Reactions of Nitroanisoles. 4.[1,2] Reaction of 2,4- and 2,6-Dinitroanisole with Cyclohexylamine. Evidence of a "Dimer" Nucleophile

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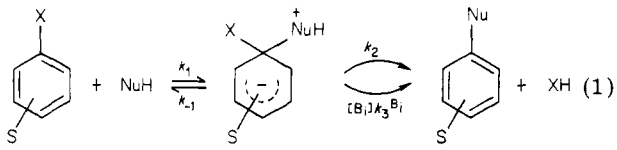
Received June 7, 1982

The reactions of 2,4- and 2,6-dinitroanisole (DNA) with cyclohexylamine in benzene and in cyclohexane were studied at three temperatures. Two unusual facts were observed: the overall reaction rate is of third order with respect to the amine concentration, and an inverse temperature effect is found for the reaction of 2,4-DNA in cyclohexane. Both experimental findings and some other "anomalous" results reported in the literature are satisfactorily accommodated in a reaction scheme in which the *dimer* of the amine is operating.

The occurrence of base catalysis in reactions of 1-substituted 2,4-dinitrobenzenes with amines (eq 1) has been



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extensively studied since its discovery by Bunnett and his co-workers.[3] The subject has been recently reviewed,[4] and the detailed mechanism for the reactions in protic solvents seems now firmly established after the works of Bernasconi et al.[5] When the reactions are run in aprotic solvents, however, "the situation is certainly more complicated."[5a] For these cases, a fast acid–base equilibrium between the zwitterionic σ intermediate complex and its conjugate base was proposed[6] followed by a rate-limiting general-acid-catalyzed departure of the nucleofugue (SB-GA mechanism).[6] However, the generality of this mechanism has been recently questioned.[7,8]

Since, according to the two-step mechanism devised by Bunnett,[9] the reaction is subject to base catalysis when the expulsion of the nucleofugue is at least partially rate determining,[3] dinitroanisoles (DNA) are appropriate substrates for the study of the decomposition of the σ-zwitterionic intermediate complex. Steric effects seem to influence the incidence of the base-catalyzed path,[3d,10] and therefore, comparison of the 2,4- and 2,6-DNA reactivities is relevant.

The reactions of both substrates with *n*-butylamine[1] show a very peculiar dependence of the rate coefficient with the amine concentration, and we report now a similar behavior in the reactions of 2,4- and 2,6-DNA with cyclohexylamine in aprotic solvents.

Table I. Kinetics of the Reaction of 2,4-Dinitroanisole with Cyclohexylamine (CHA) in Cyclohexane[a,b]

	$10^5 k_A$, s^{-1} M^{-1}		
[CHA], M	60 °C	80 °C	100 °C
0.0578	0.753	0.574	0.299
0.113	2.80	2.34	1.73
0.150	4.33		
0.210	8.07	7.96	6.03
0.306	14.3	16.7	14.7
0.402	20.1	27.1	25.5
0.514	26.8	43.0	43.5

[a] [DNA] ca. 1.7×10^{-4} M; $10^6 k_{S_N2}$ values at 60, 80, and 100 °C are 0.13, 0.37, and 3.95 s^{-1} M^{-1}, respectively. [b] Cyclohexane/benzene ratio of 99:1 (see Experimental Section).

Table II. Kinetics of the Reaction of 2,4-Dinitroanisole with Cyclohexylamine (CHA) in Benzene[a]

	$10^5 k_A$, s^{-1} M^{-1}		
[CHA], M	60 °C	80 °C	100 °C
0.0528	0.359	0.406	0.564
0.0751	0.686	0.776	0.810
0.107	1.21	1.33	1.57
0.212	3.69	4.26	4.80
0.314	6.12	8.53	9.74
0.612	12.5	24.3	32.8

[a] [DNA] ca. 1.8×10^{-4} M; $10^6 k_{S_N2}$ values at 60, 80, and 100 °C are 0.9, 1.2, and 2.1 s^{-1} M^{-1}, respectively.

Results

The reaction between 2,4- and 2,6-DNA with cyclohexylamine, both in benzene and in cyclohexane, yields mainly the expected *N*-(2,4- or *N*-(2,6-dinitrophenyl)-cyclohexylamine, respectively. The S_N2 demethylation that was important in the reactions of the same substrates with piperidine[11] was only slightly detectable in some cases here or not detected at all. For those reactions in which S_N2 demethylation occurs, its value was deduced from the observed overall rate coefficients to obtain the second-order rate coefficient, k_A, for the aromatic nucleophilic substitution (ANS).

The kinetics of the reactions were studied in the presence of varying excess of nucleophile under pseudo-first-order conditions. The reactions proved to be first order in substrate, and on division of the pseudo-first-order rate coefficients, k_ψ, by the appropriate concentration of cyclohexylamine, the second-order rate coefficients, k_A, were calculated. The data for the reaction of 2,4-DNA with cyclohexylamine in cyclohexane are reported in Table I,

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(2) Presented in part at the 2nd Conference on Physical Chemistry, Córdoba, Argentina, Sept 1980.
(3) (a) Bunnett, J. F.; Garst, R. H. *J. Am. Chem. Soc.* **1965**, *87*, 3879. (b) Bunnett, J. F.; Bernasconi, C. F. *Ibid.* **1965**, *87*, 5209. (c) Bunnett, J. F.; Garst, R. H. *J. Org. Chem.* **1968**, *33*, 2320. (d) Bunnett, J. F.; Randall, J. J. *J. Am. Chem. Soc.* **1958**, *80*, 6020. (e) Bunnett, J. F.; Pruitt, K. M. *J. Elisha Mitchell Sci. Soc.* **1957**, *73*, 297.
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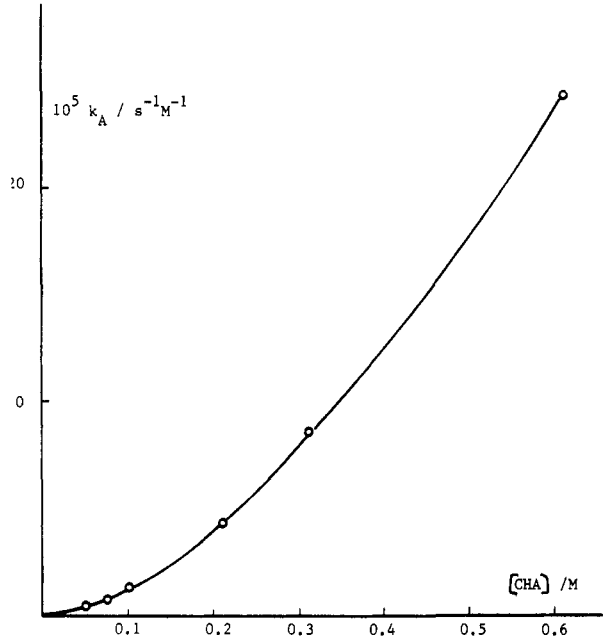

Figure 1. Reaction of 2,4-dinitroanisole with cyclohexylamine (CHA) in benzene at 80 °C.

Table III. Kinetics of the Reaction of 2,6-Dinitroanisole with Cyclohexylamine (CHA) in Benzene[a]

	10^5k_A, s^{-1} M^{-1}		
[CHA], M	27 °C	35 °C	45 °C
0.0264	1.15	1.38	1.99
0.0524	2.53	2.96	3.76
0.0794	4.22	4.84	5.92
0.154	10.8	11.8	13.5
0.213	17.4	18.6	20.7
0.262	23.5	25.0	27.7
0.461	61.2	64.1	66.3

[a] [DNA] ca. 1.8×10^{-4} M; the $k_{S_N^2}$ value in all cases is less than 7×10^{-7} s^{-1} M^{-1}. $\Delta H^{\ddagger}$ ranged from 6.4 to 1.4 kcal mol^{-1} and $-\Delta S^{\ddagger}$ ranged from 62 to 70 cal K^{-1} mol^{-1}.

and those in benzene are summarized in Table II. The reactions were studied at 60, 80, and 100 °C. It can be observed in both tables that the rate coefficients increase steadily with increasing amounts of amine. But when k_A is plotted against the cyclohexylamine concentration, [B], a parabolic curve is obtained instead of the straight line expected if the classical base catalysis mechanisms were operating. Figure 1 shows the dependence of k_A with [B] for the reaction of 2,4-DNA with cyclohexylamine in benzene at 80 °C. Similar plots are obtained for the reactions in cyclohexane at the three temperatures.

Table III gathers the kinetic results of the reaction of 2,6-DNA in benzene with varying amounts of cyclohexylamine at 27, 35, and 45 °C. Again the plot of k_A vs. [B] (not shown) is curvilinear at the three studied temperatures.

Discussion

The kinetic expression derived with reference to the mechanism depicted in eq 1 on the basis of the steady-state assumption is represented in eq 2; where the term B_i

$$\frac{\text{rate}}{[\text{ArX}][\text{NuH}]} = k_A = \frac{k_1k_2 + k_1\sum_i k_3^{B_i}[B_i]}{k_{-1} + k_2 + \sum_i k_3^{B_i}[B_i]} \quad (2)$$

symbolizes any base present in the system. The variety of factors that make $k_{-1} \gg k_2 + \sum_i k_3^{B_i}[B_i]$, or vice versa,

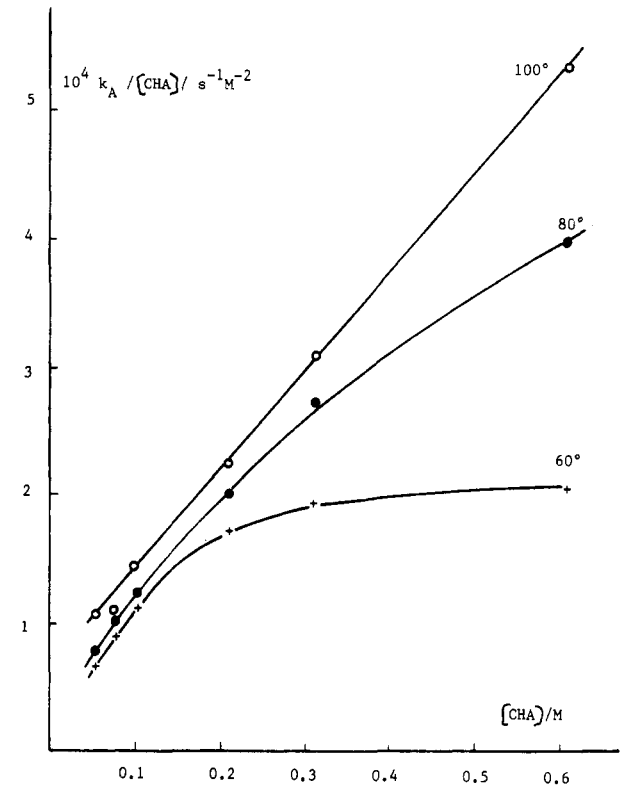

Figure 2. Reaction of 2,4-dinitroanisole with cyclohexylamine (CHA) in benzene.

have been discussed previously.[4,5] When the first inequality holds, eq 2 simplifies to eq 3, and a linear dependence of the second-order rate coefficient, k_A, with $[B_i]$ is observed.

$$k_A = \frac{k_1k_2}{k_{-1}} + \frac{k_1\sum_i k_3^{B_i}[B_i]}{k_{-1}} \quad (3)$$

According to eq 3 the plot of k_A against any present base concentration, [B], should give a straight line with intercept k_1k_2/k_{-1} and slope $k_1k_3^B/k_{-1}$. That plot for the present reactions studied is a curve instead of a straight line (Figure 1), but a linear dependence is observed between $k_A/[B]$ and [B]. Figure 2 shows the behavior for the reaction of 2,4-DNA with cyclohexylamine in benzene, and Figure 3 shows that for the reaction of the same system in cyclohexane. Similar plots are obtained for the reaction of 2,6-DNA with cyclohexylamine in benzene (Figure 4) and for the previously reported reactions of 2,4- and 2,6-DNA with *n*-butylamine in benzene.[1]

This observation of a linear variation of $k_A/[B]$ with [B] admits different interpretations. Among others, either of the following mechanisms is consistent with the quadratic dependence of k_A with [B].

Mechanism I is a base-catalyzed formation of the intermediate, followed by its base-catalyzed breakdown. A mechanism by which this base catalysis of the addition step could operate may be by hydrogen bonding of the base to the high-electron-density centers of the initial state (oxygen atoms of the nitro groups and the methoxyl group) or to the negative ring charge in the intermediate. An alternative possibility could be a concerted attack of both amine molecules (the nucleophile and the catalyst), but the energies of the involved states are different, making the two-step pathway preferred to the concerted one.[12]

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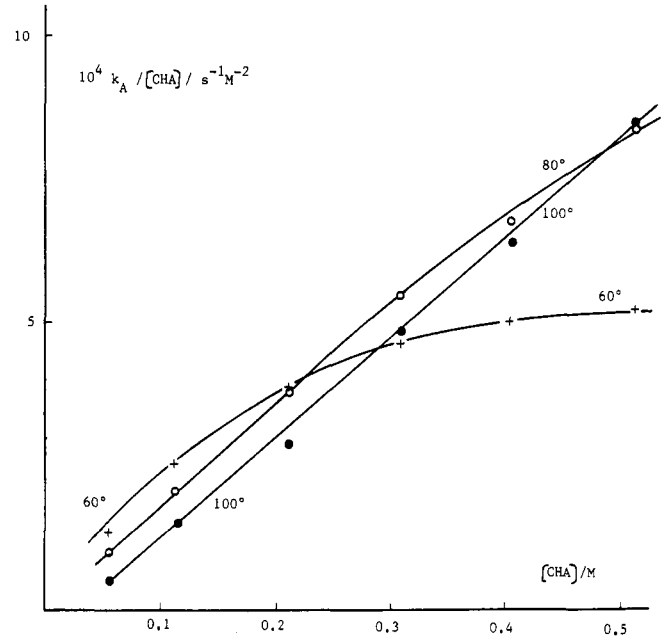


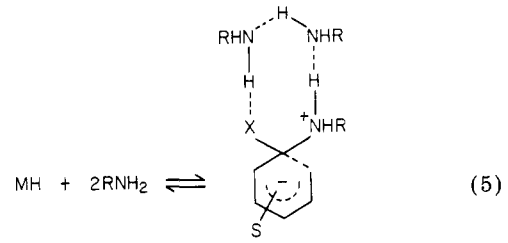
Figure 3. Reaction of 2,4-dinitroanisole with cyclohexylamine (CHA) in cyclohexane.

Hydroxide ion catalysis of the first step has been observed in the reaction of *p*-nitrophenyl phosphate with piperidine in aqueous solutions;[13] in that case the kinetic law reduces to eq 4 at high [OH^-] which accounts for the small con-

$$k_A' = k_1 + k_4[OH^-] \quad (4)$$

tinued increase in the observed rate; a behavior quite different from the present one.

Mechanism II. Two molecules of amine intervene in the base-catalyzed decomposition of the zwitterionic intermediate to form a cyclic transition step (eq 5) as has been recently proposed.[8a]



(5)

Mechanism III. A cyclic intermediate (II in the Scheme I) is formed straightforwardly in the addition step[14] through the *dimer* of the amine which exists in aprotic solvents due to equilibrium 6. A cyclic transition

$$2NH_2R \overset{K_1}{\rightleftharpoons} RNH_2\cdots NH_2R \quad (6)$$

step similar to II has been recently proposed[8b] but for the second step (decomposition of the intermediate complex III).

Mechanism I is the less favored for the reasons already mentioned. Mechanism II requires the encounter of three molecules in the second step and concerted formation of three hydrogen bonds. Furthermore, it does not explain some experimental results (apart from the quadratic dependence of k_A with [B]) related to the temperature dependence. For these reasons it is less favored than mechanism III.

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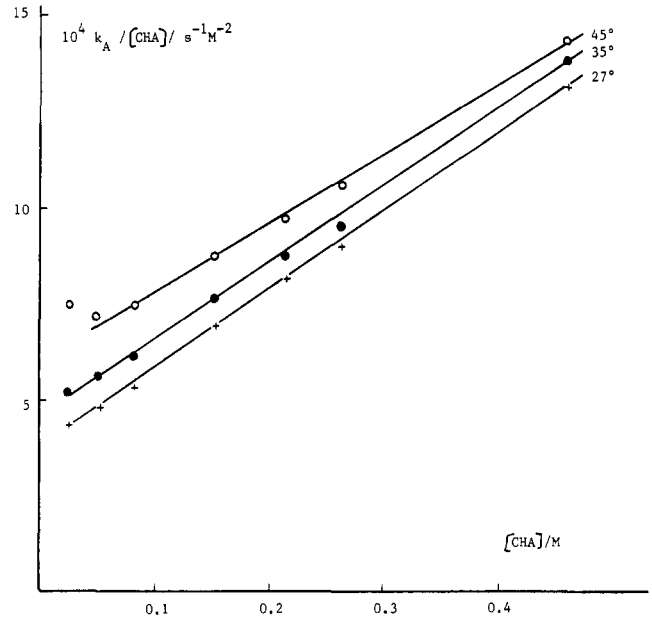
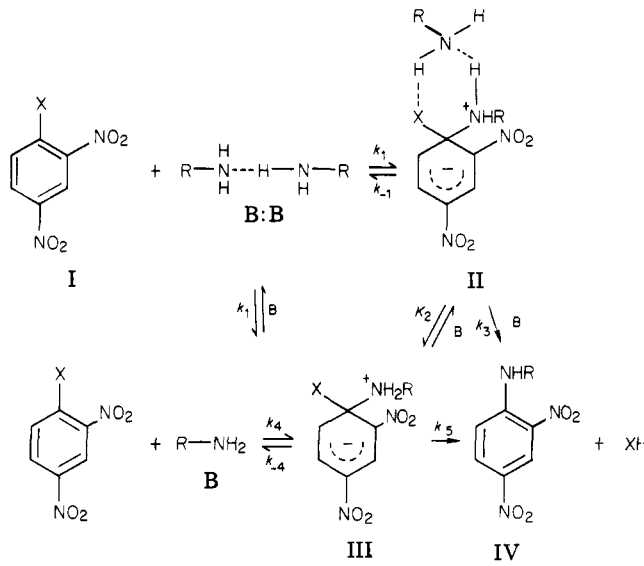


Figure 4. Reaction of 2,6-dinitroanisole with cyclohexylamine (CHA) in benzene.

Scheme I



Mechanism III takes into account equilibrium 6 that prevails in nonpolar aprotic solvents. Association of aliphatic amines in that media is a very well established phenomenom known since early times.[15] The intermediate II formed in the first step is in mobile equilibrium with the second classical intermediate III, and either of them can react to form ultimate products. The whole reacting system is depicted in Scheme I. Application of the steady-state treatment to this mechanism gives eq 7

$$k_A = \frac{d[IV]}{dt[I][B]} = \frac{k_4k_5K_2 + k_1k_5K_1K_2[B] + k_3k_4[B] + k_1k_3K_1[B]^2}{k_{-4}K_2 + k_5K_2 + (k_3 + k_{-1})[B]} \quad (7)$$

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for the observed second-order rate coefficient,[1] where K_1 has been approximated to $[B:B]/[B]_0^2$ since the association constant of the amine is small.[15]

The proposed mechanism does not preclude attack by the monomer which straightforwardly would form intermediate III, proposed in previously reported two-step mechanisms.

Mechanisms such as substrate + dimer $\rightleftharpoons$ II $\rightleftharpoons^{\text{amine}}$ transition state $\rightleftharpoons$ products and substrate + amine $\rightleftharpoons$ III $\rightleftharpoons^{\text{dimer}}$ transition state $\rightleftharpoons$ products are kinetically indistinguishable, as well as a four-step mechanism in which each molecule of amine is added stepwise; nevertheless, the experimental evidence presented in this and the next paper is consistent with the operation of a dimer of the amine.

From Figure 1 and the data of Tables I–III it can be noticed that in these reactions $k_A = 0$ at nul base concentration, and therefore $k_4k_5/(k_{-4} + k_5)$ must be nul. Since k_4 measures the rate of the monomer attack, it is reasonable to assume that its value is not negligible; consequently, the quotient $k_5/(k_{-4} + k_5) \simeq 0$, and this is probably due to the very small value of k_5 in aprotic solvents. With this assumption eq 7 simplifies to eq 8.

$$\frac{k_A}{[B]} = \frac{k_3k_4 + k_1k_3K_1[B]}{(k_{-1} + k_3)[B] + k_{-4}K_2} \quad (8)$$

This equation agrees with the experimental results of the dependence between $k_A/[B]$ and [B] (Figures 2–4), and its also accounts for its peculiar temperature dependence.

As can be seen in Tables I–III, the reaction exhibits a very small overall energy of activation, and even in some cases (e.g., reactions of 2,4-DNA with cyclohexylamine in cyclohexane, Figure 3, and with *n*-butylamine in benzene)[1] the reaction at 60 °C at low [B] is faster than the reaction at higher temperatures. As it is known, the equilibrium association constant K_1 diminishes with increasing temperatures.[15] This is a reasonable explanation for the surprising apparently "inverse" temperature effect. A similar unexplained behavior has been previously observed in the reaction of 2-phenoxy-1,3,5-triazine with piperidine in isooctane[16] over a large range of temperatures (23–71 °C), where the rates were found to decrease slightly with increasing temperatures ([piperidine] = 0.092 M). In these reactions k_A also shows a departure from linearity (upward concavity) at relatively high concentrations of piperidine (up to 0.33 M) and was ascribed to a medium effect.[17] But a plot of $k_A/[B]$ vs. [B] is linear (correlation coefficient 0.998).

Some other reactions reported in the literature were also found to show a quadratic plot of k_A vs. [B], e.g., the reaction of 2,4-dinitrofluorobenzene with *p*-anisidine in benzene[18] and with aniline in toluene[19] and the reaction of 2-methoxy-3-nitrothiophene with piperidine in benzene.[20] These anomalous departures from linearity were ascribed to "unspecific solvent effects", but the determination of the changes in the dielectric constant, *D*, of the bulk solvent due to the increasing amounts of amine[21] shows that these changes are not enough to account for the increase in rate, if the classical dependence of *k* with *D* is applied.[22] All the above-mentioned anomalous results[16,18–20] can be easily explained on the basis of the mechanism proposed in Scheme I. It also explains the low energy of activation (or even the apparent absence of it) over a wide range of temperatures: the rate-determining step is preceded by a fast equilibrium, whereby the expected increase in rate for the slow step with increasing temperatures would be compensated for by a shift of the preceding equilibrium toward the monomer.

Although this is the first time that a complex of two molecules of amine is proposed for the addition step in ANS, it has been invoked several times in the reactions of di- and trinitrobenzenes with amines,[23–25] and recently Nagy et al.[26] explained the third-order dependence with respect to butylamine in its reaction with tetrachloro-*N*-butylphthalimide in aprotic media as being due to a catalytic effect of the amine present as a dimer.

In the cyclic intermediate proposed here, the second molecule of amine acts as a proton donor to the leaving group as well as a proton acceptor from the positively charged nitrogen atom of the zwitterion, thus stabilizing the dipolar transition state that otherwise should be quite unstable in benzene. Acid assistance of the nucleofugue departure has been shown to be important in aprotic solvents.[6,16,27] The decomposition of the zwitterionic intermediate to the reaction products through a cyclic transition state like intermediate II was formerly proposed by Capon and Rees[28] and invoked several times by other authors,[16,29] and it is also clearly related to the bifunctional catalysis found in ANS.[30] The original contribution of the present paper is the operation of the dimer of the amine as an entity, according to experimental evidence.

This decomposition also explains why diisopropyl ethylamine or quinuclidine led to a very slight decrease in the rate of substitution of the already mentioned reaction of 2-phenoxy-1,3,5-triazine in isooctane.[16] 2-Pyridone, instead, has a 10 times more effective catalytic effect than piperidine, and association between this and the carbonyl oxygen of 2-pyridone should be certainly stronger than the hydrogen-bonding between two molecules of piperidine; the cyclic intermediate is greatly favored, and its decomposition to reaction products is preferred to the same decomposition of an intermediate equivalent to III.

Further Treatment of the Kinetic Results. In order to fit the experimental findings, one can simplify the general eq 8 as follows.

(1) At high base concentration, eq 8 reduces to eq 9.

$$\frac{k_A}{[B]} = \frac{k_1k_3K_1}{k_3 + k_{-1}} \quad (9)$$

According to eq 9 the plot of $k_A/[B]$ should give a plateau at high [B], and this is observed in the reactions of 2,4-DNA with cyclohexylamine in benzene (Figure 2) and in cyclohexane (Figure 3) and with *n*-butylamine in benzene[1] for the reactions at 60 °C; the reactions at 80 °C

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Table IV. Rate Coefficient Relationships for ANS of Dinitroanisoles

amine	substrate	solvent	temp, °C	$10^4k_3k_4/k_{-4}K_2$[a]	$10^3k_1k_3K_1/k_{-4}K_2$[a]	$10^3k_1k_3K_1/k_{-4}K_2$[b]	k_1K_1/k_4
cyclohexylamine	2,4-DNA	benzene	100	0.602	0.781		13[c]
			80	<0.34	>0.86	1.26	>37[d]
			60	<0.13	>1.0	1.81	>140[d]
		cyclohexane[e]	100	0	1.73		∞
			80	0	1.81	1.89	∞
			60	0	>2.65	4.0	∞
	2,6-DNA	benzene	45	6.06	1.78		2.9[c]
			35	4.57	2.00		4.4[c]
			27	3.78	2.04		5.4[c]
n-butylamine	2,4-DNA[f]	benzene	100	3.61	5.78		16[c]
			80	<3.2	>6.8	12.9	>40[d]
			60	<4.0	>6.6	22.7	>57[d]
	2,6-DNA[f]	benzene	45	19.0	9.5		5.0[c]
			35	15.0	10.9		7.3[c]
			27	13.0	12.3		9.5[c]

[a] From eq 10. [b] From the inverted slope of eq 13. [c] From the quotient between the slope and the intercept of eq 10. [d] From the quotient between the inverted slope of eq 13 and the intercept of eq 10. [e] Cyclohexane/benzene ratio of 99:1. [f] Data from ref 1.

show a slight curvature, tending to a farther asynthotic behavior.

(2) If $(k_{-4}K_2) \gg (k_3 + k_{-1})[B]$, eq 8 transforms into eq 10, which is the expression for the linear dependence of

$$\frac{k_A}{[B]} = \frac{k_3k_4}{k_{-4}K_2} + \frac{k_1k_3K_1}{k_{-4}K_2}[B] \qquad (10)$$

$k_A/[B]$ observed in most of the reactions. This equation holds for the reactions at 100 °C in all the range of [B] studies and at the three temperatures for the reactions of 2,6-DNA with cyclohexylamine and *n*-butylamine.[1] The slopes and the intercepts for the reaction data in Tables I–III are gathered in Table IV as well as values for the quotient k_1K_1/k_4.

(3) At low [B], eq 8 then simplifies to eq 11 which shows

$$k_A = \frac{k_3k_4}{k_{-4}K_2}[B] \qquad (11)$$

that the plot of k_A vs. [B] at very low [B] should give a straight line with a nul intercept, which is consistent with the experimental results.

Inversion of eq 8 gives expression 12 which allows some

$$\frac{[B]}{k_A} = \frac{(k_3 + k_{-1})[B] + k_{-4}K_2}{k_3k_4 + k_1k_3K_1[B]} \qquad (12)$$

estimation of the different k's involved. When $k_1K_1[B] \gg k_4$, eq 12 transforms into eq 13.

$$\frac{[B]}{k_A} = \frac{k_3 + k_{-1}}{k_1k_3K_1} + \frac{k_{-4}K_2}{k_1k_3K_1[B]} \qquad (13)$$

A plot of $[B]/k_A$ vs. $[B]^{-1}$ should be linear, except where the conditions which allow simplification to eq 13 are not fulfilled. Such a plot is presented as Figure 5A for the reaction with cyclohexylamine in cyclohexane based on the data in Table I and as Figure 5B for the reaction with *n*-butylamine in benzene (data in ref 1), both at 80 °C. They are satisfactorily linear, and if the slopes are inverted, one may evaluate $k_1k_3K_1/k_{-4}K_2$. Inversion plots were also constructed for the other reactions of Tables I and II, and the inverted slopes are tabulated in Table IV. The reactions at 80 °C exhibit useful behavior for estimation of the same expression from the plot of $k_A/[B]$ vs. [B]. Indeed, at low [B], eq 8 simplifies to eq 10, and the slope of the plot of $k_A/[B]$ vs. [B] agrees satisfactorily with the values obtained from the inversion plot (Table IV). These results can be interpreted as evidence that eq 8 holds and that the simplification to eq 10 is justified.

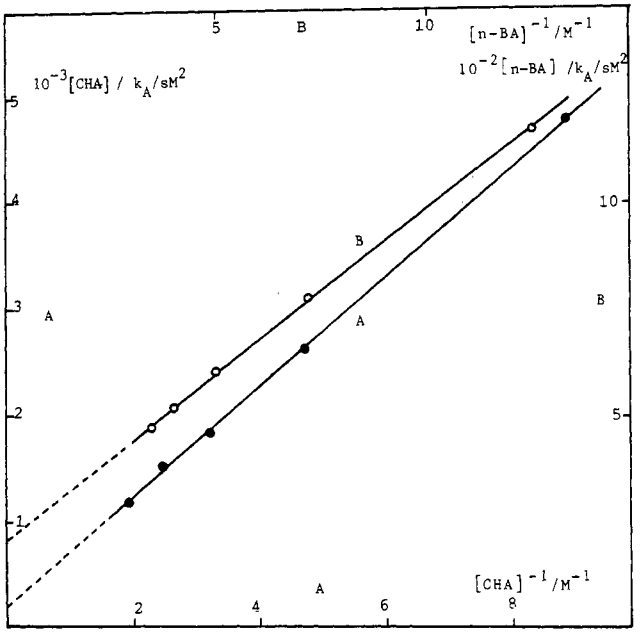

Figure 5. Inversion plot: A, reaction of 2,4-dinitroanisole with cyclohexylamine at 80 °C (●); B, reaction of 2,4-dinitroanisole with *n*-butylamine (*n*-BA) in benzene in 80 °C (○, data from ref 1).

The intercepts of the same plots allow an estimation of the order of magnitude of $k_3k_4/k_{-4}K_2$, and from these values and the $k_1k_3K_1/k_{-4}K_2$ values, the quotient k_1K_1/k_4 can be reckoned (Table IV). As can be observed, the quotient increases with decreasing temperatures, if we assume a similar energy of activation for the addition step of monomer and dimer. This result manifests the increase of the association constant with decreasing temperature in accord with the known data.[15d]

In the reaction of 2,6-DNA with cyclohexylamine in benzene a quadratic dependence of k_A with [B] is also observed; the slope of the curve at the origin is not nul. Similar behavior is observed in the reaction of the same substrate with butylamine in benzene.[1] For this last case, the rate of the reaction allows several kinetics measurements at low [B], and it is possible to calculate exactly the slope at the origin of the plot of k_A vs. [B] for a range of [B] (0–0.03 M, five data in ref 1). At 45 °C, a value of 2.2×10^{-3} s^{-1} M^{-2} is obtained which agrees satisfactorily with the value $k_3k_4/k_{-4}K_2 = 1.9 \times 10^{-3}$ s^{-1} M^{-2} obtained from the intercept of the plot of $k_A/[B]$ vs. [B] constructed with

Table V. Molar Extinction Coefficients[a] of the Products

compd	solvent	λ, nm 370	390	400	428
N-(2,4-dinitrophenyl)cyclohexylamine	benzene	9867		5550	
	cyclohexane/benzene (99:1)	4906		5609	
N-(2,6-dinitrophenyl)cyclohexylamine	benzene		3425		6086
2,4-dinitrophenoxyde[b]	benzene	12159		8714	
	cyclohexane/benzene (99:1)	8525		6966	
2,6-dinitrophenoxyde[b]	benzene		3083		7800

[a] In L mol^{-1} cm^{-1}; error <2%. [b] Measured in a ratio of [cyclohexylamine]:[dinitrophenol] > 1000.

the data obtained at higher [B].[1] The values for the reaction at 35 and at 27 °C are 1.6×10^{-3} and 1.4×10^{-3} s^{-1} M^{-2}, respectively, also in fairly good agreement with the data obtained at higher [B] (Table IV).

For the reactions of the same substrate with cyclohexylamine in benzene (Table III), the values are 4.0×10^{-4} (27 °C), 4.5×10^{-4} (35 °C), and 6.3×10^{-4} s^{-1} M^{-2} (45 °C), which compare satisfactorily with the data of Table IV.

The agreement between the $k_3k_4/k_{-4}K_2$ values obtained from both sets of data represents fulfillment of eq 8, 10, and 13 derived from the mechanism proposed in Scheme I and indicates that the assumptions made and the whole treatment are justified.

General Remarks. Several kinetics phenomena observed in this work and further results presented in next paper are in accordance with the existence of a *dimer* of the amine and its nucleophilic reactivity as sketched in Scheme I. These include the quadratic dependence of k_A with [B], the inverse temperature effect consistent with the association constant temperature dependence, and the sameness of a relation of rate constants obtained from different sets of data. Other conceivable alternative mechanisms failed to accommodate these, earlier, and further[31] observations. The clue cyclic intermediate proposed here, in which the amine exerts the dual role of both proton acceptor and donor, is the same as that proposed by Capon and Rees[28] and that was considered by Bunnett to be "an attractive possibility for reactions in benzene".[32] We feel the dimer mechanism provides satisfactory answers for certain ANS in aprotic solvents.

Experimental Section

Reagents and Solvents. 2,4-Dinitroanisole, 2,4-dinitrophenol, 2,6-dinitroanisole, and 2,6-dinitrophenol were purified as previously described.[11] *N*-(2,4-Dinitrophenyl)cyclohexylamine [mp 155.5–156.5 °C (ethanol) (lit.[33] mp 156 °C)] and *N*-(2,6-dinitrophenyl)cyclohexylamine [mp 77.5–78 °C (methanol) (lit.[34] mp 78.5 °C)] were prepared by standard procedures. Cyclohexylamine was kept over sodium wire, refluxed, and then fractionated under nitrogen; the 134.5–135 °C fraction was used. Benzene and cyclohexane were kept over sodium and stored in a special vessel which allows delivery without air contamination.

Kinetic Procedures. The reactions were studied spectrophotometrically.[35] A Beckman DU 2 spectrophotometer was used with 1.0-cm silica cells. Inasmuch as 2,4-dinitroanisole is slightly soluble in cyclohexane, 1.0-mL aliquots of standard benzene solutions of the substrates were used in all the cases and delivered into a 100-mL volumetric flask containing a weighed amount of cyclohexylamine and the desired solvent; the reaction mixture was shaken, the flask was filled to the mark with solvent, and portions were put into sealed bulbs and immersed in a thermostat. Samples were taken at intervals and cooled, and the optical densities were measured at 400 and 428 nm for the reactions of 2,4- and 2,6-DNA, respectively. Pseudo-first-order rate coefficients, k_ψ, were obtained by the least-squares method as the slope of the correlation ln $(A_\infty - A_t)$ against t, where A_∞ is the optical density of the reaction mixture measured at "infinity" time (more than 10 half-lives). In most of the cases the A_∞ values correspond within 2% to the "mock" infinity solutions prepared from the appropriated substitution products. At low amine concentrations, a parallel reaction of demethylation takes place, yielding the corresponding nitrophenols; the ratio of dinitrophenol to substitution product, R, was determined as previously described,[1] and the reported second-order rate coefficients, k_A, were calculated from $k_A = k_T/(1 + R)$ and $k_{S_N2} = k_T - k_A$, where the k_Ts are second-order overall rate coefficients, calculated from the correlation of ln $(A_\infty - A_t)$ against t. Rate coefficients were reproducible to ±2%. Correction of the amine concentration by using thermal expansion coefficients shows that it is negligible; therefore, the stated amine concentrations and second-order rate coefficients are uncorrected.

Ancillary Spectrophotometric Measurements. UV and visible spectra of the substrates and of the products of their interaction with cyclohexylamine were recorded in a Beckman DK 2A spectrophotometer. The extinction coefficients were determined in a Beckman DU 2 spectrophotometer, the solutions were found to obey Beer's law, and the spectral characteristics are gathered in Table V.

Acknowledgment. We are grateful to the National Research Council (CONICET) and to the Science and Technology Secretariat (SUBCYT) from Argentina for financial support. We also thank IBM Argentina (Buenos Aires) for computer facilities and UMYMFOR (FCEN-CONICET) for the NMR determinations.

Registry No. 2,4-DNA, 119-27-7; 2,6-DNA, 3535-67-9; CHA, 108-91-8; *N*-(2,4-dinitrophenyl)cyclohexylamine, 52790-66-6; *N*-(2,6-dinitrophenyl)cyclohexylamine, 30332-87-7; 2,4-dinitrophenoxide, 20350-26-9; 2,6-dinitrophenoxide, 20650-73-1.

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