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262. *Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part VIII.*[1] *The Reaction of* N-*Methylaniline with Tetracyanoethylene in Chloroform.*

By Zvi Rappoport and Abraham Horowitz.

The formation of *N*-methyl-4-tricyanovinylaniline by the reaction of tetracyanoethylene with *N*-methylaniline in chloroform has been studied kinetically. The initially formed π-complex was transformed rapidly into a σ-complex which, in turn, gave the final product. The equilibrium constant and the thermodynamic parameters of the π-complex have been determined. The second-order rate coefficients for both the decomposition of the π-complex (first-order in the amine and in the π-complex) and for the formation of the product (first-order in the amine and in the σ-complex) decreased when the amine concentration was reduced. The reactivities of various aromatic amines as proton abstractors from the σ-complex were related to their basicities in water. Both steps of the reaction were accelerated by an increase in the dielectric constant of the solvent. The mechanism of the reaction is discussed.

NN-Dialkylanilines and *N*-alkylanilines are tricyanovinylated in the *para*-position.[2] The kinetics of this reaction were studied previously with *NN*-dimethylaniline,[3] and a mechanism was suggested involving the formation of both π- and σ-complexes in the substitution pattern. This investigation in now extended to *N*-methylaniline, and the reaction is again formulated as:

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

Results

The reaction was studied spectrophotometrically in chloroform at 32·5, 40, and 48°, and found to consist of three consecutive steps, involving formation of π-complex, formation of σ-complex, and formation of the final product.

Formation of the π-Complex.—A blue colour ($\lambda_{\max}$ 640 mμ) is formed immediately when the reactants are mixed in chloroform, and becomes deeper when the temperature is decreased to —70°. This colour is ascribed to a 1 : 1 π-complex of the two reactants, and the equilibrium constants, $K = [\pi]/[\text{TCE-}\pi][\text{MMA}]$ (where $[\pi]$, [TCE], and [MMA] are the concentrations of the π-complex, tetracyanoethylene, and *N*-methylaniline, respectively, the last being always in excess), were calculated in the usual way [4,5] with the aid of eqn. (1), where l is the cell length, D is the measured optical density, and ε is the molar extinction

$$y \equiv [\text{TCE}]l/D = (1/K\varepsilon[\text{MMA}]) + 1/\varepsilon \qquad (1)$$

coefficient of the π-complex. Although straight lines are obtained by plotting y against 1/[MMA], the values of the equilibrium constants are sensitive to the numerical value of the intercept ($1/\varepsilon$) which is usually a small number, resulting in a relatively large error. Least-squares calculations gave a scatter in the ε values at various temperatures which is too large to be a result of the temperature-dependence of ε and probably results from the equal weight given to all the D values in this treatment, although the error is larger with small D values. A further complication in our system is the rapid decomposition of the π-complex, so that most of the D values are obtained by extrapolation. To calculate

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[1] Part VII, preceding paper.

[2] McKusick, Heckert, Cairns, Coffman, and Mower, *J. Amer. Chem. Soc.*, 1958, **80**, 2806.

[3] Rappoport, *J.*, 1963, 4498.

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

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

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the equilibrium constants (Table 1), the ε value (3100) was obtained from the intercept of the best line (at 40°) and used in the calculation of K from individual points at all the temperatures. From the average of the equilibrium constants at different temperatures the thermodynamic parameters for the formation of the π-complex ($\Delta F = -1\cdot210$ kcal. mole^{-1}, $\Delta H = -5\cdot100$ kcal. mole^{-1}, $\Delta S = -15\cdot6$ e.u. at 40°) were calculated. A value differing by 15% was found for the equilibrium constant at 675 mμ. The method of calculation of such equilibrium constants is usually not very satisfactory,[6] and so the differences are not surprising.

TABLE 1.

Equilibrium constants in chloroform for the 1 : 1 π-complex of tetracyanoethylene (TCE) and N-methylaniline (MMA) from the absorption data at 625 mμ.[a]

10^3[MMA] (moles l.$^{-1}$)	14·7	29·4	44·1	58·8	73·5	103	
			At 32·5°.				
10^3D	230	390	532	665	753	1020	
10^3y [b] (moles cm. l.$^{-1}$)	2·92	1·72	1·26	1·01	0·89	0·657	
K (l. mole^{-1}) [c]...........	8·4	7·9	7·8	8·1	7·8	9·2	Av. $K = 8\cdot2 \pm 0\cdot5$
			At 40°.				
10^3D	196	369	500	638	735	917	
10^3y [d] (moles cm. l.$^{-1}$)	3·50	1·86	1·37	1·08	0·936	0·751	
K (l. mole^{-1})	6·9	7·1	6·9	7·4	7·1	7·3	Av. $K = 7\cdot1 \pm 0\cdot2$
			At 48°.				
10^3D	49	123	177	261	425		
10^3y [e] (moles cm. l.$^{-1}$)	5·55	2·24	1·55	1·05	0·646		
K (l. mole^{-1})	4·2[f]	5·7	5·9	6·0	5·5	Av. $K = 5\cdot8 \pm 0\cdot2$	

[a] Calc. from eqn. (1) in the rearranged form, $K = 1/[\text{MMA}](\varepsilon y - 1)$; ε taken as 3100. [b] [TCE] = $6\cdot70 \times 10^{-4}$ mole l.$^{-1}$. [c] The equilibrium constant measured by the same method at 675 mμ is $9\cdot4 \pm 0\cdot2$ l. mole^{-1}. [d] [TCE] = $6\cdot88 \times 10^{-4}$ mole l.$^{-1}$. [e] [TCE] = $2\cdot75 \times 10^{-4}$ mole l.$^{-1}$. [f] This value was not used in the calculation of the average equilibrium constant.

Disappearance of the π-Complex (π-Complex ⟶ σ-complex Reaction).—This reaction was followed by measuring the decrease in the absorption of the π-complex at 560 mμ. The amine concentrations were 100—400-fold higher than those of the tetracyanoethylene, and 30—80% of the latter was usually incorporated in the π-complex. The reaction was first-order in the π-complex and hence in the tetracyanoethylene (Table 2). The order in the amine was higher than unity, as shown by the steady increase of the second-order rate coefficients (the first-order ones divided by the amine concentration) with increasing amine concentrations at all the temperatures studied (Table 2). The π-complex concentrations were calculated from the relationship, $\pi = K[\text{MMA}][\text{TCE}]/(1 + K[\text{MMA}])$. The reaction was usually followed up to 95% completion, and the rate coefficients remained steady almost to the end of each run. The reaction is practically irreversible, and the pale yellow solution of the σ-complex obtained does not yield again the free reactants or the π-complex. This is discussed further below. A sample run is included in Table 3.

Formation of the Final Product from the σ-Complex (σ-Complex ⟶ final Product Reaction).—As the π ⟶ σ-reaction with N-methylaniline is faster than the corresponding reaction with dimethylaniline, while the σ ⟶ final product reaction was slower, no correction is needed for the tetracyanoethylene remaining during the decomposition of the σ-complex, and the initial concentration of the σ-complex at the beginning of its decomposition was taken as equal to that of the initial tetracyanoethylene. Initial rates for the formation of the final product from the σ-complex were calculated from the slopes of the plots of optical density against time, according to the equation, $k_2 = (\Delta D/\Delta t)/[\sigma]\varepsilon_1[\text{MMA}]$, where $\varepsilon_1 (= 40{,}400)$ is the molar extinction coefficient of N-methyl-4-tricyanovinylaniline and the measurements were conducted at its $\lambda_{\text{max.}}$ (= 486 mμ).

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[6] Andrews, *Chem. Rev.*, 1954, **54**, 713; Halevi and Nussim, *J.*, 1963, 876.

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A sample run is given in Table 3. The second-order rate coefficients, first-order both in the amine and in the σ-complex, were found again to increase with increase in the amine concentration, although the increase was somewhat smaller than in the $\pi \longrightarrow \sigma$-reaction (Table 4). The increase in the rates is linear with increase in the amine concentrations as shown in Fig. 1. Final values showed that although a 70% yield was recorded[2] the reaction is not quantitative under the kinetic conditions in chloroform, and maximum values of 18—30% reaction were found under various conditions. Even if the $\sigma \longrightarrow$ final product reaction was conducted in the presence of various bases or ethanol (which increases the reaction rate) only 25% of the final product was found. The spectra of various reaction mixtures showed no maximum at 335 mμ, which is the wavelength of maximum absorption of *N*-methyl-*N*-tricyanovinylaniline in chloroform and which, therefore, could account for the loss of tetracyanoethylene without formation of the *C*-tricyanovinyl compound.* Higher yields are obtained when higher concentrations of the two reactants are used in chloroform solvent.

TABLE 2.

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

10^4[TCE] (moles l.$^{-1}$) ...	8·25	8·25	8·25	8·25	8·25	2·75	4·13	5·50	6·68	11·00
10^2[MMA] (moles l.$^{-1}$)	7·34	11·0	18·35	25·7	36·7	36·7	36·7	36·7	36·7	36·7
At 32·5°.										
$10^4[\pi]$ (moles l.$^{-1}$)	—	3·90	4·95	5·59	6·19	2·07	3·11	—	5·16	8·25
10^3k_1 (sec.$^{-1}$)	—	0·864	1·91	3·22	5·37	5·56	5·40	—	5·12	5·32
10^2k_2 (l. mole^{-1} sec.$^{-1}$)	—	0·785	1·04	1·25	1·46	1·51	1·47	—	1·40	1·45
At 40°.										
$10^4[\pi]$ (moles l.$^{-1}$)	2·82	3·62	4·67	5·33	5·96	1·99	2·98	3·98	4·97	7·95
10^3k_1 (sec.$^{-1}$)	0·519	1·02	2·64	4·60	6·78	7·41	7·44	6·54	6·70	6·68
10^2k_2 (l. mole^{-1} sec.$^{-1}$)	0·707	0·927	1·44	1·79	1·85	2·01	2·01	1·78	1·82	1·82
At 48°.										
$10^4[\pi]$ (moles l.$^{-1}$)	2·46	3·21	4·23	4·94	5·61	1·87	—	3·74	4·68	7·48
10^3k_1 (sec.$^{-1}$)	0·729	1·60	3·28	6·15	8·82	8·73	—	8·53	8·42	8·15
10^2k_2 (l. mole^{-1} sec.$^{-1}$)	1·00	1·45	1·79	2·39	2·40	2·38	—	2·32	2·30	2·22

TABLE 3.

Sample run for the reaction of *N*-methylaniline (MMA; 0·367 mole l.$^{-1}$) and tetracyanoethylene (6·88 × 10^{-4} mole l.$^{-1}$) in chloroform at 32·5°.

π-Complex $\longrightarrow$ σ-complex reaction,* at 560 mμ.

Time (sec.)	0	40	60	90	110	140	180	210	240	300
$10^3 \log (I/I_0)$	1250 †	1025	925	778	700	605	500	438	370	264
Reaction (%)	0	18	26	38	44	51·5	60	65	70·5	79
10^3k_1 (sec.$^{-1}$)	—	4·95	5·02	5·49	5·26	5·19	5·09	5·00	5·06	5·18

Average $k_1 = 5{\cdot}14 \times 10^{-3}$ sec.$^{-1}$; $k_2 = k_1/[\text{MMA}] = 1{\cdot}40 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$.

σ-Complex $\longrightarrow$ *N*-methyl-4-tricyanovinylaniline reaction,‡ at 486 mμ.

Time (sec.)	900	1260	1860	2460	3390	4380	5640	6780	8100
$10^3 \log (I/I_0)$	27	44	61	84	115	156	205	245	294

$s = \Delta \log (I/I_0)/\Delta t = 3{\cdot}80 \times 10^{-5}$ sec.$^{-1}$;

$k_1 = s/\varepsilon[\sigma] = 1{\cdot}365 \times 10^{-6}$ l. mole^{-1} sec.$^{-1}$; $k_2 = k_1/[\text{MMA}] = 3{\cdot}74 \times 10^{-6}$ l. mole^{-1} sec.$^{-1}$.

* Initial π-complex concentration = 4·96 × 10^{-4} mole l.$^{-1}$. † Extrapolated value. ‡ The σ-complex concentration was taken as equal to that of the initially introduced tetracyanoethylene.

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* Although tricyanovinylation by tetracyanoethylene occurs usually in the *para*-position,[2] and that by tricyanovinyl chloride on the nitrogen,[7] when *N*-alkylanilines are attacked, we found spectrophotometrically that small amounts of the *p*-tricyanovinylation product are obtained in the reaction of tricyanovinyl chloride with *N*-methylaniline in chloroform, in addition to the major *N*-tricyanovinylation product.

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

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TABLE 4.

First-order (k_1) and second-order ($k_2 = k_1$/[MMA]) rate coefficients for the formation of *N*-methyl-4-tricyanovinylaniline from the σ-complex of *N*-methylaniline (MMA) and tetracyanoethylene (TCE) in chloroform at various temperatures.

10^4[TCE] * (moles l.$^{-1}$)	2·75	4·13	5·50	6·88	8·25	11·00	8·25	8·25	8·25	8·25
10^2[MMA] (moles l.$^{-1}$)	36·7	36·7	36·7	36·7	36·7	36·7	7·34	11·0	18·35	25·7
At 32·5°.										
10^8k_1 (sec.$^{-1}$)	14·4	14·9	14·2	13·7	14·1	14·9	—	3·08	5·62	10·0
10^6k_2 (l. mole^{-1} sec.$^{-1}$)	3·90	4·06	3·86	3·72	3·83	4·06	—	2·80	3·06	3·89
Average $10^6k_2 = 3·91 \pm 0·13$ l. mole^{-1} sec.$^{-1}$.										
At 40°.										
10^8k_1 (sec.$^{-1}$)	23·0	23·2	23·8	22·8	24·0	22·6	2·38	4·33	8·38	14·4
10^6k_2 (l. mole^{-1} sec.$^{-1}$)	6·25	6·28	6·48	6·20	6·55	6·15	3·25	3·93	4·56	5·60
Average $10^6k_2 = 6·32 \pm 0·13$ l. mole^{-1} sec.$^{-1}$.										
At 48°.										
10^8k_1 (sec.$^{-1}$)	44·0	—	39·6	41·8	37·5	37·5	3·95	7·26	14·6	23·5
10^6k_2 (l. mole^{-1} sec.$^{-1}$)	12·0	—	10·9	11·4	10·2	10·2	5·38	6·60	7·96	9·15
Average $10^6k_2 = 11·2 \pm 1·0$ l. mole^{-1} sec.$^{-1}$.										

* This concentration was taken as equal to the concentration of the σ-complex at the beginning of the measurements of product formation.

In order to show that the disappearance of the π-complex and the formation of the σ-complex have the same rates, the decrease in the absorption at 560 mμ corresponding to the π-complex, and the simultaneous increase at 380 mμ corresponding to the formation of the σ-complex, were measured concurrently in some experiments. Although the last wavelength was chosen as a compromise, being the position where neither the absorption of the π-complex nor that of the amine interfere too strongly, considerable corrections had to be made. In four different runs ([MMA] = $7·34 \times 10^{-2}$ and [TCE] = 5·50, 6·88, and $8·25 \times 10^{-4}$; [MMA] = $11·0 \times 10^{-2}$ and [TCE] = $5·50 \times 10^{-4}$ mole l.$^{-1}$) the rate coefficients of the σ-complex formation up to 10—20% reaction were found to be about 10% lower than the rate coefficients for the disappearance of the π-complex. This is possibly due to the above mentioned corrections since, in the 20—65% range (in which the corrections are smaller), the increase of the σ-complex concentration was exactly the same as the decrease in the π-complex concentration.

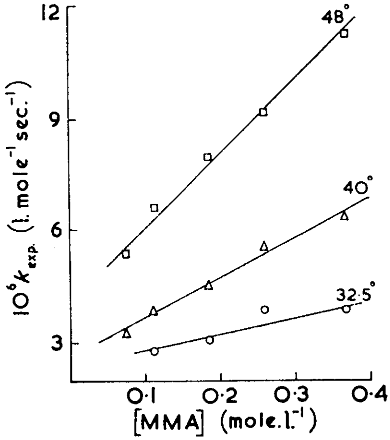

FIG. 1. Dependence on amine concentration of the second-order rate coefficients for the σ-complex ⟶ final product reaction.

The possibility that at different amine concentrations the formation of the σ-complex is not quantitative but dependent on the amine concentration was checked by treating $3{\cdot}44 \times 10^{-4}$ mole $l.^{-1}$ tetracyanoethylene with 0·92, 0·46, 0·18, 0·092, and 0·046 mole $l.^{-1}$ of *N*-methylaniline, respectively, and measuring the final absorption corresponding to the σ-complex at 380 mμ. The respective optical densities, 0·990, 0·992, 1·050, 1·050, and 1·020, show that in this range of amine concentrations, which is much higher than that used in the kinetic runs, the concentration of the σ-complex is practically the same. On the other hand, the amount of σ-complex formed is proportional to the initial amount of the tetracyanoethylene. The molar extinction coefficient of the σ-complex, calculated for $\lambda = 380$ mμ is 3100.

Effect of Aromatic Amines on the σ-Complex ⟶ Final Product Reaction.—Tables 2 and 4 show that practically all the tetracyanoethylene is incorporated in the σ-complex before any appreciable elimination of hydrogen cyanide from it takes place. Therefore, the effect of bases on the σ-complex ⟶ final product reaction can be studied. *N*-methylaniline and tetracyanoethylene were allowed to react until the disappearance of all the π-complex, and to the σ-complex so formed more *N*-methylaniline, *N*-n-butylaniline, or one of four dialkylanilines were added; the formation of *N*-methyl-4-tricyanovinylaniline was followed as usual. No evidence was found for the formation of a π-complex of any of the amines added in the second stage. The complete absence of *NN*-dialkyl-4-tricyanovinylanilines in all the reactions show that all the tetracyanoethylene is included in the σ-complex and that the π-complex ⟶ σ-complex reaction is irreversible under these conditions. The rate coefficients, $k_{obs.}$, which were calculated by using only the concentration of the added amine, and which include therefore both the effect of the original *N*-methylaniline and that of the added amine, were corrected by substracting the part of the rate due to *N*-methylaniline (measured independently in a " blank " experiment). The correction was small for the four more reactive amines (*i.e.*, diethyl-, dipropyl-, dibutyl-, and monobutyl-aniline), and was appreciable only when the added amine was *NN*-dimethylaniline of *N*-methylaniline. With the two *N*-alkylanilines, the rate coefficients increased with increasing amine concentration, and the effect is very high with *N*-n-butylaniline. This amine is also " abnormal " in having a very high reaction rate, although its p*K* is similar to that of *N*-methylaniline. With the dialkylanilines no systematic trend in the rate coefficient at the two temperatures was found by changing the amine concentrations. The rate coefficients obtained after the correction, $k_{cat.}$, which is a measure of the reactivity of the added amine, are given in Table 5. The relation between the p*K* values and the relative reactivities (*N*-methylaniline = 1·00 at an amine concentration of $18{\cdot}35 \times 10^{-2}$ mole $l.^{-1}$) and the activation parameters for the elimination of proton by the aromatic amines are given in Table 6. The order of reactivity of the amines parallels their basicity in water (*N*-n-butylaniline is an exception). However, a Brönsted plot of the p*K* values in water against the logarithms of the rate coefficients is not linear, as shown in Fig. 2. The low reactivity of *N*-methylaniline and *NN*-dimethylaniline is a result of a higher activation energy by some kcal. mole^{-1} over that of the more reactive

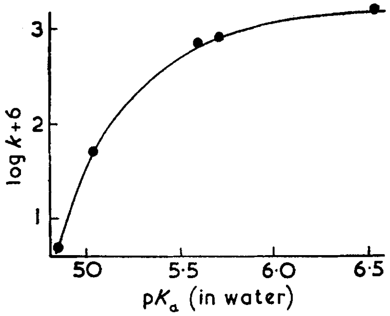

FIG. 2. Proton abstraction from the σ-complex by various amines (*N*-n-butyaniline is not included); dependence of the logarithms of the rate coefficients on the basicity of the amines.

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TABLE 5.

Observed ($k_{\text{obs.}}$) and catalytic ($k_{\text{cat.}}$) second-order rate coefficients (l. mole^{-1} sec.$^{-1}$) for the *N*-methylaniline–tetracyanoethylene σ-complex ⟶ final product reaction, catalysed by various amines * in chloroform.†

	At 32·5°.			At 48°.			At 32·5°.			At 48°.	
10^2[MMA] †	18·35	32·45	43·5	18·35	25·4	10^2[DPA]	3·67	10·2	13·95	3·39	7·02
$10^5k_{\text{obs.}}$	0·306	‡	‡	0·905	‡	$10^5k_{\text{obs.}}$	84·6	70·5	66·5	141	123
$10^5k_{\text{cat.}}$	0·306	0·374	0·430	0·905	1·120	$10^5k_{\text{cat.}}$	82·5	70·0	66·2	137	121
10^2[DMA]	3·57	14·1	19·7	3·49	6·64	10^2[DBA]	3·56	7·2	14·0	3·55	7·04
$10^5k_{\text{obs.}}$	7·33	5·25	5·45	21·4	20·5	$10^5k_{\text{obs.}}$	92·2	89·6	80·6	179	193
$10^5k_{\text{cat.}}$	5·76	4·97	4·99	16·9	17·8	$10^5k_{\text{cat.}}$	90·3	88·6	80·2	177	191
10^2[DEA]	3·58§	6·85	13·5	3·53	7·65	10^2[MBA] ¶	0·185	0·370	0·555	—	—
$10^5k_{\text{obs.}}$	187	167	181	333	351	$10^5k_{\text{obs.}}$	1170	2700	4350	—	—
$10^5k_{\text{cat.}}$	185	167	180	328	349	$10^5k_{\text{cat.}}$	1170	2700	4350	—	—

* Abbreviations as shown in Table 6. † $k_{\text{obs.}}$ is the first-order rate coefficient divided by the concentration of the added amine. $k_{\text{cat.}}$ is obtained by dividing the first-order rate coefficient, after correcting it for the "blank" reaction with *N*-methylaniline, by the added amine concentration. [Tetracyanoethylene] = $9·64 \times 10^{-4}$ mole l.$^{-1}$; [*N*-methylaniline] = $18·35 \times 10^{-2}$ mole l.$^{-1}$. ‡ These values are obtained from the original reaction mixture without added amine, and used as the blanks for the corrections. § Calc. final value of optical density = 39; found = 8·0. The same final value was obtained on addition of $11·45 \times 10^{-2}$ mole l.$^{-1}$ of *NN*-diethylaniline. ¶ [Tetracyanoethylene] = $6·60 \times 10^{-4}$ mole l.$^{-1}$.

TABLE 6.

Relative reactivities and activation parameters for the proton abstraction reaction from the σ-complex by various amines in chloroform.

Amine	pK_a *	Rel. k_2 at 32·5°	E_a (kcal. mole^{-1}) †	$-\Delta S^{\ddagger}$ (e.u.) ‡
N-Methylaniline (MMA)	4·85	1·00	12·0 §	46
NN-Dimethylaniline (DMA)	5·06	18·8	14·8	31
NN-Diethylaniline (DEA)	6·56	580	8·1	46
NN-Dipropylaniline (DPA)	5·59	238	7·3	50
NN-Dibutylaniline (DBA)	5·7	282	9·5	43
N-n-Butylaniline (MBA) ¶	4·95	3820		
NN-Dimethylaniline (DMA) **	5·06	38·2	12·4	37

* In water at 25°. Taken from Brown, McDaniel, and Hafliger in Braude and Nachod's "Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955, p. 608. † Estimated ±2 kcal. mole^{-1}. ‡ Estimated ±5 e.u. § Average value (from Table 8). ¶ The relative rate coefficient was calculated from the rate coefficient in the presence of $1·85 \times 10^{-3}$ mole l.$^{-1}$ of amine. ** Data for the proton abstraction from the σ-complex of *NN*-dimethylaniline with tetracyanoethylene.[3]

amines. The values for the entropy of activation are similar for all the amines (except for *NN*-dimethylaniline). The final absorption values in the reactions catalysed by various additional amines were the same (23—27% of the final product were formed).

Effect of the Solvent on the Reaction Rates.—Increasing the dielectric constant of the medium by the addition of ethylene dichloride to chloroform increased the reaction rates (Table 7). An approximately linear relationship exists between the rate coefficients for the two processes and the percentage of ethylene dichloride in the medium, as shown by the good agreement of the observed values and those calculated by the least-squares method. The increase in the rate coefficients for the π ⟶ σ-reaction is relatively small, being 1·8-fold on going from pure chloroform to 80% ethylene dichloride–chloroform, while the increase in the rate coefficients in the σ ⟶ final product reaction is 5-fold for the same solvent mixtures. The corresponding increase in the rates in the *NN*-dimethylaniline–tetracyanoethylene system,[3] in the same solvent mixtures, was 5·2- and 2·4-fold for the π ⟶ σ and σ ⟶ final product reactions, respectively. This inversion in the solvent sensitivity of the two reaction stages is best demonstrated by the values, *b*, of the slope of the least-squares line, which measure the sensitivity of the reaction to solvent effects. 10^3b = 10·9 and 48·5 for the π ⟶ σ-reaction of *N*-methylaniline and *NN*-dimethylaniline, respectively, and 50 and 16·2 for the σ ⟶ final product reactions for the two systems, respectively. Here again, as with dimethylaniline, the extrapolated optical densities decreased with increasing polarity of the medium, as shown in Table 7. However, the lower equilibrium constant and the higher reactivity prevents the use of high amine concentrations to determine whether this is a result of a decrease in the equilibrium constant or a shift in the $\lambda_{\text{max.}}$,[8] or both.

Activation Parameters.—The activation parameters for the two reactions were calculated for the reactions in the presence of different concentrations of amine, from the rate coefficients of Table 2 and 4, and are given in Table 8. The average rate coefficients for the reaction in the presence of 0·367 mole l.$^{-1}$ of *N*-methylaniline and different concentrations of tetracyanoethylene were used. The energies and entropies of activation for the two processes show no trend with the variation of the amine concentration, and the differences are usually within the accuracy of these values. The activation energies and entropies for the $\pi \longrightarrow \sigma$-reaction are somewhat higher than the corresponding values for the dimethylaniline reaction. The activation energies are similar, and the activation entropies are somewhat lower for the $\sigma \longrightarrow$ final product reaction than the corresponding values in the dimethylaniline system.

TABLE 7.

Second-order rate coefficients (k_2) for the π-complex $\longrightarrow$ σ-complex and the σ-complex $\longrightarrow$ final product reactions in the *N*-methylaniline–tetracyanoethylene system, in chloroform–ethylene dichloride mixtures at 32·5°.

[Ethylene dichloride] (%, v/v) *	0	20	30	40	60	80	100
10^3D † at 560 mμ	1000	890	845	820	745	705	650
π-Complex $\longrightarrow$ σ-complex reaction.							
10^2k_2 (l. mole^{-1} sec.$^{-1}$)	1·02	1·25	1·36	1·48	1·68	1·81	2·20
10^2k_2 (calc.) ‡ (l. mole^{-1} sec.$^{-1}$)	1·02	1·24	1·36	1·47	1·69	1·91	2·14
σ-Complex $\longrightarrow$ final product reaction.							
10^6k_2 (l. mole^{-1} sec.$^{-1}$)	2·80	5·38	7·50	8·70	11·00	13·60	14·70
10^6k_2 (calc.) § (l. mole^{-1} sec.$^{-1}$)	2·80	5·60	7·00	8·40	11·20	14·00	16·80

* The values given are the v/v constitution of the solvent only; each reaction mixture contains also 2% (v/v) of *N*-monomethylaniline (18·35 × 10^{-2} mole l.$^{-1}$); [Tetracyanoethylene] = 8·25 × 10^{-4} mole l.$^{-1}$ in all the experiments. † The extrapolated optical density of the π-complex. ‡ Calc. from the least-squares equation, $k = 1{\cdot}022 \times 10^{-2}\ (1 + 1{\cdot}09 \times 10^{-2}$[ethylene dichloride]). § Calc. from the least-squares equation, $k = 2{\cdot}80 \times 10^{-6}\ (1 + 0{\cdot}05$[ethylene dichloride]), which was obtained by using all the points except the last.

TABLE 8.

Activation parameters for the $\pi \longrightarrow \sigma$-reaction and the $\sigma \longrightarrow$ final product reaction, in chloroform.

10^2[*N*-Methylaniline] (moles l.$^{-1}$)	7·34	11·0	18·35	25·7	36·7
π-Complex $\longrightarrow$ σ-complex reaction.					
E_a (kcal. mole^{-1}) *	8·7	7·7	7·0	8·2	6·5
$-\Delta S^{\ddagger}$ (e.u.) †	42	44	46	42	47
σ-Complex $\longrightarrow$ final product reaction.					
E_a (kcal. mole^{-1}) ‡	12·7	10·7	11·6	11·0	13·8
$-\Delta S^{\ddagger}$ (e.u.) †	44	50	46	49	41

* Estimated ±1·5 kcal. mole^{-1}. † Estimated ±4 e.u. ‡ Estimated ±2 kcal. mole^{-1}.

Side-product.—When low and similar concentrations of the two reactants were used, evidence was found for the formation of a coloured side-product (see Experimental section). Owing to its low concentrations it was not investigated further.

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[8] Cram and Bauer, *J. Amer. Chem. Soc.*, 1959, **81**, 5971.

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Discussion

From the kinetic viewpoint the *N*-methylaniline–tetracyanoethylene system is more complicated than the *NN*-dimethylaniline–tetracyanoethylene system studied previously.[3] The straightforward second-order kinetics in both stages of the latter reaction suggested a mechanism in which the π-complexed tetracyanoethylene had reacted first with *NN*-dimethylaniline, and proton abstraction from the resulting σ-complex preceded the elimination of cyanide ion. Now, the decrease in the rate coefficients in both stages of the present reaction shows that this analysis is not sufficient for both reaction systems, and a more complete analysis is needed.

Let us analyse first the possibilities for the π $\longrightarrow$ σ-reaction. There are two states of tetracyanoethylene in the reaction mixture, one free $[\mathrm{TCE}]_f$ and one incorporated in the π-complex with concentration $[\mathrm{TCE}]_\pi$. Hence, the total concentration of the tetracyanoethylene is $[\mathrm{TCE}]_t = [\mathrm{TCE}]_f + [\mathrm{TCE}]_\pi$. By using the expression for the equilibrium constant K, and the above relationship, the concentrations of the total, complexed, and free tetracyanoethylene are given by eqns. (2)—(4). The rate of formation of the σ-complex is equal to that of the disappearance of $[\mathrm{TCE}]_t$, and six different mechanisms are possible for its formation.

$$[\mathrm{TCE}]_t = (1 + K[\mathrm{MMA}])[\pi]/K[\mathrm{MMA}] \tag{2}$$

$$[\mathrm{TCE}]_\pi = K[\mathrm{MMA}][\mathrm{TCE}]_t/(1 + K[\mathrm{MMA}]) \tag{3}$$

$$[\mathrm{TCE}]_f = [\mathrm{TCE}]_t/(1 + K[\mathrm{MMA}]) \tag{4}$$

(*a*) The σ-complex is formed by unimolecular transformation of the π-complex. The corresponding rate equation is:

$$-\mathrm{d}[\mathrm{TCE}]_t/\mathrm{d}t = k_1[\pi] \tag{5}$$

By multiplying both sides by $K[\mathrm{MMA}]/(1 + K[\mathrm{MMA}])$, which is constant for a kinetic run, the second-order experimental rate coefficient, $k_{\mathrm{exp.}} = (\mathrm{d}[\pi]/\mathrm{d}t)/[\mathrm{MMA}][\pi]$, is given by eqn. (6).

$$k_{\mathrm{exp.}} = k_1K/(1 + K[\mathrm{MMA}]) \tag{6}$$

(*b*) The σ-complex is formed by bimolecular reaction of uncomplexed tetracyanoethylene with *N*-methylaniline. Eqns. (7) and (8) apply.

$$-\mathrm{d}[\mathrm{TCE}]_t/\mathrm{d}t = k_1[\mathrm{TCE}]_f[\mathrm{MMA}] \tag{7}$$

$$k_{\mathrm{exp.}} = k_1/(1 + K[\mathrm{MMA}]) \tag{8}$$

(*c*) The σ-complex is formed with equal rate coefficients from all the tetracyanoethylene present, $[\mathrm{TCE}]_t$, in a bimolecular reaction. Eqns. (9) and (10) apply.

$$-\mathrm{d}[\mathrm{TCE}]_t/\mathrm{d}t = k_1[\mathrm{TCE}]_t[\mathrm{MMA}] \tag{9}$$

$$k_{\mathrm{exp.}} = k_1 \tag{10}$$

(*d*) The σ-complex is formed only by a bimolecular reaction of the π-complexed tetracyanoethylene with a second molecule of *N*-methylaniline. Eqns. (11) and (12) apply.

$$-\mathrm{d}[\mathrm{TCE}]_t/\mathrm{d}t = k_1[\mathrm{TCE}]_\pi[\mathrm{MMA}] \tag{11}$$

$$k_{\mathrm{exp.}} = k_1K[\mathrm{MMA}]/(1 + K[\mathrm{MMA}]) \tag{12}$$

(*e*) The σ-complex is formed in two concurrent reactions, in a monomolecular one from the π-complex, and in a bimolecular one with the free tetracyanoethylene. Eqns. (13) and (14) apply.

$$-\mathrm{d}[\mathrm{TCE}]_t/\mathrm{d}t = k_1[\pi] + k_2[\mathrm{TCE}]_f[\mathrm{MMA}] \tag{13}$$

$$k_{\mathrm{exp.}} = (k_1 + k_2)K/(1 + K[\mathrm{MMA}]) \tag{14}$$

(*f*) The σ-complex is formed by two bimolecular reactions of *N*-methylaniline with the complexed and uncomplexed tetracyanoethylene, each having a different rate coefficient. Eqns. (15) and (16) apply.

$$-\mathrm{d}[\mathrm{TCE}]_t/\mathrm{d}t = k_1[\mathrm{TCE}]_\pi[\mathrm{MMA}] + k_2[\mathrm{TCE}]_f[\mathrm{MMA}] \tag{15}$$

$$k_{\mathrm{exp.}} = (k_1K[\mathrm{MMA}] + k_2)/(1 + K[\mathrm{MMA}]) \tag{16}$$

From the above six equations, $k_{\mathrm{exp.}}$ of eqn. (10) is independent of the amine concentration, and pathway (*c*) is rejected immediately. Eqns. (6), (8), and (14) contain the [MMA] term only in the denominator, *i.e.*, in these cases increase in the amine concentration must decrease the corresponding rate coefficients. Only eqns. (12) and (16) are in agreement with the increase of the rate coefficient with the increase in the amine concentration in the *N*-methylaniline–tetracyanoethylene system. A constancy in the rate coefficients, as found experimentally for the dimethylaniline–tetracyanoethylene system,[3] is possible only if, in the equation corresponding to (12), $K[\mathrm{DMA}] \gg 1$, and then $k_{\mathrm{exp.}} = k_1$. The same result is obtained if most of the tetracyanoethylene is included in the π-complex, as in this case situation (*c*) reduces to (*d*), or when $k_2 \ll k_1K[\mathrm{DMA}]$ in the equation corresponding to (16), but then (*f*) reduces to (*d*). In the dimethylaniline–tetracyanoethylene system most of the tetracyanoethylene was incorporated in the π-complex. By using the values of *K* at 32·5° and the region of concentration of *NN*-dimethylaniline studied in the previous work,[3] a decrease of only 15% in the rate coefficient is expected in this system. The scatter of the rate coefficients is of this order of magnitude, but the rate coefficients seems to decrease slowly rather than increase with increasing amine concentration. This is probably a secondary effect, as the concentration of *NN*-dimethylaniline in the medium is changed from 4 to 12%, so that the corresponding decrease in the dielectric constant may be responsible for the decrease of the rate coefficients. Effects of such magnitude were found for the addition of similar concentrations of benzene or carbon tetrachloride to the reaction medium.[3]* Eqn. (12) and pathway (*d*) thus describe the behaviour of the *NN*-dimethylaniline–tetracyanoethylene system. In the *N*-methylaniline–tetracyanoethylene system both *K* and the amine concentrations used are lower, and 1 cannot be neglected in comparison to *K*[MMA]. At 32·5° the values of *K*[MMA] vary from 3 to 0·6 at the concentrations studied. Thus a graph of $k_{\mathrm{exp.}}$ against $K[\mathrm{MMA}]/(1 + K[\mathrm{MMA}])$ has to be linear, with a slope equal to k_1. Such plot is given in Fig. 3 for the three temperatures studied. The graphs are linear, but the intercept is zero only at 48°, while at the two other temperatures small negative intercepts (—0·25 and —0·27) are obtained, so that probably a curvature exists at low amine concentrations. Nevertheless, the values of 10^2k_2 which were obtained from the slopes (2·40, 3·04, and 3·60, at 32·5, 40, and 48°) give an activation energy of 5·4 kcal. mole^{-1} and an activation entropy of —48 e.u., which are in agreement with the similar values found in the reaction with *NN*-dimethylaniline,[3] and may be explained in the same manner. The activation energy is somewhat lower and the activation entropy is similar, when comparison is made with the values obtained when the tetracyanoethylene concentrations were varied at constant amine concentration (last values of Table 8). Hence, the kinetics are in accordance with pathway (*d*), *i.e.*,

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* There are some indications that in the low amine concentration ranges, when the medium effect of the amine is negligible, the rate coefficients decrease in this system also with decreasing amine concentrations.[9]

[9] Rappoport and Horowitz, unpublished results.

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the π-complex is again an essential intermediate in the substitution pattern. However, the present system gives no information on the nature of the process involved, and the simple " exchange " mechanism between complexes and free *N*-methylaniline during the formation of the σ-complex, as suggested previously for the interpretation of the kinetics, may be applied here, with no need for an " activated π-complex." [3]

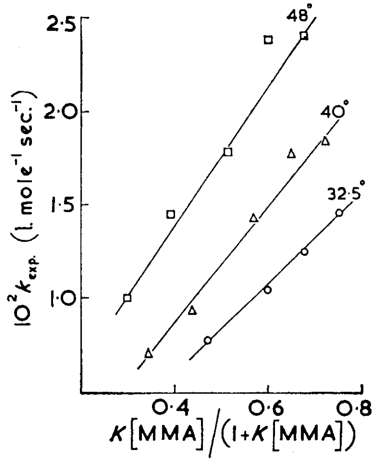
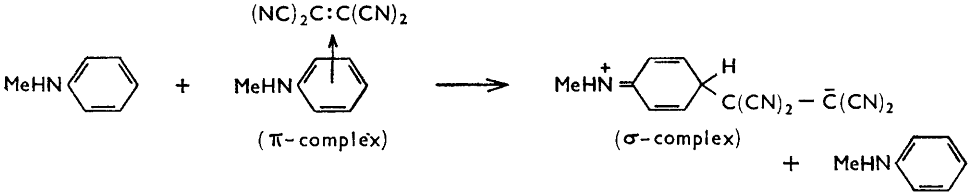
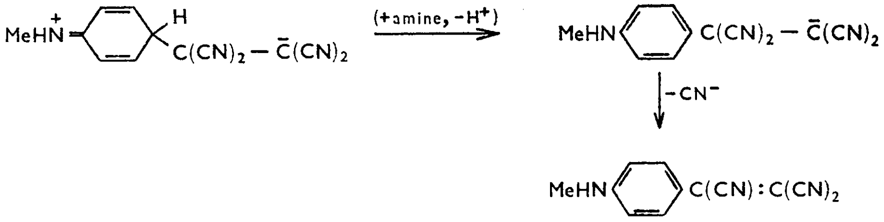


FIG. 3. Dependence on K[MMA]/(1 + K[MMA]) of the rate coefficient for the π-complex ⟶ σ-complex reaction.



The process corresponding to k_1 is a measure of the nucleophilicity of the *para*-position towards tetracyanoethylene. The fact that the attack on *N*-methylaniline is faster than that on *NN*-dimethylaniline shows that this position is more nucleophilic in *N*-methylaniline; this is due to the lower basicity of this amine, resulting in higher contributions of resonance structures having a negative charge at the *para*-position. Indeed, the order of reactivity of dialkylanilines in proton exchange in the *para*-position is the opposite of their basicity.[10]

Although measurements were conducted on the increase in the absorption due to the σ-complex, spectroscopic evidence (as $\lambda_{max.}$, ε) for its structure is missing, as it is masked by the formation of side-products at low amine concentration. However, the arguments which were put forward [3] against structures isomeric to the σ-complex are still valid in this system. The dependence of the rates of the σ ⟶ final product reaction on the nature of various amines is additional proof that this step is indeed a slow abstraction of a proton from the σ-complex, followed by departure of a cyanide ion from the resulting carbanion.



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[10] Tice, Lee, and Kendall, *J. Amer. Chem. Soc.*, **1963**, **85**, 329.

The fact that the efficiency of various bases as proton abstractors is related to their basicity in water in most cases, is again an example of the rate equilibria relationship involving protons.[11] The lack of linearity between the logarithms of the rate coefficients and the p*K* values (Fig. 2) is not surprising. The activation energies for the reactions of the various amines (Table 6) show that such a linear relationship is expected at least for the *NN*-dialkylanilines at higher temperatures. Although the order of basicity of amines is similar in protic and aprotic solvents,[12] a linear free-energy relationship including all the amines could not be expected if an important change is made in the structure. The transition from *N*-alkylanilines to *NN*-dialkylanilines is such a change, as shown by the different linear inductive free-energy relationships for di- and tri-alkylamines.[13]

The rates of proton abstraction from the two σ-complexes (that of *N*-methylaniline and that of *NN*-dimethylaniline [3]) by dimethylaniline are in a ratio of 1 : 2, and the activation energies and entropies are similar. This points both to the similar acidity of the proton in the two σ-complexes, and to the similarity of the two proton abstraction processes.

The increase in the second-order rate coefficients with the amine concentration may have three causes: (*i*) The concentration of the σ-complex is lower at lower amine concentrations, as a result of side-reactions or of incomplete formation of the σ-complex. The incomplete formation of the final product can thus be a result of loss of tetracyanoethylene by side-reactions. (*ii*) Intervention of an additional mechanism for the elimination of hydrogen cyanide from the σ-complex at low concentrations of base. (*iii*) A catalytic effect of the amine in the bimolecular proton elimination. The observation that constant final absorption at the wavelength ascribed to the σ-complex is obtained, in spite of the change in the amine concentrations which is much higher than in the kinetic runs, speaks against possibility (*i*). The dependence of the concentration of σ-complex solely on the initial concentration of tetracyanoethylene is a strong argument for the complete formation of the σ-complex, but, even if some tetracyanoethylene was lost in side-reactions prior to the formation of the σ-complex, this loss is nevertheless equal in all the experiments compared. In addition, the rate coefficients change with a change in the concentration of *N*-methylaniline when the same initial σ-complex was used (Table 5). Of the two plausible mechanisms corresponding to possibility (*ii*) a concurrent *E*2 elimination will have no effect on the kinetics. A reaction scheme in which the cyanide ion leaves first in a rate-determining step, and the proton afterwards, will be similar to that suggested for the tricyanovinylation by tricyanovinyl chloride.[1] Such a reaction, being unimolecular, will be more important at low concentrations of base, but a decrease in the rate coefficients with increase in the amine concentration is expected if this process occurs concurrently with the carbanionic elimination *E*1*cB*. Possibility (*iii*) can be augmented by the following facts. (1) The dependence of the rate coefficients on the amine concentrations is linear (Fig. 1). (2) The effect is specific to *N*-alkylanilines, and was found neither in the tetracyanoethylene–*NN*-dimethylaniline system nor in the effect of various dialkylanilines on the σ-complex $\longrightarrow$ final product reaction (Table 5). (3) From all the bases studied the *N*-alkylanilines are the most likely to form hydrogen-bonded entities with themselves, with the π-complex, or with the σ-complex. The systems studied are too limited to permit a decision as to whether the last factor is responsible for the observed effect, and, if it is, whether it operates in the ground state or in the transition state. In principle, a reaction order higher than unity in the amine would be in agreement with the presence of hydrogen-bonded entities in both the $\pi \longrightarrow \sigma$ and the $\sigma \longrightarrow$ final product reactions. The hydrogen on the positively charged alkylamino-group in the σ-complex is much more likely to form hydrogen bonds than that in the neutral amine molecule, so that the effect can be a result

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[11] Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, New York, 1959, p. 155; Pearson and Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

[12] Hall, *J. Phys. Chem.*, 1956, **60**, 63.

[13] Hall, *J. Amer. Chem. Soc.*, 1957, **79**, 5441.

of a specific solvation of the transition state, leading to the σ-complex by an amine molecule. This effect may be linear with increase in the amine concentration in a relatively large range of amine concentrations.

Much higher response to solvent effects is found for the $\sigma \longrightarrow$ final product reaction than in the $\pi \longrightarrow \sigma$ reaction. In the tetracyanoethylene–*NN*-dimethylaniline system [3] the intrinsically slower $\pi \longrightarrow \sigma$-reaction in chloroform had a higher response to solvent effects. On the other hand, the $\sigma \longrightarrow$ final product reaction, which is much slower in the present system, has a much higher response to solvent effects than the corresponding reaction in the *NN*-dimethylaniline system. This is again an example of the principle, found in some nucleophilic reactions on double bonds,[1,14] that the less reactive system is " compensated " by higher response to medium effects.

Formation of side-product at low concentrations of amine was found also in related systems. We obtained a mixture of products from the reaction of *NN*-diethylaniline with tetracyanoethylene when the concentrations of the former were low. In this mixture, the anion of pentacyanopropene [15] could be isolated as its silver salt, accompanied by low concentrations of the *p*-tricyanovinylation product, which becomes the major product if the amine concentration is high.[9] This may result from relatively rapid unimolecular transformations, or from bimolecular reactions of the σ-complex with tetracyanoethylene, competing effectively with the slower proton abstraction at low concentrations of base.

EXPERIMENTAL

N-Methylaniline (Eastman; free from dimethylaniline), dried over potassium hydroxide and distilled twice under nitrogen, had b. p. 90°/20 mm., n_D^{28} 1·570. It was stored at 0° under nitrogen. Tetracyanoethylene (Aldrich), crystallised from chlorobenzene, had m. p. 198° (sealed tube). The purification of the solvents, the kinetic procedure, and the treatment of data have been described previously.[3]

Product Analysis.—Tetracyanoethylene (370 mg.) and *N*-methylaniline (875 mg.) were dissolved in chloroform (25 ml.), and the mixture was stirred for 2 hr.; the solvent was evaporated and the residue (480 mg., 69%) gave red-violet needles, m. p. 178—179° (from ethanol).[2] Measurements during the kinetic runs showed that only one peak, at 486 mμ ($\lambda_{max.}$ of *N*-methyl-4-tricyanovinylaniline), is formed. When low and similar concentrations of the two reactants were used, a new maximum in the absorption was found at 568 mμ. When $3{\cdot}44 \times 10^{-3}$ mole $l.^{-1}$ of tetracyanoethylene reacted for 100 hr. at 32·5° with (*a*) $3{\cdot}50 \times 10^{-3}$ mole $l.^{-1}$, (*b*) $6{\cdot}85 \times 10^{-3}$ mole $l.^{-1}$, and (*c*) $13{\cdot}6 \times 10^{-3}$ mole $l.^{-1}$-*N*-methylaniline, no peak was found at 486 mμ in (*a*), but a peak with optical density of 1·088 was found at 568 mμ. The reaction mixture still contained free tetracyanoethylene (as shown by the formation of the blue π-complex with *NN*-dimethylaniline). In (*b*) the optical density at 568 mμ was 1·312, and 0·8% of *N*-methyl-4-tricyanovinylaniline was formed; the solution still contained 12% of tetracyanoethylene. In (*c*), the absorption at 568 mμ was 1·050, and 1·65% of the final product was formed. On addition of *N*-n-butylaniline to the last reaction mixture, 27% of the final product was formed.

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[14] Patai and Rappoport, *J.*, 1962, 383.

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