Kinetic Evidence for a Methanolysis Intermediate in Aromatic Nucleophilic Substitution

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The reactions of 2,4- and 2,6-dinitrochlorobenzene and 2,4-dinitroanisole with cyclohexylamine in benzene and in methanol have been examined. Computer analysis of the kinetic data shows the formation and fate of a solvolysis product in the reaction of 2,4-dinitrochlorobenzene in methanol. The results prove that an experimental failure to detect a solvolysis product is not evidence for a negligible solvolysis rate.

BUNNETT and ZAHLER [1] in their review on nucleophilic aromatic substitution reactions drew attention to a complication arising when studying nucleophilic displacement by amines in alcoholic solvents. An alcoholic solution of an amine contains an appreciable concentration of alkoxide ion [equilibrium (1)] so that substitution may be effected by either amine or alkoxide.

$$R^1NH_2 + R^2OH \rightleftharpoons R^1\overset{+}{N}H_3 + R^2O^- \qquad (1)$$

Working with 2,4-dinitrochlorobenzene Brady and Cropper [2] suggested that the amount of alkoxide ion cannot be sufficiently high for interference except in the cases of very slow acting, strongly basic amines, and Chapman and his co-workers [3] demonstrated that even with strongly basic amines the rate of ethanolysis is negligible when compared with the main reaction after a few percent of reaction. A similar pre-equilibrium was found for the reaction of the same substrate with phenoxide ion in methanol.[4]

For the case of nucleophilic displacement of fluorine Suhr made a quantitative estimation of the extent of ether formation in the reaction of *p*-fluoronitrobenzene and found sizable amounts for weakly nucleophilic amines.[5] For heterocyclic compounds no solvolysis product was found in the reaction of 2-chloro-5-nitropyridine with anilines but for the fluoro-compound there was a slow competitive solvolysis.[6]

Therefore, we thought it of interest to investigate in more detail the incidence of proton transfer equilibria on the rate of nucleophilic displacement of chlorine using more sensitive methods than quantitative determination of the secondary products. We have measured the rate of the reactions of 2,4- and 2,6-dinitrochlorobenzenes and 2,4-dinitroanisole with cyclohexylamine in benzene and in methanol.

EXPERIMENTAL

Reagents and Solvents.—2,4- and 2,6-dinitrochlorobenzene (Fluka) were crystallised from ethanol until constant m.p. 51.0 and 87.5°, respectively. Cyclohexylamine (Fluka) was kept over sodium and then fractionated through a 20 (Fenske) theoretical plates column, fraction of b.p. 134.5° (lit.,[7] 134.75°) being used. *N*-(2,4)- and 2,6-dinitrophenylcyclohexylamine were prepared by dissolving the corresponding dinitrochlorobenzenes in the minimum amount of ethanol and adding 10 mol. equiv. of cyclohexylamine. The reaction mixture was refluxed for 3 h. The products were crystallized from ethanol and were identical with authentic samples.[8] M.p.s were 153 and 78.5°, respectively.

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[1] J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, 271.

[2] O. L. Brady and F. R. Cropper, *J. Chem. Soc.*, 1950, 507.

[3] (*a*) E. A. S. Cavell and N. B. Chapman, *J. Chem. Soc.*, 1953, 3392; (*b*) N. B. Chapman, R. E. Parker, and P. W. Soanes, *ibid.*, 1954, 2109.

[4] A. G. Catchpole and R. H. Lynch, *Chem. and Ind.*, 1966, **49** 2058.

[5] H. Suhr, *Tetrahedron Letters*, 1966, **47**, 5871.

[6] D. M. Brewis, N. B. Chapman, J. S. Paine, J. Shorter, and D. J. Wright, *J.C.S. Perkin II*, 1974, 1787.

[7] J. Timmermans and H. Roland, *J. chim. Phys.*, 1959, **56**, 984.

2,4-Dinitroanisole was prepared by treating 2,4-dinitrochlorobenzene with sodium methoxide in excess. Crystallisation from methanol gave material, m.p. 95—96° (lit., 88,[9] 94.8—96.5° [10]). Attempts to prepare 2,6-dinitroanisole by the same procedure failed because 2,6-dinitroanisole reacts with the excess of sodium methoxide to give sodium 2,6-dinitrophenoxide, m.p. >300°, which by acidification gave 2,6-dinitrophenol, m.p. 58° (lit.,[11] 60°). 2,6-Dinitroanisole was prepared by mixing stoicheiometric amounts of 2,6-dinitrochlorobenzene with sodium methoxide. Crystallisation from methanol gave material, m.p. 118° (lit.,[12] 117—119°). Cyclohexylammonium chloride was prepared by flushing hydrogen chloride into an ethereal solution of cyclohexylamine; it was crystallised twice from ethanol and had m.p. 206—207° (lit.,[13] 206). Methanol was dried by the Lund and Bjerrum method,[14] and was stored in a special vessel which allowed delivery without air contamination. Benzene was kept over sodium wire for several days, then distilled over sodium, and stored in the kind of vessel used for methanol.

Kinetic Procedure.—All reactions were studied spectrophotometrically.[15] A Beckman DU 2 spectrophotometer was used, with 1.00 cm silica cells. Standard solutions of the halogeno-compound (*ca.* 1—5 × 10^{-4}M) and the aromatic amine (in large excess, not less than 100-fold) in methanol or in benzene were prepared, mixed at 0° C, and aliquot portions were put in separate reaction tubes (at 35 °C) or in sealed bulbs (at 45 and 60°) and immersed in a thermostat. Samples were taken at intervals, cooled, and quenched by the addition of methanolic sulphuric acid. The optical density of the reaction mixtures of 2,4-dinitrochlorobenzene with cyclohexylamine in methanol were measured at 290 and 350 nm; the optical density of the other reaction mixtures were measured at the wavelength of the maximum absorption of the *N*-cyclohexylaminophenyl derivative.

Except for the reactions of 2,4-dinitrochlorobenzene with cyclohexylamine in methanol, pseudo-first-order rate coefficients, k_ψ, were obtained by the least-squares method as the slope of $\ln(d_\infty - d_t)$ against t; where d_∞ is the optical density of the reaction mixture after more than 10 half-lives and which was coincident with the optical density of a solution of the *N*-(2,6-dinitrophenyl)cyclohexylamine derivative in the same solvent. The second-order rate coefficients, k_T, were obtained by dividing k_ψ by the cyclohexylamine concentration. Rate coefficients were reproducible to ±2%. Values of $\Delta H^\ddagger$ are accurate to *ca.* ±0.3 kcal mol^{-1} and values of $\Delta S^\ddagger$ to ±1 cal K^{-1} mol^{-1}.

For the reactions of 2,4-dinitrochlorobenzene in benzene a correction is applied since the substrate absorbs at the wavelength at which the optical density is measured (350 nm). The measured optical density, d_t, is corrected by expression (2) where ε_a and ε_b are the molar extinction co-

$$d_t' = (d_t\varepsilon_\mathrm{b} - d_\infty\varepsilon_\mathrm{a})/(\varepsilon_\mathrm{b} - \varepsilon_\mathrm{a}) \qquad (2)$$

efficients of the substrate and the product, respectively. This correction was introduced into the computer program and the pseudo-first-order rate coefficient was calculated in the way described for the 2,6-dinitrochlorobenzene reactions.

The reaction of 2,4-dinitrochlorobenzene in methanol produces 2,4-dinitroanisole as a relatively stable intermediate and a different treatment is applied which is described in the Discussion section.

Ancillary Spectrophotometric Measurements.—The spectral properties of the substrates and of the products of their interaction with cyclohexylamine and/or sodium methoxide are recorded in Table 1. The solutions were found to obey Beer's law. Spectrophotometric determination of the reaction mixtures at ' infinity ' revealed that the *N*-(dinitrophenyl)cyclohexylamine derivative was the only product in quantitative yield.

TABLE 1

Spectral properties of 2-R^1-3-R^2-5-R^3-nitrobenzenes

R^1	R^2	R^3	Solvent	λ/nm	ε/l mol^{-1} cm^{-1}	
Cl	NO_2	H	Methanol	425	0	
Cl	NO_2	H	Benzene	425	0	
Cl	H	NO_2	Methanol	350	325	ε_{11}
				290	3 081	ε_{21}
Cl	H	NO_2	Benzene	350	327	
OCH_3	NO_2	H	Methanol	307	1 735	
ONa	NO_2	H	Methanol	425	6 920	
OCH_3	H	NO_2	Methanol	290	10 740	ε_{22}
				350	912	ε_{12}
$C_6H_{11}N$	NO_2	H	Methanol	425	5 612	
$C_6H_{11}N$	H	NO_3	Methanol	350	17 250	ε_{13}
				290	1 902	ε_{23}
$C_6H_{11}N$	H	NO_2	Benzene	350	17 200	

DISCUSSION

General Comments on the Kinetics of the Reaction of 2,4-*Dinitrohalogenobenzenes with Amines.*—Examples of aromatic nucleophilic substitutions with amines which proceed by an addition–elimination mechanism have been summarized by Bernasconi.[16] When the halogen displaced is chlorine most of the decomposition of the intermediate complex proceeds spontaneously and rapid acceleration by bases has not been observed.[17]

In the reaction of 2,4-dinitrochlorobenzene with cyclohexylamine we have studied the influence of base concentration in benzene in which it would be more likely to detect base acceleration. The results are gathered in Table 2. As can be observed a small increase in the total second-order rate coefficient is found for increasing amounts of cyclohexylamine.

Table 3 gathers the calculated k_0 and k_B values according to the equation $k_\mathrm{T} = k_0 + k_\mathrm{B}$ [B]. As can be

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[15] J. F. Bunnett, T. Kato, and N. S. Nudelman, in ' Fundamental Organic Chemistry Laboratory Manual,' eds. K. Thomas Finley and J. Wilson, Prentice Hall, New Jersey, p. 112.

[16] C. F. Bernasconi, *M.T.P. International Rev. Sci. Org. Chem. Ser. 1*, 1973, **3**, 33.

[17] J. F. Bunnett and C. F. Bernasconi, *J. Org. Chem.*, 1970, **35**, 70.

observed $k_B/k_0 \leqslant 5$ and the low acceleration can be interpreted as a medium effect. The working temperatures are close to the isokinetic temperature [18] and a slight increase in rate is expected with increasing polarity of the solvent, although it is an *ortho*-substituted compound and the inverse effect is more usual.[19,20]

TABLE 2

Reaction of 2,4-dinitrochlorobenzene with cyclohexylamine (CHA) in benzene

[CHA]/M	T/°C	$10^4\ k_T$/ l mol^{-1} s^{-1}	$\Delta H^{\ddagger}_{45°}$/ kcal mol^{-1}	$-\Delta S^{\ddagger}_{45°}$/ cal K^{-1} mol^{-1}
0.049	35	0.703		
	45	1.92	9.4	45.5
	60	4.00		
0.098	35	1.10		
	45	2.02	9.2	46.5
	60	4.47		
0.452	35	1.66		
	45	3.06	9.6	46.1
	60	7.33		
0.997	35	3.42		
	45	6.00	9.3	45.5
	60	14.5		

TABLE 3

Reaction of 2,4-dinitrochlorobenzene with cyclohexylamine in benzene

T/°C	$10^4 k_0$/ l mol^{-1} s^{-1}	$10^4 k_B$/ l mol^{-1} s^{-1}	k_B/k_0
35	0.5	2.6	5
45	1.6	4.2	2.6
60	3.5	8.5	2.4
$\Delta H^{\ddagger}$/kcal mol^{-1}	10.2	4.4	
$-\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	44	61	

The thermodynamic parameters confirm this assumption. If base catalysis were important the entropy of activation for the total reaction should be smaller (*ca.* -60 cal K^{-1} mol^{-1}), while the experimental data resembles the values for an uncatalysed reaction.

We conclude that the reaction of 2,4-dinitrochlorobenzene with cyclohexylamine is not amine catalysed (in this term we include catalysis by the amine B and catalysis by its conjugate acid BH$^+$).

TABLE 4

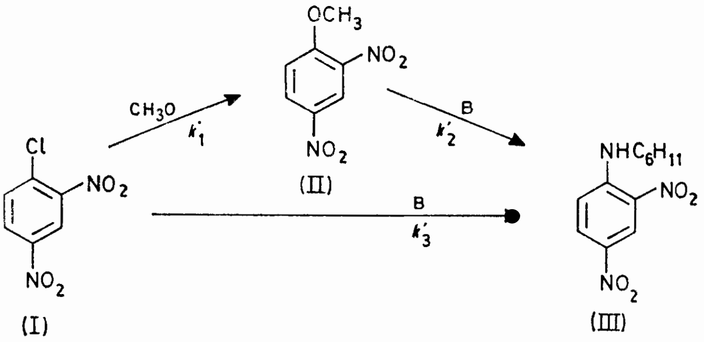
Reaction of 2,4-dinitrochlorobenzene with cyclohexylamine in methanol [a]

T/°C	$10^5 k'_1$ [b]/ s^{-1}	$10^5 k'_3$ [b]/ s^{-1}	10^4[MeO$^-$]/ M	pK_B	$10^4 k_T$ [c]/ l mol^{-1} s^{-1}	$10^4 k_T$ [d]/ l mol^{-1} s^{-1}
35	3.5	2.4	4.7	6.13	1.45	1.19
45	6.4	6.7	3.6	6.36	2.71	2.08
60	20.5	19.4	3.3	6.44	10.0	7.15
$\Delta H^{\ddagger}$/kcal mol^{-1}	11.4	13.4				12.2
$-\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	25	33				40.0

[a] [Cyclohexylamine] = 0.297M. [b] Calculated pseudo-first-order rate coefficients from measurements of the optical density at 290 and 350 nm. [c] Calculated second-order rate coefficients from measurements at 350 nm for a direct reaction. [d] *Idem*, 10^{-2}M-cyclohexylammonium chloride added.

2,4-Dinitroanisole as an Intermediate in the Reactions in Methanol.—Because of equilibrium (1) for a methanolic solution of cyclohexylamine there is a constant amount of methoxide ion able to react with the 2,4-dinitrochlorobenzene. When performing the reaction with cyclohexylamine we found *N*-(2,4-dinitrophenyl)-cyclohexylamine as the only product in quantitative yield.

Nevertheless, this result cannot dispose of the possibility of a parallel reaction of 2,4-dinitrochlorobenzene (I) with methoxide ion to give 2,4-dinitroanisole (II) followed by the reaction of this with cyclohexylamine (B) to produce the same final product (III), as in the Scheme.



This is a very simplified mechanism as each of the reactions involves several steps. Nevertheless, we have demonstrated that the direct reaction (I) ⟶ (III) is not subject to amine catalysis and we have found a similar result for reaction (II) ⟶ (III) (see Table 5).

For the experimental conditions used in the present work $[B] \gg [(I)]$. According to the pK_B value of cyclohexylamine in methanol (5.89) * the amount of methoxide ion is not much greater than [(I)] but it remains constant because of equilibrium (1). Therefore, assuming that each step behaves as a pseudo-first-order reaction, the differential equations (3)—(5) are obtained.

$$-d[(I)]/dt = (k_1' + k_3')[(I)] \quad (3)$$

$$d[(II)]/dt = k_1'[(I)] - k_2'[(II)] \quad (4)$$

$$d[(III)]/dt = k_3'[(I)] + k_2'[(II)] \quad (5)$$

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* The pK value was determined spectrophotometrically following the procedure of ref. 21 using Bromocresol Purple as indicator.

[18] N. S. Nudelman and J. A. Brieux, unpublished results.

[19] J. F. Bunnett and R. J. Morath, *J. Amer. Chem. Soc.*, 1955, **77**, 5051.

[20] S. D. Ross and M. Finkelstein, *J. Amer. Chem. Soc.*, 1963, **85**, 2603.

[21] (*a*) I. M. Kolthoff and L. S. Guss, *J. Amer. Chem. Soc.*, 1938, **60**, 2516; (*b*) J. R. Schaefgen, M. S. Newman, and F. H. Verhoek, *ibid.*, 1944, **66**, 1847.

Equation (3) is easily integrated to yield (6) where $[(\mathrm{I})]_0$ is the initial concentration of (I).

$$[(\mathrm{I})] = [(\mathrm{I})]_0\,\mathrm{e}^{-(k_1'+k_3')t} \qquad (6)$$

Since at the beginning $[\mathrm{II}]_0 = 0$, equation (4) may be integrated by the usual integrating factor methods to give (7). $[(\mathrm{III})]$ may

$$[(\mathrm{II})] = [(\mathrm{I})]_0 \cdot \frac{k_1'}{k_1' + k_3' - k_2'}\,(\mathrm{e}^{-k_2'} - \mathrm{e}^{-(k_1'+k_3')t}) \qquad (7)$$

be found most conveniently from the stoicheiometric relation obtained by integrating the sum of equations (3)—(5), *i.e.* $[(\mathrm{I})]_0 = [(\mathrm{I})] + [(\mathrm{II})] + [(\mathrm{III})]$, thus yielding equation (8). To determine the amount of each

$$\frac{[(\mathrm{I})]_0 - [(\mathrm{III})]}{[(\mathrm{I})]_0} = \left(\frac{k_3' - k_2'}{k_1' + k_3' - k_2'}\right)\mathrm{e}^{-(k_1'+k_3')t} + \left(\frac{k_1'}{k_1' + k_3' - k_2'}\right)\mathrm{e}^{-k_2't} \qquad (8)$$

compound at different intervals the optical densities A_1 and A_2 of the reaction mixtures were measured at two wavelengths, λ_1 350 and λ_2 290 nm, respectively. The three compounds show measurable optical density at these two wavelengths and equations (9)—(11) are valid

TABLE 5

Reaction of 2,4-dinitrochlorobenzene with cyclohexylamine in methanol [a]

t/s	$10^5[(\mathrm{I})]/\mathrm{M}$	$10^5[(\mathrm{II})]/\mathrm{M}$	$10^5[(\mathrm{III})]/\mathrm{M}$
180	7.83	0.508	0.591
360	6.78	0.976	1.17
780	5.19	1.46	2.28
1 200	3.99	1.89	3.04
1 620	3.34	1.87	3.34
2 040	2.57	2.12	4.24
2 880	1.98	2.22	4.62
3 780	1.24	2.40	5.10
4 980	0.91	2.45	5.32
7 080	0.01	2.34	6.58
8 100	0.002	1.87	7.03

[a] T 60°; $[\text{Dinitrochlorobenzene}]_0 = 8.9 \times 10^{-5}\mathrm{M}$; $[\text{cyclohexylamine}] = 0.297\mathrm{M}$.

$$A_1 = \varepsilon_{11}[(\mathrm{I})] + \varepsilon_{12}[(\mathrm{II})] + \varepsilon_{13}[(\mathrm{III})] \qquad (9)$$

$$A_2 = \varepsilon_{21}[(\mathrm{I})] + \varepsilon_{22}[(\mathrm{II})] + \varepsilon_{23}[(\mathrm{III})] \qquad (10)$$

$$A_\infty = \varepsilon_{13}[(\mathrm{I})] + \varepsilon_{13}[(\mathrm{II})] + \varepsilon_{13}[(\mathrm{III})] \qquad (11)$$

where the ε values are the molar extinction coefficients of Table 1 and A_∞, is the ' infinity ' optical density.

Using equations (3)—(5) and (9)—(11) a computer program written in Fortran IV * allowed the calculation of the pseudo-first-order rate constants, k_1' and k_3', providing the value of the pseudo-first-order rate constant, k_2', is known.

The rate of the reaction of (II) with cyclohexylamine was measured (see below) and the calculated values of k_1' and k_3' are recorded in Table 4.

From the same program it is possible to obtain the amount of each of the three compounds at each interval (Table 5). As can be observed the amount of compound (II) increases at the beginning and then decreases as it is transformed in (III). A plot of [(III)] against time shows the sigmoidal curve expected for composite (parallel and consecutive) reactions. The time, $t_{\text{max.}}$, at which the concentration of (II) is a maximum can be calculated from equation (12). For reaction at 60°,

$$t_{\text{max.}} = \frac{\ln(k_1' + k_3') - \ln k_2'}{k_1' + k_3' - k_2'} \qquad (12)$$

$t_{\text{max.}}$ is 4 890 s which compares fairly well with the experimental value, $t_{\text{max.}}$ 4 980 s, obtained from the plot of [(II)] against time. The experiment was repeated and *ca.* 80 min after the start, a spectrum of the reaction mixture was recorded in the region 250—400 nm. This showed a maximum at 290 nm, which is not present in the ' infinity ' mixture.

If the assumptions involved are correct it would be possible to obtain the amount of methoxide ion present in the methanolic cyclohexylamine solution by equation (13) where k_T is the second-order rate coefficient for

$$[\mathrm{MeO}^-] = k_1'/k_\mathrm{T} \qquad (13)$$

reaction (I) $\longrightarrow$ (II) which has been determined by Miller *et al.*,[22] the extrapolated $10k_\mathrm{T}$ l mol^{-1} s^{-1} values are 0.767 (35°), 1.76 (45°), and 6.31 (60°). The calculated methoxide ion concentrations are shown in Table 4. These values agree well with that calculated from the pK value determined at room temperature, $[\mathrm{MeO}^-] = 6.0 \times 10^{-4}\mathrm{M}$, and therefore confirm the above assumptions. The method is thus useful for kinetic determinations of pK, similar to that described previously.[23] Using the calculated methoxide ion concentrations it is possible from equation (14) to obtain the pK_B values at the three

$$K_\mathrm{B} = [\mathrm{MeO}^-]^2/[\mathrm{B}] \qquad (14)$$

experimental temperatures. As shown in Table 4, dissociation of the amine diminishes as the temperature increases. These pK_B values, and the one determined at *ca.* 25° by an independent method fall on a parabola in the plot of —log K against T; 60° seems to be close to the θ value *i.e.* the temperature at which the maximum of the parabola is found.[24]

When the reaction was performed in the presence of $10^{-2}\mathrm{M}$-cyclohexylammonium chloride no formation of 2,4-dinitroanisole was detected by t.l.c. nor by computer calculation. The rate constants calculated in the usual way obey the Arrhenius equation (k_T in Table 4), while the rate constants measured in the absence of the salt ($k_\mathrm{T}{}^\mathrm{C}$), do not, giving a concave upward Arrhenius plot,

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* The program is available by writing to N.S.N.

[22] A. L. Beckwith, J. Miller, and G. D. Leahy, *J. Chem. Soc.*, 1952, 3552.

[23] J. F. Bunnett and N. S. Nudelman, *J. Org. Chem.*, 1969, **34**, 2043.

[24] R. W. Gurney, ' Ionic Processes in Solution,' Dover, New York, 1953, p. 122.

as expected for a complex reaction.[25] Cyclohexylammonium chloride was used, as earlier,[26] to force equilibrium (1) to the left.

Reaction of 2,4-*Dinitroanisole with Cyclohexylamine.*—The results are gathered in Table 6. Despite expectation for this poor leaving group, a very mild acceleration ($k_B/k_0 = 0.6$) is observed for increasing amounts of amine. For this reason amine catalysis was neglected in the above treatment.

The absence of base catalysis in this reaction may be due to the fact that as cyclohexylamine is an aliphatic, primary, and sterically hindered amine, the formation (k_1) of the intermediate complex is the rate-controlling step. Comparison with the second-order rate coefficient of the reaction with piperidine [10] reveals that this is 10^5 times faster than the reaction with cyclohexylamine. But, contrary to the results found with piperidine, the reaction with cyclohexylamine goes to completion with only one product; neither an equilibrium nor side reactions are detected. For the three concentrations of amine studied the rate coefficients obey the Arrhenius equation as would be expected for a simple reaction. The average thermodynamic parameters are $\Delta H^\ddagger$ 13.5 kcal mol^{-1}, $\Delta S^\ddagger$ −36 cal K^{-1} mol^{-1}.

TABLE 6

Reaction of 2,4-dinitroanisole with cyclohexylamine in methanol

[Cyclohexylamine]/ M	T/°C	10^4k_T/ l mol^{-1} s^{-1}
0.101	35	0.161
	45	0.366
	60	1.08
0.306	35	0.177
	45	0.421
	60	1.39
0.592	35	0.205
	45	0.497
	60	1.54

Reaction of 2,6-*Dinitrochlorobenzene with Cyclohexylamine.*—Contrary to the behaviour of the 2,4-dinitrochlorobenzene the 2,6-isomer undergoes a simple reaction with cyclohexylamine in methanol. The presence of 2,6-dinitroanisole was not detected and the absorbance at 307 nm ($\lambda_{max.}$ of 2,6-dinitroanisole) showed the expected slight increase due to the formation of *N*-(2,6-dinitrophenyl)cyclohexylamine, $\lambda_{max.}$ 425 nm. The 'infinity' spectrum corresponds to the *N*-substituted product in quantitative yield.

As can be observed in Table 7 the reaction is not subject to amine catalysis and for the three amine concentrations studied the second-order rate coefficients for the three experimental temperatures give a linear Arrhenius plot. The thermodynamic parameters are $\Delta H^\ddagger$ 11.5 kcal mol^{-1}, $\Delta S^\ddagger$ −38.4 cal K^{-1} mol^{-1}.

TABLE 7

Reaction of 2,6-dinitrochlorobenzene with cyclohexylamine in methanol

[Cyclohexylamine]/ M	T/°C	10^4k_T/ l mol^{-1} s^{-1}
0.174	35	2.88
	45	5.97
	60	17.8
0.432	35	3.28
	45	7.68
	60	20.5
0.591	35	3.40
	45	7.22
0.586	60	20.5

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[25] J. F. Bunnett, 'Techniques of Chemistry,' ed. E. S. Lewis, Wiley, New York, 1974, vol. VI, part I, ch. VIII, p. 406.

[26] J. F. Bunnett, T. Kato, and N. S. Nudelman, *J. Org. Chem.*, 1969, **34**, 785.