HCN; (*d*) TCE + 2DMA. However, (*a*), (*b*), and (*c*) each demand an additional intermediate, according to the current views on electrophilic aromatic and nucleophilic vinylic substitutions; otherwise (*a*) is obtained by a one-step electrophilic aromatic substitution, (*b*) by a one-step vinylic nucleophilic substitution, and (*c*) by both taking place simultaneously. With no evidence for additional intermediates, and considering that the activation energy is too low for a simple bond-breaking reaction, we prefer formulation (II) which can account for the reaction sequence and is formed in the simplest route. Reaction (*d*) can be excluded by the general base catalysis (including dimethylaniline) required for the proton abstraction in the transition from (II) to the end-product, as in (*d*) the proton could be removed by the second dimethylaniline molecule incorporated in (*d*).

[23] Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[24] Brown and Brady, *J. Amer. Chem. Soc.*, 1952, **74**, 3570.

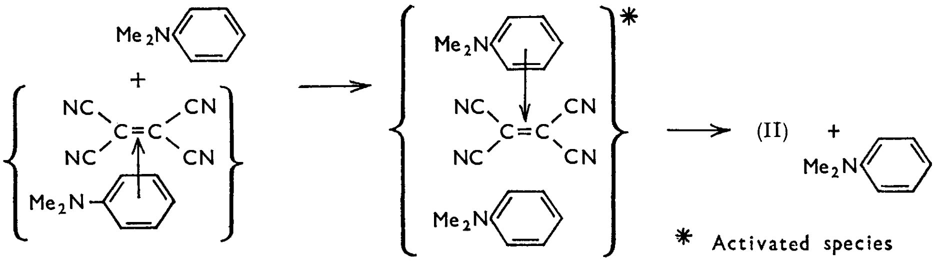
[25] Williams, Wiley, and McKusick, *J. Amer. Chem. Soc.*, 1962, **84**, 2210.

energy content for the formation of the σ-complex. On using a steady-state treatment for the scheme,

$$(\pi) + (\mathrm{DMA}) \underset{k_{-E}}{\overset{k_E}{\rightleftharpoons}} (\pi)^* \xrightarrow{k_D} (\sigma)$$

where k_E, k_{-E}, and k_D are the rate coefficients for the activation, deactivation, and σ-complex-formation processes, respectively, the concentration of the activated π-complex $(\pi)^*$ is given by:

$$(\pi)^* = k_E\,(\pi)[\mathrm{DMA}]/(k_{-E} + k_D) \quad \ldots\ldots\ldots \quad (7)$$



The expected first-order dependence on the " activated " π-complex in the formation of the σ-complex (eqn. 8) (the reverse reaction being negligible) leads to a second-order rate equation (9), as found experimentally,

$$\mathrm{d}\sigma/\mathrm{d}t = k_D\,(\pi)^* \quad \ldots\ldots\ldots \quad (8)$$

$$\mathrm{d}\sigma/\mathrm{d}t = k'\,[\pi][\mathrm{DMA} \quad \ldots\ldots\ldots \quad (9)$$

where $k' = k_D k_E/(k_{-E} + k_D)$.

Similar unusual kinetics were observed in electrophilic aromatic isomerization of *o*- and *p*-xylene to *m*-xylene by aluminium bromide–hydrogen bromide, and were explained by " exchange " of proton between σ-complex (of proton with the solvent) and xylene molecule.[26] The high negative entropy of activation in the present case is a result of the formation of charges in the π-complex ⟶ σ-complex reaction. Previous workers attributed the exclusive *para*-substitution to steric strain in the final product.[11a] We believe that only the π-complex directed as in (I) is formed, and explain substitution *via* (II) in the *para*-position.

The spectrum of (II) is consistent with a σ-complex structure. The high extinction coefficient (34,300) and its position (279 mμ) can be related to the following facts. Quinonoid intermediates of electrophilic aromatic substitution of the structures (IV)–(VI) [27–29] have $\lambda_{\max.}$ near 280 mμ and ε within the order of 10^4. In our formulation for (II) no conjugation exists between the two parts of the molecule which are in different planes, and we can assume additivity in the respective absorption. Taking the quinonoid portion as having similar $\lambda_{\max.}$ and absorption intensity to those of (IV)–(VI), we may postulate a molar extinction coefficient of 2×10^4 for the tetracyanoethylene carbanionoid portion of (II) at 279 mμ, which is comparable with the extinction coefficients (2—3×10^4) for carbanions from 1,1,2,3,3-pentacyanopropene.[30] $\lambda_{\max.}$ for the latter is in the region 310—360 mμ, while that of the cyanoform carbanion is at 211 mμ. On the assumption that the carbanion of tetracyanoethylene occupies an intermediate position in conjugation properties between the two above mentioned types of carbanions, an absorption maximum

[26] Brown and Jungk, *J. Amer. Chem. Soc.*, 1955, **77**, 5579.

[27] Cannell, *J. Amer. Chem. Soc.*, 1957, **79**, 2927, 2932.

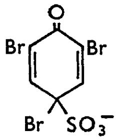
[28] Price, *J. Amer. Chem. Soc.*, 1955, **77**, 5436.

[29] Elston, Peters, and Rowe, *J.*, 1948, 367.

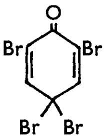
[30] Middleton, Little, Coffman, and Engelhardt, *J. Amer. Chem. Soc.*, 1958, **80**, 2795.

in the range 260—290 mμ can be predicted, and the superposition of this on the quinonoid spectra would lead to the observed absorption.

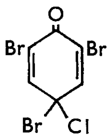
There remains the problem of the unusual stability of (II) compared with that of other σ-complexes. Molecular models show that the positive amino-nitrogen is near the cyano-groups carrying in part the negative charge. Electrostatic attraction between the opposite charges may have considerable importance for its stability, partially counteracting the loss of part of the resonance energies of the reactants. Three main pathways (*E*1, *E*2, and *E*1c*B*) all of which are first-order in the σ-complex should be considered for the formation of the final product by elimination of hydrogen cyanide from (II); *E*1 elimination is excluded since it requires no dependence on the dimethylaniline concentration, while rapid loss of cyanide ions from similar carbanions is slow.[31] *E*2 elimination from conformation (II), which requires the coplanarity of the four atoms taking place in the elimination, leads to a very strained transition state. We believe that *E*2 elimination from conformation (VII), obtained by rotation around the central carbon–carbon bond, is consistent with the kinetics but is unlikely compared with *E*1c*B*, as the rotation (II) ⟶ (VII) involves considerable loss of electrostatic energy. The carbanion mechanism (*E*1c*B*), in which abstraction of proton from (II) by another dimethlyaniline molecule is rate-determining, fits the kinetic results, the general base catalysis, and the energy considerations. In the new carbanion (VIII) the electrostatic attraction between the two opposite charges in (II) is destroyed, and electrostatic repulsion develops between the amino-nitrogen lone-pair and the negative charge on the tetracyanoethylene portion. This repulsion assists the rotation during the formation of (IX) and elimination of cyanide ion gives *NN*-dimethyl-4-tricyanovinylaniline.


(IV)

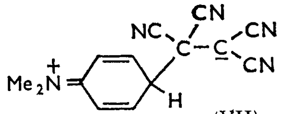
($\lambda_{max.}$ 279 mμ, ε 11,400)

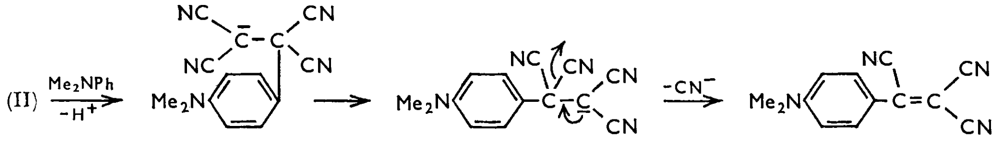

(V)

($\lambda_{max.}$ 280 mμ, ε 9270)


(VI)

($\lambda_{max.}$ 275 mμ, ε 10,000)


(VII)



(VIII) (IX)

Formation of (VII) directly from the starting materials, if occurring at all, must be insignificant. According to Table 6, even at those stages of the reaction when the concentration of (II) is still very small compared with the concentration of the unchanged reactants and of (I), product formation is strictly dependent on the concentration of (II).

We found no reference to solvent effect on the reactions σ-complex ⟶ final product. However, the disappearance of the blue colour of the π-complex of tetracyanoethylene with 4-methoxystyrene is much more rapid in the more polar solvents.[25] Our results are similar, and in mixtures of structurally similar solvents (chloroform, carbon tetrachloride, and ethylene dichloride) a linear relation is observed between the logarithms of the rate coefficients and the fraction of the more polar component of the solvent between 16%

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[31] McKusick, Heckert, Cairns, Coffman, and Mower, *J. Amer. Chem. Soc.*, 1958, **80**, 2808.

and 80% of the latter. This fits the more polar nature of the transition state than of the ground state, and Hughes and Ingold's theory of solvent effects.[32] Similar results are obtained in the analogous quaternization reaction.[33] The same theory accounts for the increase of the rate coefficients with the polarity of the medium in the reaction $\sigma \longrightarrow$ final product. The zwitterionic ground-state (II) is polar, but the close proximity of the opposite charges probably prevents the complete solvation of the charge-carrying groups. In the transition state this " internal solvation " is lost to some degree and substituted by more lyate solvation as more space becomes available for solvent molecules. Owing to the small differences in the rate coefficients, the values of activation entropy cannot be used to examine this suggestion. By use of Ingold's scheme of solvent effects,[34] the formation of two different charges from a zwitterion is intermediate in character between the S_N1 reaction (two charges are formed from neutral molecule; high positive solvent effect [34]) and the *E*1c*B* mechanism (large carbanion giving a smaller one and neutral molecule; low negative solvent effect [35]). In the overall reaction, reactants $\longrightarrow$ (IX) + H^+, two ions are obtained from two neutral molecules. The reasonable assumption that the stage in which charges are formed ($\pi \longrightarrow \sigma$) must be more sensitive to solvent effects than the removal of the charges from each others vicinity ($\sigma \longrightarrow$ final product) fits our results (Table 7).

The controversy about the formation and role of π- and σ-complexes in electrophilic aromatic substitutions is best demonstrated by various suggested energy profiles. While the one-stage mechanism has been ruled out,[36] in some energy profiles a quinonoid σ-complex is the lone intermediate.[27,37] In others, π- and σ-complexes are essential, either the former [2,3] or the latter [24,38,39] being suggested as being formed in the rate-determining step. In most cases mentioned above there is no information concerning the interconversion of the intermediates. In the present work, the heat of formation and the equilibrium constant for the π-complex formation, as well as the rates and activation parameters for the reactions $\pi \longrightarrow \sigma$ and $\sigma \longrightarrow$ final product were measured, and both π- and σ-complexes were found to be kinetically essential and identified spectrophotometrically in a single reaction system. Thus, the energy profile for the reaction is similar to that suggested by Brown *et al.*[38]

The detection of π-complexes is, however, not essential for their postulation as reaction intermediates. For a reaction without π-complexes, $(\text{ArX}) + (\text{Y}) \xrightarrow{k_1} (\sigma)$, the rate of formation of the σ-complex (neglecting the reverse reaction) is given by:

$$d\sigma/dt = k_1[\text{ArX}][\text{Y}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and for the reaction *via* a π-complex $(\text{ArX}) + (\text{Y}) \overset{K}{\rightleftharpoons} (\pi) \xrightarrow{k_2} (\sigma)$ by:

$$d\sigma/dt = k_2K[\text{ArX-}\pi][\text{Y-}\pi] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

When the equilibrium constant for the formation of the π-complex is very small, eqn. (11) reduces to (12) which cannot be distinguished kinetically from (10). Hence, if formation

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[32] Hughes and Ingold, *J.*, 1935, 244.

[33] Menschutkin, *Z. phys. Chem.*, 1890, **5**, 589.

[34] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell University Press, New York, 1953, p. 347.

[35] Patai, Weinstein, and Rappoport, *J.*, 1962, 1741.

[36] Melander, *Arkiv Kemi*, 1950, **2**, 211.

[37] Kresge and Chiang, *J. Amer. Chem. Soc.*, 1961, **83**, 2877; Zollinger, *Experientia*, 1956, **12**, 165; *Helv. Chim. Acta*, 1955, **38**, 1617; Melander and Myhre, *Arkiv Kemi*, 1959, **13**, 507; Berglund-Larsson and Melander, *ibid.*, 1953, **6**, 219; Berglund-Larsson, *ibid.*, 1957, **10**, 549; Lauer and Noland, *J. Amer. Chem. Soc.*, 1953, **75**, 3689; Halvarson and Melander, *Arkiv Kemi*, 1957, **11**, 77; de la Mare, Dunn, and Harvey, *J.*, 1957, 923.

[38] Brown and Nelson in Brooks, Kurtz, Boord, and Schmerling, " The Chemistry of Petroleum Hydrocarbons," Reinhold, New York, 1955, Vol. 3, Ch. 56.

[39] Gold and Satchell, *J.*, 1955, 3609, 3619, 3622; 1956, 2743.

of the final product is dependent on the σ-complex, even straightforward second-order kinetics for the reaction may be consistent with the formation of a π-complex of low stability as an intermediate.

$$d\sigma/dt = k_2K[ArX][Y] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The present reaction can also be regarded as a vinylic nucleophilic substitution on the tetracyanoethylene, with dimethylaniline as the nucleophile. Although conditions that favour π-complex formation with vinylic systems will also favour the nucleophilic attack on them, usually the concentrations and the equilibrium constants for such intermediates will be so small that they could be detected only by using strongly activated double bonds. In all cases studied previously, only carbanionic intermediates were suggested. However, all the systems investigated kinetically were relatively unreactive,[1,9,40] not permitting the detection of complexes even if formed at all. With very active double bonds, as in tetracyanoethylene, tricyanovinyl chloride,[41] and dicyanodiethoxycarbonylethylene,[42] both π-complexes and vinylic substitutions were demonstrated separately. The reaction sequence suggested for tetracyanoethylene, namely, initial formation of a π-complex, followed by transition to a carbanionic intermediate, in turn yielding the final product, is most probably applicable at least for other similar reactive double bonds which were shown to give π-complexes. Less reactive systems may also react according to the same scheme, and the kinetic treatment [eqns. (10)—(12), with σ denoting the carbanionic intermediate] may apply. This mechanism is consistent with the characteristic features of nucleophilic vinylic substitution, as both the " element effect " and the stereochemistry (retention of configuration) are dependent on the carbanion alone and independent of the π-complex formation.

By this extension, all types of nucleophilic vinylic substitution are covered by the same scheme, including both very active and relatively unreactive systems. It is reasonable to assume a general scheme for similar reactions with a wide range in the stability of the intermediate. This mechanism also emphasizes the similarity between the π-complex route in electrophilic[43] and nucleophilic reactions on double bonds, and points to quantitative differences in the magnitude of the equilibrium constants rather than to qualitative ones in the various types of reactions.

EXPERIMENTAL

Materials.—Tetracyanoethylene (Aldrich), crystallized three times from chlorobenzene,[44] had m. p. 198—199° (sealed tube). When stored at 0° it was stable for several months. Dimethylaniline (British Drug Houses) was distilled twice under reduced pressure in a nitrogen stream immediately before use and the middle fraction, b. p. 95°/25 mm., n_D 1·558,[25] was used. *NN*-Dimethyl-4-tricyanovinylaniline, m. p. 173—175° (from acetic acid) was prepared according to the literature.[11] Triethylamine was distilled twice from solid potassium hydroxide.

Solvents.—Chloroform (Mallinckrodt) was treated twice with 10% sulphuric acid, then twice with 10% sodium hydroxide solution, and washed three times with water. It was dried (K_2CO_3), stored in completely filled brown bottles, and redistilled under nitrogen immediately

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[40] Silversmith and Smith, *J. Org. Chem.*, 1958, **23**, 427; Miller and Yonan, *J. Amer. Chem. Soc.*, 1957, **79**. 5931; Carra and Beltrame, *Gazzetta*, 1959, **89**, 2027; Truce and Boudakian, *J. Amer. Chem. Soc.*, 1956, **78**, 2748; Modena, *Ricerca sci.*, 1958, **28**, 341. Maioli and Modena, *Gazzetta*, 1959, **89**, 854; Modena and Todesco, *ibid.*, p. 866; Modena, Todesco, and Tonti, *ibid.*, p. 878; Campagni, Modena, and Todesco, *ibid.*, 1960, **90**, 694; Maioli, Modena, and Todesco, *Boll. sci. Fac. Chim. ind. Bologna*, 1960, **18**, 66; Ghersetti, Modena, Todesco, and Vivarelli, *Gazzetta*, 1961, **91**, 620; Modena, Taddei, and Todesco, *Ricerca sci.*, 1960, **30**, 894. Patai and Rappoport, *J.*, 1962, 383, 392.

[41] Dickinson, Wiley, and McKusick, *J. Amer. Chem. Soc.*, 1960, **82**, 6132.

[42] Kudo, *Bull. Chem. Soc. Japan*, 1962, **35**, 1490, 1730.

[43] Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 5372; Taft, Purlee, Riesz, and DeFazio, *ibid.*, 1955, **77**, 1584; Purlee and Taft, *ibid.*, 1956, **78**, 5807; Boyd, Taft, Wolf, and Christman, *ibid.*, 1960, **82**, 4729.

[44] Carboni, *Org. Synth.*, **39**, p. 64.

before use into a Polythene flask (b. p. 58°/720 mm.) After storage for more than one week the strong characteristic odour pointed to formation of phosgene.[45] It was found later that kinetically pure chloroform can be obtained by washing the commercial solvent three times with water portions each equal to its volume. After distillation, this chloroform gave the same results as the one described above and tended less to form phosgene. Ethylene dichloride, b. p. 80—81°/720 mm., was purified as described in the first procedure for chloroform. Carbon tetrachloride, b. p. 74°/720 mm., was dried ($CaCl_2$) and distilled.

Kinetic Procedure and Treatment of Data.—A new stock solution of tetracyanoethylene in chloroform was prepared daily in a Polythene flask. A high molar excess of dimethylaniline was added slowly to the appropriately diluted tetracyanoethylene stock solution in a Polythene flask so that two phases with a blue intercept were formed. The time of mixing of the two phases was taken as the zero time. The blue reaction mixture was transferred rapidly to a stoppered 1 cm. (or 1 mm.) silica absorption cell in a thermostat-controlled spectrophotometer chamber of Beckman DU spectrophotometer with a Beckman dual thermospacer. The decrease in the absorbance at 675 mμ, the wavelength of the maximum absorption of the π-complex, was measured as a function of time, and after more than 90% of the original π-complex had disappeared, the measurements of the increase in absorption of the final product, *NN*-dimethyl-4-tricyanovinylaniline, were continued at its $\lambda_{max.}$ (515 mμ, ε 48,400) in chloroform. The starting materials have no appreciable absorption at these wavelengths. After sufficient time to obtain 2—4% of the product, an additional measurement was conducted at 675 mμ, from which the % decomposition of the π-complex at the end of the measurements was calculated. In the cases where measurements were conducted at 515 mμ from the start of the reaction, the absorption first decreased (owing to the decomposition of the π-complex) and afterwards increased (final-product formation). Measurements at other wavelengths showed the continuous increase of the absorption below 350 mμ during the time of the decomposition of the blue colour (owing to σ-complex formation).

Data of the $\pi \longrightarrow \sigma$ reaction and the $\sigma \longrightarrow$ final product reaction were each treated according to the usual first-order equation, and second-order rate coefficients (k_2) were obtained by dividing k_1 by the dimethylaniline concentration. The concentration of the σ-complex was obtained from eqn. (6); 85—95% of the final product was obtained after 48 hr. at room temperature. The solution of the final product in chloroform is stable for at least 36 hr.

Product Analysis.—*NN*-Dimethyl-4-tricyanovinylaniline (45 mg., 90%) was obtained from the reaction of tetracyanoethylene (25 mg.) and dimethylaniline (25 mg.) in chloroform (25 ml.), by evaporating the solvent after 24 hr. It was identified by m. p., mixed m. p., and ultraviolet spectra.

Reaction of Tetracyanoethylene with Isoprene.—In each of two experiments, tetracyanoethylene (5×10^{-4} mole $l.^{-1}$) was treated with 2 ml. and 4 ml. of pure isoprene, respectively, the volume of the solution being made up to 10 ml. by addition of chloroform. The solution containing more isoprene was slightly darker (yellow-brown) at the beginning of the reaction than the other, but its colour disappeared more rapidly, so that after 1 min. the dilute solution had a slightly stronger colour. After 3 min. the more concentrated solution was completely colourless while the dilute one was still faintly yellow.

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[45] Richards and Wallace, *J. Amer. Chem. Soc.*, 1932, **54**, 2705.