**261.** *Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part VII.[1] The " Element Effect " in Tricyanovinylation. The Reaction of Tricyanovinyl Chloride with* NN-*Dialkylanilines.*

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The kinetics of the formation of NN-dialkyl-4-tricyanovinylanilines from tricyanovinyl chloride and NN-dialkylanilines in chloroform has been studied by a spectrophotometric method. The reactions are second-order (first-order in each of the reactants). The order of reactivity was: NN-dibutyl- > NN-diethyl- > NN-dipropyl- > NN-dimethyl-aniline. The product was formed much faster than in the corresponding reaction with tetracyanoethylene, and a small inverse deuterium isotope effect occurred in the reaction with dimethyl[4-^{2}H]aniline. The activation energies for all the dialkylanilines were very low (1·4—2·6 kcal. mole^{-1}), and the activation entropies had high negative values ($\sim$—55 e.u.). No general base-catalysis was observed in the presence of amines. The reaction rates were enhanced by an increase in the dielectric constant of the medium. A detailed reaction mechanism is suggested, involving a zwitterionic intermediate which loses, first the chloride anion, and afterwards the proton.

THE reaction in chloroform of NN-dimethylaniline with tetracyanoethylene, giving NN-dimethyl-4-tricyanovinylaniline, is a three-step process,[2] involving formation of a π-complex of the reactants and its decomposition to a relatively stable σ-complex (I) which in turn gives the final product. The amine-catalysed elimination of hydrogen cyanide from the complex (I) was suggested to proceed through a carbanionic mechanism.
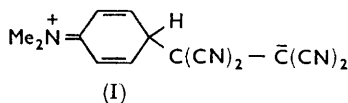
The complex (I) may be regarded both as the σ-complex of an electrophilic aromatic substitution and as the carbanionic intermediate of a vinylic aliphatic substitution. Hence, it was hoped that here, in a single reaction system, both the deuterium isotope effect[3a] and the

Me$_2$N$\overset{+}{=}$⟨ ⟩$\overset{H}{\underset{C(CN)_2 - \bar{C}(CN)_2}{\diagup}}$

(I)

" element effect "[3b,4] could be utilised in order to evaluate the relative importance of the C–H and C–CN bond-breaking in the rate-determining step of the reaction. Furthermore, the effect of the substituent X in the system (NC)$_2$C:C(CN)X on the formation and decomposition of the π-complexes could be studied. To this end the reactions of tricyanovinyl chloride, which was shown to tricyanovinylate NN-dimethylaniline,[5] were studied kinetically with various NN-dialkylanilines.

$$(NC)_2C \colon C(CN)Cl + C_6H_5 \cdot NR_2 \longrightarrow p\text{-}R_2N \cdot C_6H_4 \cdot C(CN) \colon C(CN)_2 + HCl$$

RESULTS

The reactions of four dialkylanilines C$_6$H$_5$·NR$_2$ (R = Me, Et, Pr^n, Bu^n) with tricyanovinyl chloride were studied spectrophotometrically in chloroform by following the formation of the NN-dialkyl-4-tricyanovinylanilines at their $\lambda_{max.}$, where both reactants show negligible absorption. The reaction was second-order (first-order in both the tricyanovinyl chloride and the dialkylaniline, the latter being always in at least a twenty-fold excess). The initial concentration of the tricyanovinyl chloride was usually changed 3—5 fold and that of the amine ten-fold, at least at one temperature. The pseudo-first-order rate coefficients, which were obtained from the slopes of the log $(D_\infty - D_t)$

[1] Part VI, Rappoport, Degani, and Patai, *J.*, 1963, 4513.
[2] Rappoport, *J.*, 1963, 4498.
[3] Melander, "Isotope Effects on Reaction Rates," Roland Press Co., New York, 1960, (a) p. 98; (b) p. 122.
[4] Bunnett, Garbisch, and Pruitt, *J. Amer. Chem. Soc.*, 1957, **79**, 385; Bender and Jones, *J. Org. Chem.*, 1962, **27**, 3771.
[5] Dickinson, Wiley, and McKusick, *J. Amer. Chem. Soc.*, 1960, **82**, 6132.

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TABLE 1.

First-order (k_1) and second-order $(k_2 = k_1/[\text{Amine}])$ rate coefficients for the reaction of NN-dialkylanilines with tricyanovinyl chloride (TCVC) in chloroform at various temperatures.

NN-Dimethylaniline (DMA)   At 32·5°

$10^5[\text{TCVC}]$ [a] (moles l.$^{-1}$)...	0·76	1·51	3·02	3·02	3·02 [b]	3·02	3·12 [c]	4·06
$10^4[\text{DMA}]$ (moles l.$^{-1}$) ...	51	119	68	34	137	274	0·156	49
10^3k_1 (sec.$^{-1}$)	0·53	1·24	0·73	0·35	1·45	2·79	0·00167	0·54
k_2 (l. mole^{-1} sec.$^{-1}$)	0·104	0·104	0·107	0·103	0·106	0·102	0·107	0·109
$10^5[\text{TCVC}]$ [d] (moles l.$^{-1}$)...	2·4	2·4	2·4	2·4	2·4			
$10^4[\text{DMA}]$ [e] (moles l.$^{-1}$) ...	86·2	109	110	138	215·5			
10^3k_1 (sec.$^{-1}$)	0·922	1·16	1·17	1·46	2·29			
k_2 (l. mole^{-1} sec.$^{-1}$)	0·107	0·106	0·106	0·106	0·106			

Average $k_2 = 0·106 \pm 0·002$ l. mole^{-1} sec.$^{-1}$.

At 40°.   At 48°.

$10^5[\text{TCVC}]$ (moles l.$^{-1}$) ...	1·39	3·48	3·48	4·35	1·39	2·09	2·78	3·48
$10^4[\text{DMA}]$ (moles l.$^{-1}$) ...	27·6	36·8	165·6	73·6	32·3	53·9	107·8	172·4
10^3k_1 (sec.$^{-1}$)	0·336	0·444	2·00	0·91	0·419	0·708	1·43	2·25
k_2 (l. mole^{-1} sec.$^{-1}$)	0·122	0·121	0·121	0·122	0·130	0·131	0·133	0·131

Average $k_2 = 0·121 \pm 0·001$ Average $k_2 = 0·131 \pm 0·001$
l. mole^{-1} sec.$^{-1}$.   l. mole^{-1} sec.$^{-1}$.

NN-Dimethyl[4-^{2}H]aniline (DDMA)   At 32·5°.

$10^5[\text{TCVC}]$ (moles l.$^{-1}$) ...	1·62	1·65	2·16	2·28	2·9	3·01	3·48	3·48	3·48
$10^4[\text{DDMA}]$ [f] (moles l.$^{-1}$)	137	182	227	182	110	206	15·9	47·1	79·5
10^3k_1 (sec.$^{-1}$)	1·65	2·21	2·74	2·26	1·32	2·51	0·197	0·549	0·95
k_2 (l. mole^{-1} sec.$^{-1}$)	0·121	0·122	0·121	0·124	0·121	0·122	0·124	0·117	0·120

Average $k_2 = 0·121 \pm 0·002$ l. mole^{-1} sec.$^{-1}$.

$10^5[\text{TCVC}]$ (moles l.$^{-1}$) ...	1·74	2·44	3·48	3·48	3·48
$10^4[\text{DMA}]$ [g] (moles l.$^{-1}$) ...	11·2	48·6	56·1	97·2	112·2
10^3k_1 (sec.$^{-1}$)	0·122	0·518	0·618	1·03	1·205
k_2 (l. mole^{-1} sec.$^{-1}$)	0·110	0·107	0·111	0·107	0·109

Average $k_2 = 0·109 \pm 0·002$ l. mole^{-1} sec.$^{-1}$.

NN-Diethylaniline (DEA)   At 32·5°.

$10^5[\text{TCVC}]$ (moles l.$^{-1}$) ...	0·76	1·51	3·02	3·02	3·02 [h]	3·37
$10^4[\text{DEA}]$ (moles l.$^{-1}$) ...	4·12	5·47	5·47	13·7	137·0	12·90
10^3k_1 (sec.$^{-1}$)	0·505	0·655	0·683	1·78	14·7	1·50
k_2 (l. mole^{-1} sec.$^{-1}$)	1·23	1·20	1·25	1·30	1·07 [h]	1·17

Average $k_2 = 1·20 \pm 0·08$ l. mole^{-1} sec.$^{-1}$.

At 40°.

$10^5[\text{TCVC}]$ (moles l.$^{-1}$) ...	2·09	2·09	2·44	2·78	2·78	2·78	3·48
$10^4[\text{DEA}]$ (moles l.$^{-1}$)......	3·75	12·9	12·5	6·45	7·5	9·62	25·5
10^3k_1 (sec.$^{-1}$)	0·479	1·585	1·51	0·86	0·88	1·18	3·02
k_2 (l. mole^{-1} sec.$^{-1}$)	1·28	1·23	1·22	1·25	1·17	1·20	1·18

Average $k_2 = 1·22 \pm 0·04$ l. mole^{-1} sec.$^{-1}$.

At 48°.

$10^5[\text{TCVC}]$ (moles l.$^{-1}$) ...	1·39	2·78	2·78	3·13	3·13
$10^4[\text{DEA}]$ (moles l.$^{-1}$) ...	3·75	6·0	7·5	15·0	21·0
10^3k_1 (sec.$^{-1}$)	0·757	0·805	1·03	1·98	2·81
k_2 (l. mole^{-1} sec.$^{-1}$)	1·31	1·34	1·37	1·32	1·34

Average $k_2 = 1·34 \pm 0·02$ l. mole^{-1} sec.$^{-1}$.

NN-Dipropylaniline (DPA)   At 32·5°.

$10^5[\text{TCVC}]$ (moles l.$^{-1}$) ...	1·21	2·42	2·42	3·02	3·02	3·62
$10^4[\text{DPA}]$ (moles l.$^{-1}$) ...	3·06	4·90	8·75	6·12	17·5	21·9
10^3k_1 (sec.$^{-1}$)	0·310	0·477	0·823	0·573	1·64	2·02
k_2 (l. mole^{-1} sec.$^{-1}$)	1·01	0·97	0·94	0·94	0·94	0·92

Average $k_2 = 0·95 \pm 0·03$ l. mole^{-1} sec.$^{-1}$.

TABLE 1. *(Continued.)*

	At 40°.					At 48°.			
10^5[TCVC] (moles l.$^{-1}$) ...	1·51	3·02	3·02	3·59	3·62	1·21	1·81	2·42	3·02
10^4[DPA] (moles l.$^{-1}$) ...	5·11	7·2	14·4	19·0	14·1	3·20	6·39	12·78	19·17
$10^3 k_1$ (sec.$^{-1}$)	0·534	0·750	1·505	2·00	1·415	0·364	0·715	1·50	2·26
k_2 (l. mole^{-1} sec.$^{-1}$)	1·04	1·04	1·05	1·05	1·00	1·14	1·12	1·17	1·18

Average $k_2 = 1·03 \pm 0·02$ l. mole^{-1} sec.$^{-1}$.   Average $k_2 = 1·15 \pm 0·03$ l. mole^{-1} sec.$^{-1}$.

NN-Dibutylaniline (DBA)   At 32·5°.

10^5[TCVC] (moles l.$^{-1}$) ...	0·38	0·76	1·22	1·22	1·51	2·39
10^4[DBA] (moles l.$^{-1}$) ...	20·6	8·22	1·09	13·7	27·4	17·2
$10^3 k_1$ (sec.$^{-1}$)	2·72	1·09	0·142	1·82	3·78	2·19
k_2 (l. mole^{-1} sec.$^{-1}$)	1·32	1·33	1·30	1·33	1·32	1·27

Average $k_2 = 1·31 \pm 0·02$ l. mole^{-1} sec.$^{-1}$.

	At 40°.				At 48°.			
10^5[TCVC] (moles l.$^{-1}$) ...	1·39	2·02	2·44	2·78	1·39	2·08	2·78	3·13
10^4[DBA] (moles l.$^{-1}$) ...	2·65	5·3	15·9	10·6	2·65	5·3	10·6	15·9
$10^3 k_1$ (sec.$^{-1}$)	0·374	0·756	2·34	1·53	0·414	0·836	1·658	2·50
k_2 (l. mole^{-1} sec.$^{-1}$)	1·41	1·43	1·47	1·44	1·56	1·58	1·56	1·57

Average $k_2 = 1·44 \pm 0·02$ l. mole^{-1} sec.$^{-1}$.   Average $k_2 = 1·57 \pm 0·01$ l. mole^{-1} sec.$^{-1}$.

a Prepared from tetramethylammonium tricyanoethenolate. *b* Average of three experiments ($k = 0·108$, $0·106$, and $0·104$ l. mole^{-1} sec.$^{-1}$). *c* Very slow run; final value had been measured after one month. Rate coefficient calculated only from one point (at $\tau_{\frac{1}{2}} = 48$ hr.). *d* Prepared from tetraethylammonium tricyanoethenolate. *e* Prepared for these experiments by the decomposition of the 4-iodomagnesium derivative with water. *f* Prepared by the decomposition of 4-iodomagnesium-*NN*-dimethylaniline with D$_2$O. The 4-position is 54% deuterated. *g* Different preparation of amine by method *f*; it contained 53% of 4-deuterium. *h* $\tau_{\frac{1}{2}} = 47$ sec.

against time graphs, where D_t and D_∞ are the optical densities at time t and at the end of the reaction, were divided by the amine concentration, giving the second-order rate coefficients. The reactions were followed to completion, when the final value taken after ten or more half-lives had remained constant for one day. No evidence was found for any formation of *NN*-dialkyl-4-(1-chloro-2,2-dicyanovinyl)aniline, a product that would have been formed by elimination of hydrogen cyanide. The reproducibility of the rate coefficients was good (± 1—2%) even when using different preparations of tricyanovinyl chloride and different batches of chloroform. It is interesting to note that the intrinsically labile tricyanovinyl chloride, in its reaction with dimethylaniline, is much less susceptible to impurities in the solvent than is tetracyanoethylene; a batch of chloroform which gave reproducible rate coefficients in the tricyanovinyl chloride–*NN*-dimethylaniline reaction gave, under the same conditions, erratic and irreproducible rate coefficients in the tetra-cyanoethylene–dimethylaniline reaction. The rate coefficients, and the mean values

TABLE 2.

Sample run for the reaction of tricyanovinyl chloride ($3·02 \times 10^{-5}$ mole l.$^{-1}$) with
NN-dimethylaniline ($0·34 \times 10^{-2}$ mole l.$^{-1}$) in chloroform at 32·5°.

Time (sec.) ...	104	240	450	570	690	900	1500	2040	2520	4200	4920	7380	9960
$10^3 D$ at 518 mμ	43	105	183	233	277	378	547	680	782	1045	1093	1238	1305
Reaction (%)	3·18	7·77	13·6	17·3	20·5	26·2	40·5	50·4	58·0	77·5	81·0	91·5	96·5
$10^4 k_1$ (sec.$^{-1}$)	3·3	3·4	3·3	3·4	3·4	3·5	3·5	3·6	3·6	3·6	3·5	3·4	3·4

Average $k_1 = 3·5 \times 10^{-4}$ sec.$^{-1}$; $k_2 = k_1/[\text{DMA}] = 1·03 \times 10^{-1}$ l. mole^{-1} sec.$^{-1}$.

with the corresponding standard deviations at three temperatures, are given in Table 1, and a sample run is given in Table 2.

Deuterium Isotope Effect.—The rate of the reaction of dimethyl[4-^{2}H]aniline with tricyanovinyl chloride was measured under the same conditions as for the non-deuterated

compound. For control experiments, dimethylaniline which was prepared by the same procedure as the 4-deuterio-compound (*i.e.*, by iodination of dimethylaniline, Grignard reaction, and decomposition with water instead of deuterium oxide) was used; the rate coefficients were the same as those with " ordinary " dimethylaniline. Two independent preparations of the 4-deuterio-compound (53% 4-^{2}H and 54% 4-^{2}H) gave rate coefficients which were higher than with the non-deuterated compound, but which differed by 10% from each other. From the average of the rate coefficients for the two series of experiments, the measured deuterium isotope effect is $k_D/k_H = 1.085$ at 54% deuteration. Extrapolation to the fully deuterated compound gives an inverse isotope effect, $k_D/k_H = 1.16$.

Lack of Accumulation of Intermediate.—No evidence was found for the accumulation of intermediates in the course of the reactions. If such intermediates are formed in measurable quantities, their formation is reversible; this is shown by the free availability of all the tricyanovinyl chloride, not incorporated in the end-product, during the intermediate stages of the reaction. To a reacting mixture of tricyanovinyl chloride and dimethylaniline (DMA) (the less reactive amine) after 22% reaction, *NN*-diethylaniline (DEA) was added in a concentration similar to that of the dimethylaniline, while a second portion of the original mixture was allowed to react further without interference. The increase in rate of the modified reaction compared to the unmodified one is in agreement with the intrusion of a competitive reaction of the diethylaniline on 78% of the initially present

TABLE 3.

Apparent ($k_{app.}$) and calculated [$(k_1 + k_1')_{calc.}$] rate coefficients for the reactions of tricyanovinyl chloride (TCVC) with various amines, with interference by a second amine.

No.	Reaction	10^4[Amine] ‡ (moles l.$^{-1}$) First	Second	10^5[TCVC] (moles l.$^{-1}$)	Temp.	% Reaction before addn. of 2nd amine	10^4k_1 * (sec.$^{-1}$)	10^4k_1' † (sec.$^{-1}$)	10^4($k_1 + k_1'$) (calc.) (sec.$^{-1}$)	10^4$k_{app.}$ (sec.$^{-1}$)
1	Single	DBA 5·62	— —	3·02	32·5°	28	5·98	3·17	9·15	—
1	Concurrent	DBA 4·50	DMA 30·2	2·42	32·5	—	—	—	—	9·05
2	Single	DMA 15·1	— —	3·02	32·5	22	0·127	1·695	1·822	—
2	Concurrent	DMA 12·1	DEA 14·43	2·42	32·5	—	—	—	—	1·840
3	Single	DMA 18·4	— —	2·78	40	12·5	0·178	2·440	2·618	—
3	Concurrent	DMA 14·7	DBA 16·9	2·22	40	—	—	—	—	2·440
4	Single	DMA 15·1	— —	3·02	32·5	21	0·130	1·450	1·580	—
4	Concurrent	DMA 12·1	DPA 15·3	2·42	32·5	—	—	—	—	1·500

‡ Abbreviations as in Table 1. * Rate coefficient for the reaction of tricyanovinyl chloride with the first amine; calculated from the single (unmodified) reaction. † Rate coefficient for the reaction of the second amine with tricyanovinyl chloride (from Table 1).

tricyanovinyl chloride. Thus, the reaction was first-order in the residual tricyanovinyl chloride, with an apparent rate coefficient, $k_{app.}$, in agreement with the sum ($k_{DMA} + k_{DEA}$), where k_{DMA} was obtained from the unmodified reaction, and k_{DEA} from Table 1. Similar results were obtained with other slow-amine–fast-amine systems, and, in a complementary run in which the rapid amine (di-n-butylaniline) was introduced first and a 6·7 molar excess of a slower amine (dimethylaniline) was introduced later, again $k_{app.} = k_{DMA} + k_{DBA}$. Owing to the similarity of the spectra of the various *NN*-dialkyl-4-tricyanovinylanilines the final spectra of the solutions could not be used for an analysis of the distribution of the products. These experiments are summarised in Table 3.

Irreversibility of the Reaction.—The reaction was rendered completely irreversible by

capture of the hydrochloric acid produced by the excess of the amine present, and could, accordingly, be studied up to 100%. The absorption of 9.6×10^{-6} mole l.$^{-1}$ of NN-dimethyltricyanovinylaniline (TCVDMA) in chloroform solutions of hydrochloric acid (10^{-3}M and 10^{-2}M) remained unchanged, and with 0.1M-hydrochloric acid the absorption was lowered by about 5%. If this decrease is ascribed to protonation (giving a salt which has no absorption in this region), the equilibrium constant for the reaction, [TCVDMA] + [H$^+$] $\rightleftharpoons$ [TCVDMAH$^+$], is 0.55 l. mole^{-1}. Hence, with 3×10^{-5} mole l.$^{-1}$ of tricyanovinyl chloride (a typical concentration studied) only 4.5×10^{-10} mole l.$^{-1}$ of TCVDMAH$^+$ exists at the end of the reaction, and the reaction is practically irreversible.

π-*Complex Formation.*—In none of the reactions studied was there any appearance of colour which could be attributed to the formation of a π-complex at the beginning of the reaction, and the D_0 values extrapolated to $t = 0$ were always zero, within the accuracy of the experiment. The fact that the concentration of the π-complex in kinetic conditions is too small to be detected can be justified by the following calculation. Using the value $K_{eq.} = 15$ l. mole^{-1} for the dimethylaniline–tetracyanoethylene π-complex,[2] and the value 3.44 for $K_{eq.}$(tetracyanoethylene)/$K_{eq.}$(tricyanovinyl chloride) with toluene as donor [5,6] (the value 6.1 found for durene [5] would give an even lower $K_{eq.}$), $K_{eq.} = 4.4$ l. mole^{-1} for the dimethylaniline–tricyanovinyl chloride π-complex. Using $\varepsilon = 3400$, as for the tetracyanoethylene–dimethylaniline π-complex,[2] it can be calculated that, even with the highest concentrations of the reactants studied, the expected optical density is only 0.010 (which is the limit of accuracy of the spectrophotometer) while $\Delta D_{product}/\Delta t$ is of the order or 0.003 optical density units per second at the beginning of such experiments. Owing

TABLE 4.

Second-order rate coefficients, k_2 (l. mole^{-1} sec.$^{-1}$), for the reaction of NN-dialkyl-anilines * with tricyanovinyl chloride (TCVC) in chloroform–ethylene dichloride (EDC) mixtures at $32.5°$.

[EDC] (%, v/v)	0	8	20	28	36	40	48	56	60	72	80	84	88	92
10^5[TCVC]	4.06	4.06	4.06	3.16	—	3.16	—	3.37	—	3.37	—	—	3.16	—
10^3[DMA]	4.92	4.92	4.92	4.92	—	4.92	—	4.92	—	4.92	—	—	3.94	—
k_2	0.109	0.124	0.133	0.151	—	0.167	—	0.188	—	0.203	—	—	0.232	—
k_2 (calc.) †	0.110	0.122	0.137	0.148	—	0.164	—	0.186	—	0.207	—	—	0.229	—
10^5[TCVC]	3.37	—	3.37	—	3.37	—	3.37	—	3.48	3.37	—	3.48	—	3.37
10^3[DEA]	1.29	—	1.29	—	1.29	—	0.645	—	0.645	0.645	—	0.645	—	0.645
k_2	1.17	—	1.41	—	1.53	—	1.61	—	1.70	1.72	—	1.79	—	1.79
10^5[TCVC]	3.02	3.02	3.02	—	3.02	—	3.02	—	3.02	—	3.02	—	—	3.02
10^3[DPA]	0.72	0.72	0.61	—	0.72	—	0.72	—	0.72	—	0.72	—	—	0.72
k_2	0.94	1.00	1.09	—	1.21	—	1.23	—	1.32	—	1.34	—	—	1.34
10^5[TCVC]	2.39	—	1.62	3.37	—	2.87	—	3.37	—	3.37	—	3.37	—	3.37
10^3[DBA]	1.72	—	1.72	1.72	—	1.72	—	1.72	—	1.72	—	0.86	—	0.86
k_2	1.27	—	1.51	1.61	—	1.71	—	1.74	—	1.79	—	1.79	—	1.78

* Abbreviations as in Table 1. † Calculated from the least-squares equation: $k = 0.11 + 1.35 \times 10^{-3}$[EDC].

to the higher reactivity of the other amines, their concentrations in the kinetic experiments were even lower. By using the $\Delta H°$ value of the tetracyanoethylene–dimethylaniline π-complex, it can be shown that with all amines except dimethylaniline, even at $0°$, the π-complex will be undetectable. With dimethylaniline, when the reactant concentrations were higher than in the kinetic work, a transient violet colour was observed for one second before the solution changed to the red colour of the final product.

When any of the amines was mixed with tricyanovinyl chloride in chloroform at $-60°$ or below, a blue colour appeared which we ascribe to π-complexes, but the solutions became

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

red after a few minutes. As in other cases [2,7] where the decomposition of π-complexes is decreased by lowering the dielectric constant of the solvent, the same complexes were somewhat more stable in carbon tetrachloride, and much more stable in light petroleum, *e.g.*, the blue dimethylaniline–tricyanovinyl chloride complex is stable for at least one hour in light petroleum at −60°. Moreover, as the formation of the final product is also slower under these conditions, it is observed that the formation of the blue colour is rapid and reversible and favoured by lower temperatures; these are characteristic properties of π-complexes.[8] When the blue solution at −60° was brought rapidly to room temperature it became immediately colourless, but rapid cooling soon restored the blue colour.

The Effect of Solvents.—Increase in the dielectric constant of the solvent by gradual addition of ethylene dichloride (EDC) to the chloroform solvent somewhat enhanced the reaction rates (Table 4) with all the amines studied. The rise in the rate coefficients with dimethylaniline was linear with additions of ethylene dichloride up to 88% (v/v), but curvatures appeared earlier with other amines and the rate coefficients converged to a constant value. The straight portions of the curves were treated by the least-squares method using the equation $k = k_0 (1 + b[\text{EDC}]_{\text{lin.}})$, where $[\text{EDC}]_{\text{lin.}}$ is the percentage volume of ethylene dichloride in the linear portion of the curves. The fit of the data is demonstrated for dimethylaniline in Table 4.

TABLE 5.

Response to solvent effect in tricyanovinylation of aromatic amines by tricyanovinyl chloride in chloroform–ethylene dichloride at 32·5°.

Amine	k_0 (l. mole⁻¹ sec.⁻¹)	10^3b (moles l.⁻¹)	n *	$[\text{EDC}]_{\text{lin.}}$ (max.)	$k_{92\% \text{ EDC}}/k_{\text{chl.}}$
NN-Dimethylaniline	0·110	12·3	8	88	2·13
NN-Diethylaniline	1·19	7·3	5	60	1·50
NN-Dipropylaniline	0·94	8·0	4	36	1·43
NN-Dibutylaniline	1·28	8·7	4	40	1·39
N-Methylaniline † [9]					
π ⟶ σ reaction	$1·02 \times 10^{-2}$	10·9	7	100	2·00 ‡
σ ⟶ final product reaction	$2·80 \times 10^{-6}$	50·0	6	80	5·50 ‡
NN-Dimethylaniline † [2]					
π ⟶ σ reaction	$4·4 \times 10^{-3}$	48·5	8	80	6·05 ‡
σ ⟶ final product reaction	$1·25 \times 10^{-4}$	16·2	8	80	2·52 ‡

* Number of points used for the least-squares calculation. † Reaction with tetracyanoethylene.
‡ Extrapolated value.

The parameters k_0 and b, the upper limit of the region of linearity of the k against [EDC] curves {$[\text{EDC}]_{\text{lin.}}(\text{max.})$} and the ratio of the rate coefficients in 92 and in 0% ethylene dichloride ($k_{92\% \text{ EDC}}/k_{\text{chl.}}$) are given in Table 5, which contains, for comparison, the same parameters for the reactions of *N*-methylaniline and *NN*-dimethylaniline with tetracyanoethylene. The Table shows clearly that the higher the rate of the reaction in chloroform (k_0), the lower is the response of the reaction to solvent effects shown both by b and $[\text{EDC}]_{\text{lin.}}(\text{max})$. The rate enhancement is too low to give more than a general trend, but the three reactive amines ($k_0 = 0·9$—$1·3$) give nearly the same response to solvent effects ($10^3b = 7·3$—$8·7$, $[\text{EDC}]_{\text{lin.}}(\text{max.}) = 40$—$60\%$), while the less reactive one ($k_0 = 0·11$) is more influenced ($10^3b = 12·3$, $[\text{EDC}]_{\text{lin.}}(\text{max.}) = 88\%$). This is demonstrated by the decrease of the $k_{\text{DBA}} : k_{\text{DMA}}$ ratio from 11·7 in pure chloroform to 6·6 in 92% ethylene dichloride–chloroform. The same phenomena are also found in both stages of the tricyanovinylation of *N*-mono- and *NN*-di-methylaniline by tetracyanoethylene.

Activation Parameters.—The activation parameters, which were calculated by the least-squares method from the average rate coefficients of Table 1, are given in Table 6.

[7] Williams, Wiley, and McKusick, *J. Amer. Chem. Soc.*, 1962, **84**, 2210.
[8] Hammick and Yule, *J.*, 1940, 1539; Ross, Basin, Finkelstein, and Leach, *J. Amer. Chem. Soc.*, 1954, **76**, 69.

TABLE 6.

Activation parameters for the tricyanovinylation of NN-dialkylanilines, $C_6H_5 \cdot NR_2$, by tricyanovinyl chloride in chloroform.

R	Me	Et	Prⁿ	Buⁿ
E_a (kcal. mole⁻¹) *	2·6	1·4	2·4	2·2
$\Delta S^{\ddagger}$ (e.u.) †	−56	−55	−52	−52

* Estimated $\pm$ 0·4 kcal. mole⁻¹.   † Estimated $\pm$ 1 e.u.

The most interesting features of these values are the very low activation energies (1·4—2·6 kcal. mole⁻¹) for all the amines. The high negative $\Delta S^{\ddagger}$ values are similar for all the amines (−52 to −56 e.u.).

DISCUSSION

The most striking feature of the tricyanovinylation is the change in kinetic behaviour on going from tetracyanoethylene to tricyanovinyl chloride, although the same final product is obtained. The main differences in behaviour of the two electrophilic double-bond systems, in their reaction with dimethylaniline,[2] are summarised in Table 7. The

TABLE 7.

Characteristic features of the tricyanovinylation of dimethylaniline by tetracyano-ethylene and by tricyanovinyl chloride, both giving NN-dimethyl-4-tricyanovinyl-aniline.

Tetracyanoethylene.[2,9]

1. Rapid π-complex formation with $K_{eq.} = 15$ l. mole⁻¹ at 32·5°.

2. Irreversible transformation of the π-complex to a stable σ-complex; first-order in the π-complex and in the dimethylaniline. $k_2 = 4 \times 10^{-3}$ l. mole⁻¹ sec.⁻¹ at 32·5°.

3. Transformation of the σ-complex to the final product is first-order in dimethylaniline and in the σ-complex. $k_2 = 1·2 \times 10^{-4}$ l. mole⁻¹ sec.⁻¹ at 32·5°.

4. General amine catalysis in the σ-complex ⟶ final product reaction.

5. High normal deuterium isotope effect on the σ-complex ⟶ final product reaction.

6. $E_a = 5·7$ kcal. mole⁻¹ and $\Delta S^{\ddagger} = -50$ e.u. for the $\pi \longrightarrow \sigma$ reaction. $E_a = 12·4$ kcal. mole⁻¹ and $\Delta S^{\ddagger} = -37$ e.u. for the $\sigma \longrightarrow$ final product reaction.

7. Rate increases 6·05-fold in the $\pi \longrightarrow \sigma$ reaction and 2·52-fold in the $\sigma \longrightarrow$ final product reaction on changing the medium from pure chloroform to 92% chloroform–ethylene dichloride.

Tricyanovinyl chloride.

π-Complex formed only at low temperatures; cannot be detected under kinetic conditions (*i.e.*, $K_{eq.}$ must be lower than 3 l. mole⁻¹).

σ-Complex cannot be detected in kinetic concentrations. If formed at all its reversion to the reactants is very rapid.

Formation of the final product is first-order in the dimethylaniline and in the tricyanovinyl chloride. $k_2 = 0·11$ l. mole⁻¹ sec.⁻¹ at 32·5°.

No amine catalysis was found in the tricyano-vinylation.

Small inverse deuterium isotope effect in the tricyanovinylation.

$E_a = 2·6$ kcal. mole⁻¹, $\Delta S^{\ddagger} = -56$ e.u.

Rate increases 2·13-fold from pure chloroform to 92% chloroform–ethylene dichloride.

first difference is not one of principle, as the kinetic lack of detection of the π-complex is a result of the experimental conditions (temperature, solvent, and low concentration of base). The π-complex can be detected if the formation of product is slowed down, by a reduction in temperature or a decrease in the dielectric constant of the solvent. That the equilibrium constant of the π-complex with tricyanovinyl chloride is lower than that of the corresponding complex with tetracyanoethylene was demonstrated for their durene and toluene complexes,[5,6] and can be readily explained on the basis of the less effective conjugation in the acceptor molecules. Nothing is known about the role of the π-complex in the

[9] Rappoport and Horowitz, unpublished results.

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substitution except that its decomposition becomes slower with decreasing dielectric constant of the medium, as shown previously for the analogous complexes of tetracyanoethylene.[2,7] As the π-complexes of tetracyanoethylene[2] and 1,2-dicyano-1,2-diethoxy-carbonylethylene[10] were regarded as essential intermediates in the corresponding substitution patterns with aromatic amines, the π-complex may also be essential in our system. In any case it has been shown[2] that, from the kinetic viewpoint, there is no difference if the second intermediate is formed directly from the reactants or from a low concentration of the π-complex.

The experimentally observed occurrence of the σ-complex in the tetracyanoethylene–dimethylaniline reaction was predicted on theoretical grounds, as both nucleophilic vinylic aliphatic and electrophilic aromatic substitutions are known to have at least one intermediate on the path from the reactants to the products. The same is true also for the reaction with tricyanovinyl chloride, and this intermediate, which is zwitterionic in our case, is formulated as the σ-complex (II). The almost free availability of the tricyanovinyl chloride during the reaction proves that there is a low concentration of the intermediate, and the steady-state treatment can thus be used to calculate its concentration.

The elimination of hydrogen chloride from the σ-complex can be a one-step (E2) process (pathway A), a two-step carbanionic process (*E1cB*) where the elimination of the proton is rapid and precedes the elimination of the chloride ion from the remaining carbanion (III) (pathway B), or an *E1* process in which the chloride ion leaves first and the proton afterwards from the σ'-complex (IV). If the reversal of the last step is neglected in each of the three pathways (described by k_{-2}, k_{-4}, and k_{-6}), as the reaction was found to be practically irreversible, and if an amine molecule is introduced (which may be the original or additional amine) as a kinetic entity for proton abstraction, the rate of the reaction v, by the concerted process A is given by eqn. (1). Pathway B corresponds to eqn. (2) and

$$v = k_1 k_2 [\text{Tricyanovinyl chloride}][\text{Amine}]^2/(k_{-1} + k_2[\text{Amine}]) \qquad (1)$$

$$v = k_1 k_3 k_4 [\text{Tricyanovinyl chloride}][\text{Amine}]^2/(k_{-1} k_{-3}[\text{H}^+] + k_1 k_4 + k_3 k_4[\text{Amine}]) \qquad (2)$$

$$v = k_1 k_5 k_6 [\text{Tricyanovinyl chloride}][\text{Amine}]^2/\{k_{-1} k_{-5}[\text{Cl}^-] + k_6(k_{-1} + k_5)[\text{Amine}]\} \qquad (3)$$

pathway C to eqn. (3). Thus, the experimental second-order rate coefficient in A, $k_{\text{exp.}} = k_1 k_2[\text{Amine}]/(k_{-1} + k_2[\text{Amine}])$, has to be dependent on the amine concentration. The results in Table 1 show that this is not the case, as the rate coefficients remain constant even with a 10—30-fold increase in the dialkylaniline concentration for all the amines. Moreover, if the solution contains an additional base, the terms [Amine] in all the experimental rate coefficients corresponding to eqns. (1)—(3) are replaced by Σ[B], the sum of the concentrations of all the bases in the solution, and the reaction should be general-base-catalysed. In fact, no general base-catalysis is found in any of the tricyanovinylations, as shown in Table 3. The overall rate coefficient of a concurrent reaction with two amines is equal to the sum of the rate coefficients for the two reactions independently, although in the concurrent runs the *total* base concentrations, Σ[B], are higher than in any " single " run, and generally the second amine added is much more basic than dimethylaniline. (The exceptionally high reactivity of tricyanovinyl chloride prevents the use of other types of catalyst such as aliphatic amines.) Therefore $k_{-1} \ll k_2[\text{Amine}]$, *i.e.*, the partition of the intermediate between the reverse reaction and the formation of product is highly in favour of the latter, and in this case $k_{\text{exp.}} = k_1$. However, the nucleophilic attack cannot be rate-determining, as this implies that $E_{\text{exp.}} = E_1$, and thus pathway A is rejected, as there is no way to ascribe such low activation energies (1·4—2·6 kcal. mole^{-1}) to a nucleophilic attack on carbon–carbon double bonds, or to a relatively slow aromatic substitution on

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

the dialkylaniline molecule.* For the same reasons, pathway B is rejected, as analysis of eqn. 2 gives $k_3k_4[\text{Amine}] \gg k_{-1}k_4 + k_{-1}k_3[\text{H}^+]$, and again $k_{\text{exp.}} = k_1$. Pathways A and B can also be rejected immediately, by taking into account the lack of a normal deuterium isotope effect (where $k_{\text{H}} > k_{\text{D}}$) in conjunction with the lack of base catalysis, both facts
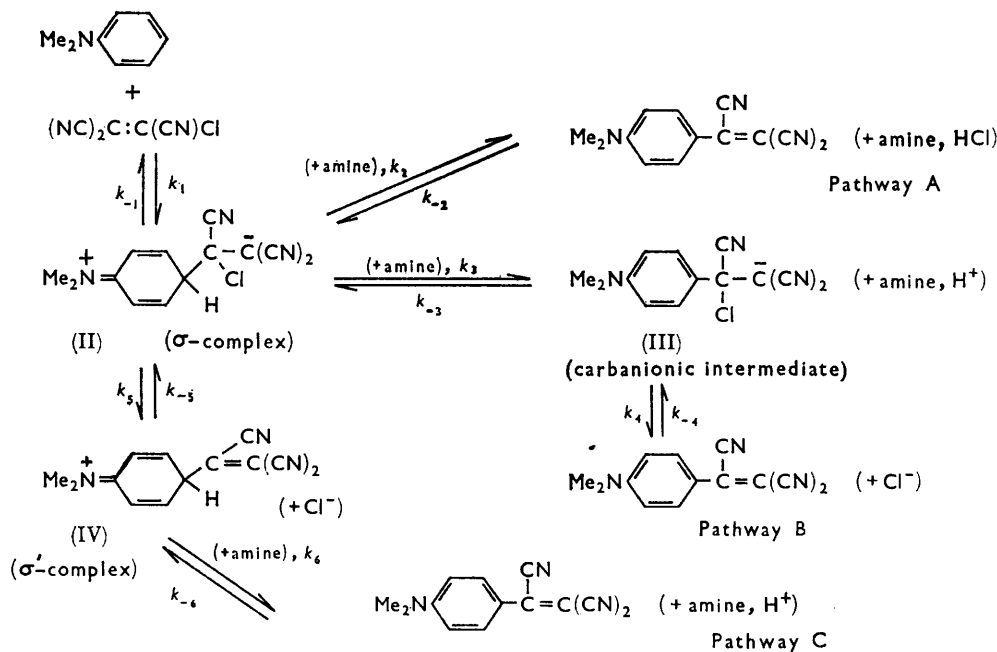
showing that the departure of the proton is not advanced very much in the rate-determining step. Pathway C, on the other hand, with the chloride leaving in the rate-determining step seems to account for these facts. The rate coefficient according to eqn. (3) is,

$$k_{\text{exp.}} = k_1k_5k_6[\text{Amine}]/\{k_6(k_{-1} + k_5)[\text{Amine}] + k_{-1}k_{-5}[\text{Cl}^-]\}$$

The lack of base-catalysis implies that $k_6(k_{-1} + k_5)[\text{Amine}] \gg k_{-1}k_{-5}[\text{Cl}^-]$, which reduces the rate coefficient to that of eqn. (4). Thus the magnitude of the rate coefficient of eqn.

$$k_{\text{exp.}} = k_1k_5/(k_{-1} + k_5) \qquad (4)$$

(4) depends on the ratio of the rates of the $E1cB$ elimination of the dimethylaniline molecule (k_{-1}) to that of the elimination of the chloride ion (k_5) from the zwitterionic intermediate. From eqn. (4) it is clear that k_5 cannot be much greater than k_{-1} (this again would give $k_{\text{exp.}} = k_1$), and the original eqn. (4) cannot be applied, as again $k_{\text{exp.}}$ can be shown to

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* In nucleophilic aromatic substitutions, which may serve as a model to our reaction, low activation energies (4·4 kcal. mole[-1]) were found only in the reaction of aniline with the highly activated 1,2,3,5-tetranitrobenzene or with picryl fluoride.[11] The activation energies for other leaving groups (including chloride ions) are much higher. The value for picryl fluoride was ascribed to the very high solvation of the incipient fluoride ion in the transition state,[11,12] and, indeed, the reaction of 4-fluoronitrobenzene with azide ions stops at the intermediate stage in solvents in which such solvation cannot be achieved.[13] However, such a situation does not exist in the present system, with chloride ion as the leaving group and with chloroform as solvent.

[11] Parker and Read, *J.*, 1962, 9.
[12] Chapman and Parker, *J.*, 1951, 3301.
[13] Bolton, Miller, and Parker, *Chem. and Ind.*, 1960, 1026; Miller and Parker, *J. Amer. Chem. Soc.*, 1961, **83**, 117.

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decrease rapidly to the value of eqn. (5) or to k_1 as the temperature is changed.   On the other hand, if $k_{-1} > k_5$, the rate coefficient is given by eqn. (5), and the corresponding activation energy by $E_{\text{exp.}} = E_1 + E_5 - E_{-1}$.   Literature values for a variety of nucleophilic reactions on double bonds gives $E_1 = 13 \pm 3$ kcal. mole^{-1} for systems of moderate

$$k_{\text{exp.}} = k_1 k_5 / k_{-1} \qquad (5)$$

reactivity,[14–18] but in more activated systems, to which tricyanovinyl chloride belongs, the value is somewhat lower ($E_1 = 10 \pm 2$ kcal. mole^{-1}).[16,19,20]   In this way ($E_{-1} - E_5$) = 8 ± 2 kcal. mole^{-1}.*   Although this is surprising at first sight, as both processes to which these activation energies correspond are carbanionic eliminations from the same intermediate, the difference can be accounted for by the nature of the two leaving groups.   In the reverse reaction an exocyclic carbon–carbon bond of a substituted cyclohexadiene is cleaved, while in the pathway to the product it is a carbon–halogen bond.   Although on these two types of bond cleavage there is superimposed the effect of the unusual structure of the zwitterion (which may reduce E_{-1} compared to E_5),[1] the readiness of carbon–halogen bond heterolysis compared to that of carbon–carbon bond heterolysis will explain the energy difference between the two transition states.

If both $k_5 < k_{-1}$ and $E_{-1} \sim E_5 + 8$ kcal. mole^{-1}, an entropy factor of about 25—35 e.u., compensating the difference between $\Delta S^{\ddagger}_{-1}$ and $\Delta S^{\ddagger}_{5}$, must exist.   Such situations, in which the increase in the energy of activation is more than offset by an increase in the activation entropy, are known,[21] and can result when the transition state is poorly solvated.   From eqn. (5) the experimental activation entropy $\Delta S^{\ddagger}_{\text{exp.}}$ is given by $\Delta S^{\ddagger}_{\text{exp.}} = -56$ e.u. $= \Delta S^{\ddagger}_1 + \Delta S^{\ddagger}_5 - \Delta S^{\ddagger}_{-1}$.   A considerable decrease in the $\Delta S^{\ddagger}_1$ term for the formation of an intermediate with two opposite charges from two neutral molecules may be assumed, especially in a solvent of low dielectric constant such as chloroform.   For the reverse step, in which the charged ground-state is more solvated than the transition state, a rise in the entropy term $\Delta S^{\ddagger}_{-1}$ can be predicted.   The contribution of the $\Delta S^{\ddagger}_5$ factor is relatively small compared to the two others as no charge is developed in this step, but only two remote charges on the same molecule are separated.   Hence, all three entropy terms contribute to the high negative value of $\Delta S^{\ddagger}_{\text{exp.}}$.   As the value of $\Delta S^{\ddagger}_5$ is small and negative, and that of $\Delta S^{\ddagger}_{-1}$ is high and positive, a difference of 25—35 e.u. for ($\Delta S^{\ddagger}_{-1} - \Delta S^{\ddagger}_5$) seems reasonable.   The reaction of the σ-complex of dimethylaniline with tetracyanoethylene, which seems from entropy considerations to be formally analogous to the transformation (II) $\longrightarrow$ (IV) and which has a high negative activation entropy (-37 e.u.), is entirely different, since the corresponding transition state contains an additional amine molecule and the " built up solvation "[22] during the charge separation is higher than in the present case owing to the " sandwich structure " of the σ-complex.[2]   If the σ-complex of tricyanovinyl chloride had the same geometry, the contribution of the $\Delta S^{\ddagger}_5$ term would be higher, and also the difference $\Delta S^{\ddagger}_{-1} - \Delta S^{\ddagger}_5$.

The suggested partition of the intermediate favouring the reverse reaction is met frequently in nucleophilic reactions on carbon–carbon double bonds.   Isomerisations of

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* If π-complex is formed initially in this system also, and the activation energy for the π-complex $\longrightarrow$ σ-complex transformation is similar to that found in the dimethylaniline–tetracyanoethylene system ($E_1 = 5\cdot7$ kcal. mole^{-1}), the difference ($E_{-1} - E_5$) will be much lower (3—4 kcal. mole^{-1}).

[14] Jones, Morris, Vernon, and White, *J.*, 1960, 2349.
[15] Modena and Todesco, *Gazzetta*, 1959, **89**, 866.
[16] Patai and Rappoport, *J.*, 1962, 383, 392.
[17] Maioli and Modena, *Gazzetta*, 1959, **89**, 854.
[18] Modena, Todesco, and Tonti, *Gazzetta*, 1959, **89**, 878.
[19] Kamlet and Glover, *J. Amer. Chem. Soc.*, 1956, **78**, 4556.
[20] Schmidt and Kubitzek, *Ber.*, 1960, **93**, 866.
[21] Bunnett, Morath, and Okamoto, *J. Amer. Chem. Soc.*, 1955, **77**, 5056; Winstein and Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 1120; Winstein and Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.
[22] Bunnett and Morath, *J. Amer. Chem. Soc.*, 1955, **77**, 5051.

the attacked molecules to more stable geometric isomers have been found to be faster than some alkaline epoxidations,[23] cleavage reactions,[24] or substitutions.[25]

Equation (5) can be written as $k_{exp.} = Kk_5$, where $K = k_1/k_{-1}$ is the equilibrium constant for the first nucleophilic step (the " carbon basicity ").[1,26] This is not readily measurable in nucleophilic attacks of this type, as the carbanions first formed enter into various types of rapid reactions. However, the existence of such an equilibrium is shown by the complete equilibration of $C^{14}N^-$ with non-labelled tetracyanoethylene.[27] Low values of K ($k_{-1} \gg k_1$) were suggested for nucleophilic cleavage.[28] The reversibility of the first step is demonstrated by the rapid isomerisation with water, compared to the cleavage, of ethyl-α-cyano-β-o-methoxyphenylacrylate.[24] Indeed, $k_{exp.}$ of this isomerisation has the same form as that of eqn. (5) except that, in this case, k_5 is the rate coefficient for the step following the nucleophilic attack, *i.e.*, the internal rotation in the carbanion. The overall isomerisation, too, has a low activation energy and a high negative entropy of activation. In cases where a special factor can stabilise the intermediate, the equilibrium constant becomes high, *e.g.*, in the formation of the completely stable zwitterion [29] p-Cl·C_6H_4·$CH(P^+Bu^n_3)$·$C^-(CN)_2$ from 4-chlorobenzylidenemalononitrile and tributylphosphine ($K = 3700$ at 34).[30] This system is the only one in which thermodynamic parameters for the equilibrium have been measured directly, and the value $\Delta S^\circ = -27\cdot4$ e.u. in methanol, which is probably much more negative in chloroform,[31] is in agreement with the estimated high negative value of ($\Delta S^\ddagger_1 - \Delta S^\ddagger_{-1}$), while $\Delta H^\circ = 13\cdot4$ kcal. mole^{-1} gives $\Delta H^\ddagger_5 = 15$—16 kcal. mole^{-1}, a value lower than that found for the activation energy of the $E1cB$ elimination from carbanions,[32] as predicted for elimination from zwitterions in a related system.[1]

Equation (5) and the $k_{exp.}$ values (1—0·1 l. mole^{-1} sec.$^{-1}$) give, for various amines, $k_{-1} = k_1k_5$ to $10k_1k_5$, and, as $k_{-1} > k_5$, a possibility exist that k_1 may be similar or higher than k_{-1}, *i.e.*, $K \geqslant 1$ l. mole^{-1}. In such a case the degree of stability of the σ-complex may be attributed to a special stabilisation in the zwitterionic structure, since the negative charge is delocalised on the cyano-groups and the positive charge on the dimethylaniline moiety.

From the above values the rate coefficients of the nucleophilic attacks (k_1) on tricyano-vinyl chloride are at least ten times higher than $k_{exp.}$, being 1—10 l. mole^{-1} sec.$^{-1}$ for various dialkylanilines. Values of k_1 of this order of magnitude were found for the following systems, barbiturate anions–β-nitrostyrene,[19] various mercaptide ions–α-arenesulphonyl-β-chloroethylenes,[15] hydroxide ion–arylmethylenemalononitriles and –arylmethylene-cyanoacetates,[16] methoxide ions–*trans*-dibenzoylethylenes,[33] and higher values only with the " living " dimer of α-methylstyrene or cumyl anion–α-methylstyrene,[34] and hydroperoxide and hypochlorite anions–2-chlorobenzylidenemalononitrile.[35] As the nucleophilicity of the above nucleophiles seems to be much higher than that of the 4-position of dialkylanilines, tricyanovinyl chloride is probably the most activated double-bond system which has been studied kinetically.

A very high " element effect " seems to exist in the tricyanovinylation by tricyano-vinyl chloride, chloride ion being eliminated much more rapidly than cyanide ion from

[23] House and Ro, *J. Amer. Chem. Soc.*, 1958, **80**, 2428.
[24] Patai and Rappoport, *J.*, 1962, 396.
[25] Ross, Leach, and Kuntz, *J. Amer. Chem. Soc.*, 1952, **74**, 2908.
[26] Parker, *Proc. Chem. Soc.*, 1961, 371.
[27] Webster, Mahler, and Benson, *J. Amer. Chem. Soc.*, 1962, **84**, 3678.
[28] Crowell and Francis, *J. Amer. Chem. Soc.*, 1961, **83**, 591.
[29] Ford and Wilson, *J. Org. Chem.*, 1961, **26**, 1433.
[30] Rappoport and Gertler, unpublished results.
[31] Pearson, *J. Chem. Phys.*, 1952, **20**, 1478.
[32] Patai, Weinstein, and Rappoport, *J.*, 1962, 1741; Hine, Wiesboeck, and Ramsay, *J. Amer. Chem. Soc.*, 1961, **83**, 1222.
[33] Crowell, Helsley, Lutz, and Scott, *J. Amer. Chem. Soc.*, 1963, **85**, 443.
[34] Vrancken, Smid, and Szwarc, *Trans. Faraday Soc.*, 1962, **58**, 2036; Lee, Smid, and Szwarc, *J. Amer. Chem. Soc.*, 1963, **85**, 912.
[35] Rosenblatt and Broome, *J. Org. Chem.*, 1963, **28**, 1290.

reaction. In the few cases where a high element effect was observed, it was ascribed to change of the mechanism from " addition–elimination " to " elimination–addition," [37a] a situation which cannot be applied to our case.

The above analysis accounts for the difference between the σ-complexes of tetracyano-ethylene and of tricyanovinyl chloride. Apart from the steric structure of the intermediate, the stability of the first one is a result of enhanced charge delocalisation by an additional cyano-group and of the slow elimination of this group. The tricyanovinyl chloride σ-complex may have some stability, but the rapid departure of chloride ion from it prevents its accumulation.

Substituents and Solvent Effects.—The activation of the benzene nucleus by the dialkyl-amino group is so high [38] that kinetic data for the reactions are rare. The order of reactivity in the present case for the series $C_6H_5 \cdot NR_2$ is Bu ~ Et ~ Pr > Me. This differs from the order (Et > Bu ~ Pr > Me) of pK values in water [39] or in chloroform (the latter judged by the effectivity of the various amines as proton acceptors from the σ-complex of mono-methylaniline and tetracyanoethylene in chloroform).[9] The dependence on R in quaternis-ation [40] is Me > Et > Pr > Bu, that for the rate of exchange of protons in the 4-position [41] is Me > Bu ~ Pr > Et, and that for the order of π-complex stability for the complexes with trinitrotoluene [42] is Me > Et ~ Pr ~ Bu (*i.e.*, opposite to the one found in tricyano-vinylation). In our system, direct steric effects exerted by various dialkylamino-groups are not important, as the change in the substituent occurs remote from the reaction site, and, indeed, $\Delta S^{\ddagger}_{exp}$ values are similar for all the amines. The differences in reactivity between the ethyl, propyl, and butyl compounds are practically negligible, and, on the assumption that k_5 is similar for all the amines (since the chloride elimination occurs from similar environments), the differences in the overall reactivities result from the K values, which include the attack on the aromatic ring. We cannot predict the direction of the change of K with the structure of the dialkylamino-group, but we have calculated the part of the basicity of the amines which results from inductive effects alone, by using Hall's linear inductive-effects relation [43] for aliphatic tertiary amines, and have obtained the order Me < Et ~ Pr ~ Bu, in agreement with our experimental results.

Inductive effects on the equilibrium also explain the small inverse deuterium isotope effect. This is a secondary effect, resulting from the greater inductive electron-releasing capacity of deuterium compared to hydrogen,[44] as found for the ionisation equilibria of carboxylic acids,[45] phenols,[46] carbonium ions,[47] and anilines.[48] The 4-position of the deutero-compound is thus more nucleophilic than that of the non-deuterated compounds by a factor of 1·16. A similar effect, smaller in magnitude, was found on C- or N-deuter-ation of aniline, in a reaction when the attacked carbonyl group of benzoyl chloride was again an unsaturated electrophilic carbon.[49]

Predicted solvent effects are a large increase for the nucleophilic attack and a large decrease for its reversal with the increase of the dielectric constant of the solvent.[50] A small decrease for the elimination step is found in other $E1cB$ systems with increasing dielectric

[38] Bell and Ramsden, *J.*, 1958, 161; Robertson, de la Mare, and Swedlund, *J.*, 1953, 782; Eaborn, *J.*, 1956, 4858; Miller, *Austral. J. Chem.*, 1956, **9**, 61.
[39] Ref. 36, p. 608.
[40] Evans, *J.*, 1944, 422; Thomas, *J.*, 1913, **103**, 594.
[41] Tice, Lee, and Kendall, *J. Amer. Chem. Soc.*, 1963, **85**, 329.
[42] Foster and Hammick, *J.*, 1954, 2685.
[43] Hall, *J. Amer. Chem. Soc.*, 1957, **79**, 5441.
[44] Halevi, *Trans. Faraday Soc.*, 1958, **54**, 1441.
[45] Bell and Jensen, *Proc. Chem. Soc.*, 1960, 307; Ropp, *J. Amer. Chem. Soc.*, 1960, **82**, 4252; Halevi, Nussim, and Ron, *J.*, 1963, 866.
[46] Klein and Streitwieser, *Chem. and Ind.* 1961, 180.
[47] Kresge, Rao, and Lichtin, *Chem. and Ind.*, 1961, 53.
[48] Bernasconi, Koch, and Zollinger, *Helv. Chim. Acta*, 1963, **46**, 1184.
[49] Elliott and Mason, *Chem. and Ind.*, 1959, 488.
[50] Hughes and Ingold, *J.*, 1935, 244; Ingold, " Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 347.

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constant.[32]   The results show that the increase in the K values with increasing dielectric constant is slightly more than compensated by the decrease in k_5.   The solvent effect is higher for the less reactive amine, in analogy to previous results,[16] showing that the slower the reaction the higher is its response to medium effects.

EXPERIMENTAL

Melting points are corrected.

Materials.—Tricyanovinyl chloride, prepared by method B of Dickinson, Wiley, and McKusick,[5] and stored under nitrogen at −70°, had m. p. 70°, $\lambda_{max.}$ (CHCl₃) 266 mμ (ε 13,200). Attempts to prepare it by using tetraethylammonium tricyanoethenolate instead of the tetramethylammonium salt resulted in very low yields.   Tetramethylammonium iodide did not react at all with tetracyanoethylene under the same conditions as the corresponding chloride.

NN-Dimethylaniline (British Drug Houses, AnalaR), b. p. 83°/24 mm. (lit.,[41] 191°), *NN*-diethylaniline (British Drug Houses), b. p. 118—120°/25 mm. (lit.,[41] 216°), *NN*-dipropylaniline, b. p. 131—134°/23 mm. (lit.,[41] 238—242°), and *NN*-dibutylaniline, b. p. 145°/14 mm. (lit.,[41] 117·5—8·5°/1 mm.) were refluxed for 3 hr. with an excess of acetic anhydride and distilled twice under reduced pressure.   *NN*-dimethyl[4-²H]aniline, b. p. 85°/20 mm., m. p. 0·5—1° was prepared by the decomposition of the iodo-Grignard reagent in deuterium oxide.[9]   *NN*-Dimethylaniline, b. p. 88°/25 mm., for the control experiments was prepared by the same method, but the Grignard reagent was decomposed with water.   *NN*-Dialkyl-4-tricyanovinylanilines were prepared according to the literature,[51] and have the following properties ($\lambda_{max.}$ in chloroform): Me₂, m. p. 178° (from acetic acid), $\lambda_{max.}$ 515 mμ (ε 48,400); Et₂, m. p. 167° (from ethanol), $\lambda_{max.}$ 524 mμ (ε 51,030); Prⁿ₂, m. p. 139—140° (from methanol), $\lambda_{max.}$ 526 mμ (ε 54,700); Buⁿ₂ m. p. 128° (from ethanol), $\lambda_{max.}$ 530 mμ (ε 56,800).

Solvents.—Chloroform (Mallinckrodt, AnalaR) was washed 5 times with half its volume of water, dried (K₂CO₃), and distilled under nitrogen immediately before use, b. p. 58°/720 mm. Ethylene dichloride (British Drug Houses) was washed once with 5% sodium hydroxide and thrice with water.   It was dried over potassium carbonate and distilled immediately before use, b. p. 80·5°/690 mm.

Kinetic Procedure.—Stock solutions of tricyanovinyl chloride in dry chloroform were prepared prior to the kinetic runs and were stored under nitrogen at −70°.   The stock solutions were stable for at least 2 weeks, as shown by the final absorption values of the products obtained in the kinetic runs.   Stock solutions of the amines stored under nitrogen at 0° were stable for at least 1 week.   The two stock solutions were mixed at the reaction temperature, and the reaction was followed spectrophotometrically at the $\lambda_{max.}$ of the products, by using 1-cm. silica cells in a thermostat-controlled (±0·1°) chamber of a Beckmann DU spectrophotometer.   The reactions were followed up to 95% completion, and the final value was determined after ten or more half-lives.   The final readings were in good agreement with those calculated for 100% reaction (*e.g.*, with diethylaniline the values of the optical density obtained in 5 different runs were 1·165, 1·420, 1·179, 1·464, and 1·416, compared with the calculated values 1·165, 1·420, 1·165, 1·420, and 1·420).   For the simultaneous reactions with two amines, 25 ml. of a reaction mixture with one of the amines was prepared, 5 ml. was withdrawn, and the reaction was measured in the spectrophotometer chamber while the remaining reaction mixture was left in the thermostat.   At a predetermined time, an additional 5 ml. containing the second amine were added to the original reaction mixture, and the two reactions were followed simultaneously.

Product Analysis.—The spectra of the reaction products were those of the pure *NN*-dialkyl-4-tricyanovinylanilines.   In addition tricyanovinyl chloride (10—20 mg.) and amine (10—20 mg.) were mixed in chloroform (20 ml.) which was allowed to evaporate slowly.   The crystalline red mass was recrystallised from methanol, and the m. p. and mixed m. p. of the crystals obtained were in agreement with those of the corresponding *NN*-dialkyl-4-tricyanovinylanilines.

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