Kinetics of the Reaction between 1,2-Dinitrobenzene and Piperidine in n-Hexane. Role of Electron Donor–Acceptor Complexes in the Mechanism. Catalysis by Pyridine

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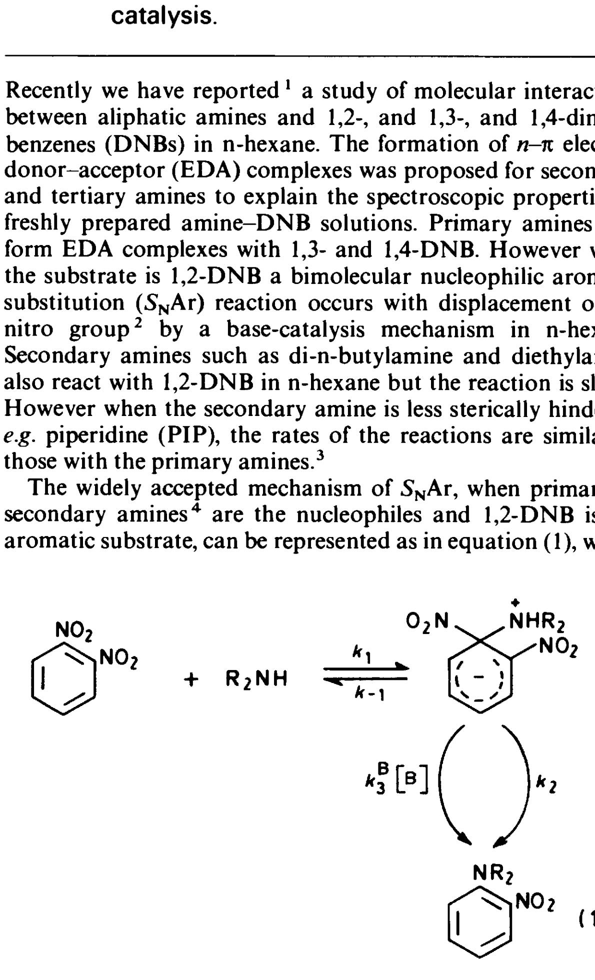
The denitration of 1,2-dinitrobenzene (1,2-DNB) by piperidine (PIP) in n-hexane follows a wholly base-catalysed S_NAr mechanism. The curvilinear dependence of the apparent second-order rate constant (k_A) on PIP concentration is explained in terms of an electron donor–acceptor (EDA) complex between 1,2-DNB and PIP prior to the formation of the σ-intermediate. The fact that the association constant for this complex calculated from kinetic data agrees quite well with the spectroscopic measurements supports this proposal. The kinetics of the reaction in the presence of pyridine are best explained in terms of an association between piperidine and pyridine in an effect that could be described as catalysis of catalysis.

Recently we have reported[1] a study of molecular interactions between aliphatic amines and 1,2-, and 1,3-, and 1,4-dinitrobenzenes (DNBs) in n-hexane. The formation of *n*–π electron donor–acceptor (EDA) complexes was proposed for secondary and tertiary amines to explain the spectroscopic properties of freshly prepared amine–DNB solutions. Primary amines also form EDA complexes with 1,3- and 1,4-DNB. However when the substrate is 1,2-DNB a bimolecular nucleophilic aromatic substitution (S_NAr) reaction occurs with displacement of the nitro group[2] by a base-catalysis mechanism in n-hexane. Secondary amines such as di-n-butylamine and diethylamine also react with 1,2-DNB in n-hexane but the reaction is slow.[1] However when the secondary amine is less sterically hindered, *e.g.* piperidine (PIP), the rates of the reactions are similar to those with the primary amines.[3]

The widely accepted mechanism of S_NAr, when primary or secondary amines[4] are the nucleophiles and 1,2-DNB is the aromatic substrate, can be represented as in equation (1), where



(1)

B is the nucleophile or any base added to the reaction medium. Application of the steady-state hypothesis to this mechanism gives equation (2), where k_A is the observed second-order rate constant.

$$k_A = \frac{k_1(k_2 + \Sigma k_3{}^B[B])}{k_{-1} + k_2 + \Sigma k_3{}^B[B]} \qquad (2)$$

Although the S_NAr reaction of halogens with PIP, in nitro-activated aromatic compounds, has been extensively studied[5] in a variety of solvents, there are only a few examples of nitro group displacement by this nucleophile. Piperidinodenitration has been reported for 1,2-DNB and 1,2,4-trinitrobenzene in benzene as solvent.[6] This reaction was found not to be base-catalysed, *i.e.* $k_2 \gg k_{-1}$ in equation (2). However, for the reaction of PIP with 2,5-dinitrothiophene in benzene, a base-catalysis mechanism was found ($k_2 \ll k_{-1}$).[7]

Thus base catalysis seems to be variable in incidence for nucleophilic substitutions of nitro groups in a non-polar solvent. It therefore seemed of interest to study the kinetics of the reaction of PIP with 1,2-DNB in n-hexane. We now report these studies, which show that the reaction is base-catalysed.

This was confirmed by studies with the addition of pyridine (Py) as a non-nucleophilic base. An unexpected dependence of the rate coefficients on Py concentration was found which might shed new light on base catalysis by this amine in non-polar solvents.

We were also interested in the role of EDA complexes between reactants[8] in the S_NAr mechanisms. The formation of such complexes has been considered either as a side reaction[9] or as a pre-equilibrium to the formation of the σ-intermediate,[10–12] or even as providing an alternative mechanism of base catalysis.[13–15]

Most of these studies have been performed with aromatic amines as nucleophiles.

We present here the evidence that allowed us to interpret the kinetic data for this reaction in terms of formation of an EDA complex between 1,2-DNB and PIP prior to the formation of the σ-intermediate.

Results and Discussion

The reaction between 1,2-DNB and PIP in hexane gives 1-nitro-2-piperidinobenzene in almost quantitative yield (>98%), as shown by t.l.c. and u.v.–visible spectroscopic analysis of the reaction mixtures at infinite time.

The apparent second-order rate constants k_A = (rate/[1,2-DNB][PIP]) for piperidino substitution in hexane as a function of PIP concentration at various temperatures are summarized in Table 1. The value of k_A increases with PIP concentration. This general behaviour is common for S_NAr reactions with aliphatic amines as nucleophiles in non-polar solvents.[16,17]

The plots of k_A *vs.* [PIP] show curvilinear dependence (downward curvature) at temperatures below 38 °C and linear

Table 1. Kinetic constants for the piperidino-substitution of 1,2-DNB in n-hexane at various temperatures

T 18.2 ± 0.1 °C								
[PIP]/M	0.10	0.22	0.30	0.42	0.51	0.60	0.72	0.76
10^4k_A/mol^{-1} dm^3 s^{-1}	0.22	0.39	0.55	0.70	0.85	0.92	1.05	1.06
T 27.4 ± 0.1 °C								
[PIP]/M	0.21	0.21	0.29	0.29	0.41	0.59	0.70	0.71
	0.71	0.79	0.79	1.09	1.19			
10^4k_A/mol^{-1} dm^3 s^{-1}	0.45	0.47	0.59	0.60	0.84	1.02	1.20	1.21
	1.25	1.34	1.30	1.54	1.67			
T 31.3 ± 0.1 °C								
[PIP]/M	0.30	0.41	0.51	0.57	0.61	0.72	0.82	0.90
10^4k_A/mol dm^3 s^{-1}	0.70	0.93	1.12	1.21	1.27	1.43	1.59	1.69
T 38.6 ± 0.1 °C								
[PIP]/M	0.15	0.20	0.30	0.36	0.41	0.48	0.56	0.60
	0.61	0.64						
10^4k_A/mol^{-1} dm^3 s^{-1}	0.75	0.82	1.28	1.62	2.04	2.35	2.75	3.09
	3.09	3.19						

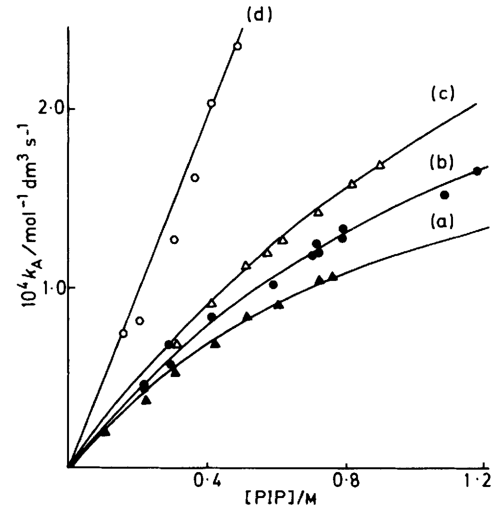


Figure 1. Dependence of k_A on amine concentration in the reaction of 1,2-DNB with piperidine in n-hexane at (a) 18.2 ± 0.1, (b) 27.0 ± 0.1, (c) 31.3 ± 0.1, and (d) 38.6 ± 0.1 °C; solid lines are the theoretical lines obtained from the kinetic parameters in Table 2

dependence at higher temperatures (Figure 1). The intercepts are always zero or near zero.

The linear dependence of k_A on [PIP] at the highest temperature studied (38.6 °C)* can be easily rationalized on the basis of Bernasconi's treatment,[5b] by assuming k_3[PIP] $\gg$ ($k_{-1} + k_2$) and $k_{-1} \gg k_2$. In this case from equation (2) a kinetic law of the type given in equation (3) can be derived. Since the

$$k_A = k_I + k_{II}^{PIP}[PIP] \qquad (3)$$

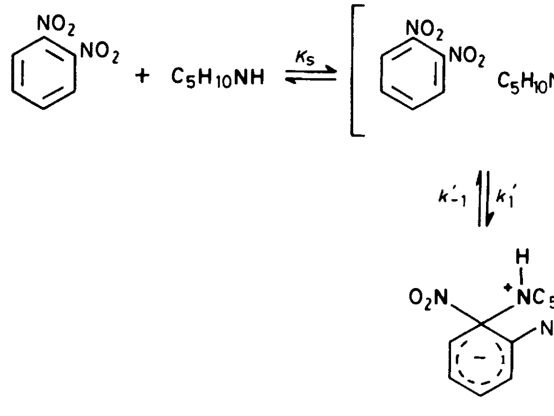
intercept of the linear plot is almost zero ($k_I = 0$), then the slope gives the value of $k_{II}^{PIP} = 4.69\ 10^{-4}$ mol^{-2} dm^6 s^{-1} ($r = 0.9988$); thus the reaction is wholly base-catalysed.

At temperatures below 38 °C, the value of k_I is still zero; thus the reaction is wholly piperidine-catalysed and no spontaneous decomposition of intermediate into products is detectable. The downward curvature of the plot can be explained in terms of two alternative mechanisms:

(*a*) Base-catalysed S_NAr with $k_{-1} \sim k_3^{PIP}$. This would permit a change of the rate-limiting step with increasing catalyst concentration.[17,18] In this case the behaviour of k_A is represented by equation (4).

$$k_A = \frac{k_1 k_3^{PIP}[PIP]}{k_{-1} + k_2^{PIP}[PIP]} \qquad (4)$$

(*b*) Base-catalysed S_NAr with a pre-equilbrium formation of an EDA complex between 1,2-DNB and PIP, as depicted in equation (5). If the condition $k_{-1} \gg k_3^{PIP}$[PIP] is maintained as



(5)

(I)

for the highest temperature studied, then k_A is described by equation (6).

$$k_A = \frac{k'_1 k_3^{PIP} K_s[PIP]}{k'_{-1} + k'_1 K_s[PIP]} \qquad (6)$$

In fact equations (4) and (6) are mathematically equivalent and our experimental data will not distinguish between them in principle.

The alternative (*a*) appears inconsistent with the following facts. Our studies of the reaction of 1,2-DNB with primary amines,[2] particularly n-butylamine[2a] in hexane, show that this reaction is wholly base-catalysed, which implies that $k_{-1} \gg k_3^{BA}$. Further, it is known that S_NAr reactions with secondary amines are more prone to base catalysis than analogous reactions with a primary amine of similar pK_a value.[16] Thus, for example, it has been shown that in the reactions of 1-fluoro-2,4-dinitrobenzene with both PIP and butylamine in benzene k_3^{BA}/k_{-1} is 7.8-fold higher than k_3^{PIP}/k_{-1}. This example was chosen not only on the basis of the amines involved, but also in view of the potential effect of the *ortho*-nitro group.[16]

In the light of these ideas, it seems to us not reasonable to suggest $k_{-1} \sim k_3^{PIP}$ for the reaction under study.

If we consider now alternative (*b*), the curvature of the k_A *vs.* [PIP] plot will depend on the value of K_s. The analytical expression of k_A used for the calculations is given in equation (7), where $k_{III} = k'_1 k_3^{PIP}/k'_{-1}$. A standard treatment of equation

$$k_A = \frac{k_{III}[PIP]}{(1/K_s) + [PIP]} \qquad (7)$$

(7) allows the calculation of k_{III} and K_s. The results are collected in Table 2; the curves drawn by making use of calculated parameters (Figure 1; solid lines) reproduce well the experimental behaviour over the whole range of [PIP] examined.

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* The low boiling points of the liquid reactant and the solvent prevented measurements at temperatures higher than 40 °C under our experimental conditions.

In support of the idea of the formation of an EDA complex prior to substitution [equation (5)], the absorbance of the reaction mixture extrapolated to zero time showed an appreciable deviation from additivity with respect to the components alone, in the region λ = 290—320 nm. These spectroscopic properties are similar to three observed for primary amines with dinitrobenzenes.[2] The equilibrium constants were calculated by a method previously described,[19] and the K values are collected in Table 3. These values, calculated from the spectroscopic measurements, agree within experimental error with those calculated from the kinetic data (Table 2). Also, since K decreases when the temperature is increased, it seems reasonable that at higher temperatures the dependence of k_A with [PIP] should become linear.

From studies of temperature effects on k_{III}, values of $\Delta H^{\ddagger}$ (40.63 kJ mol^{-1}) and $\Delta S^{\ddagger}$ (−226.8 J mol^{-1} K^{-1}) at 25 °C were calculated. These values are consistent with the complexity of the mechanism, resulting from the balance of the parameters of the single steps involved (k'_1, k'_{-1}, and k_3^{PIP}).

Piperidino-substitution of 1,2-*DNB in the Presence of Pyridine*.—The aim of this part of the work was to establish the possibility of base catalysis by Py, and the implications of EDA complex formation. The following studies were performed: (i) a spectroscopic determination of K for complex formation from 1,2-DNB and Py in n-hexane (results in Table 3); (ii) a kinetic study of the reaction of 1,2-DNB with constant [PIP], with the addition of different Py concentrations; and (iii) a study of the reaction of 1,2-DNB with different [PIP] in the presence of a constant concentration of Py (results in Table 4 and Figures 2 and 3).

The curvilinear dependence of the plots of k_A *vs.* [amine] in both experiments (ii) and (iii) fitted equation (8). The results of

$$k_A = \frac{a + b[\text{amine}]}{c + [\text{amine}]} \tag{8}$$

the regression analysis are shown in Table 5. The curves drawn with calculated parameters a, b, and c (Figures 2 and 3; dashed lines) reproduce the experimental behaviour of experiments (ii) and (iii).

The curvilinear dependence of k_A on [Py] at constant [PIP] may imply either a change in rate-determining step when [Py] is increased or association of the catalyst with starting material.[20,21] However when we calculated from equation (8) the levelling-off effect exerted by Py for all the curves in Figure 2, the b value obtained was 2.50 × 10^{-4} ± 0.07 mol^{-2} dm^6 s^{-1}, which differs from the limiting value calculated for PIP itself at the same temperature (k_{III}, Table 2, 27.4 °C). This result supports the interpretation of the curvature based on the association of the catalyst with the reactant. Two types of association could explain this behaviour: formation of the EDA complex 1,2-DNB–Py (Table 3) and a hydrogen-bonded association, PIP–Py. The value of K for the 1,2-DNB–Py complex is considered to be to low to have detectable effects on the catalytic properties of Py.[2b]

Table 2. Kinetic parameters [see equation (7)] for the reaction between 1,2-DNB and piperidine in n-hexane at various temperatures

T/°C	10^4 k_{III}/mol^{-1} dm^3 s^{-1}	K_s/mol^{-1} dm^3	10^{4}C.V.^{a}
18.2	2.547	0.945	0.13
27.4	3.811	0.656	2.05
31.3	5.430	0.502	1.53

[a] Coefficient of variability = $s100/\bar{k}_A$ (s is the standard deviation and $\bar{k}_A$ the mean value of k_A).

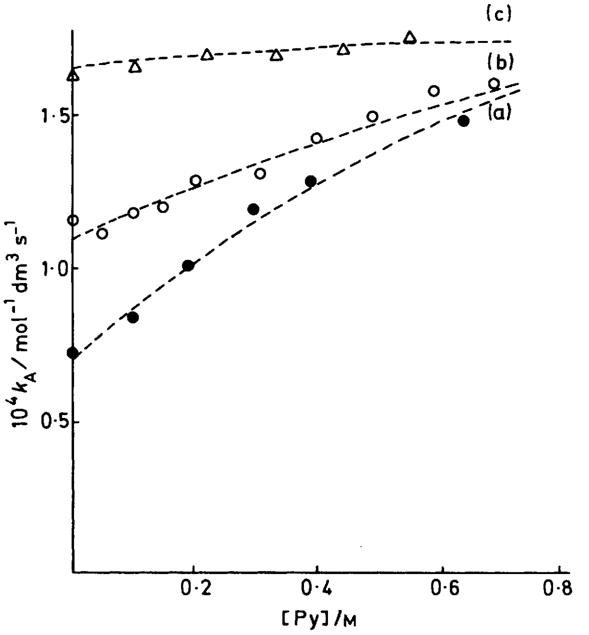


Figure 2. Plots of k_A for the reaction of 1.2-DNB with piperidine in n-hexane in the presence of pyridine against [pyridine]; T 27.0 °C; [PIP]/M (a) 0.305, (b) 0.590, (c), 0.827; dashed lines are the theoretical lines obtained from the kinetic parameters in Table 5

On the other hand, the association between PIP and Py seems the true catalyst in these systems. When the relation of k_A with [PIP] at constant [Py] is analysed (Figure 3) it is seen that k_A approaches zero when [PIP] decreases. This means that Py does not itself catalyse the decomposition of the σ-intermediate (I); if this were the case a finite intercept value would be expected in Figure 3 (*i.e.* $k'_2k_3^{Py}[\text{Py}]/k'_{-1}$). Since Py is a considerable weaker base than the nucleophile in such a non-polar solvent as n-hexane,[22] it seems reasonable that only the complex PIP–Py could act as a catalyst. Thus, we can represent the catalysed decomposition of intermediate (I) in presence of Py in terms of the competitive processes delineated in equation (9). This effect in the catalytic pathway, requiring association of a pair of amines, can be described as catalysis of catalysis, as defined by Frenna *et al.*[23]

This association could also explain the fact that Py seems to be a better catalyst at low than at high constant [PIP] as

Table 3. Formation constants of 1,2-DNB–PIP and 1,2-DNB–Py EDA complexes in n-hexane at various temperatures (λ = 300 nm)

Amine	T/°C	10^2[1,2-DNB]/M	[amine]/M	10^4[amine] [1,2-DBN]	K/mol^{-1} dm^3	r	n
PIP	18.2 ± 0.1	7.25	0.1—2.4	1.4—3.4	0.78 ± 0.08	0.9859	12
PIP	27.2 ± 0.1	4.62	0.1—2.4	2.2—5.2	0.55 ± 0.05	0.9995	6
PIP	32.0 ± 0.1	4.62	0.1—2.4	2.2—5.2	0.36 ± 0.04	0.9963	6
PIP	39.0 ± 0.1	4.62	0.1—2.4	2.2—5.2	0.19 ± 0.02	0.9996	7
Py	27.0 ± 0.1	9.23	0.3—2.3	3.6—25.2	0.30 ± 0.03	0.9956	7

Table 4. Kinetic data for the reaction of 1,2-DNB with PIP in n-hexane, at 27 °C in the presence of Py

System								
(1)	[PIP] 0.30M							
	[Py]/M	0.00	0.10	0.20	0.30	0.40	0.60	
	10^4k_A/mol^{-1} dm^3 s^{-1}	0.72	0.83	1.02	1.20	1.27	1.47	
(2)	[PIP] 0.59M							
	[Py]/M	0.00	0.05	0.10	0.15	0.21	0.31	0.41
		0.49	0.59	0.69	0.79			
	10^4k_A/mol^{-1} dm^3 s^{-1}	1.16	1.10	1.18	1.20	1.29	1.30	1.43
		1.50	1.60	1.60	1.62			
(3)	[PIP] 0.83M							
	[Py]/M	0.00	0.11	0.23	0.34	0.45	0.56	
	10^4k_A/mol^{-1} dm^3 s^{-1}	1.63	1.67	1.70	1.70	1.71	1.75	
(4)	[Py] 0.00M							
	[PIP]/M	0.21	0.21	0.29	0.29	0.41	0.59	0.70
		0.71	0.79	1.09	1.19			
	10^4k_A/mol^{-1} dm^3 s^{-1}	0.45	0.47	0.59	0.60	0.84	1.02	1.20
		1.25	1.34	1.54	1.67			
(5)	[Py] 0.25M							
	[PIP]/M	0.20	0.30	0.44	0.59	0.74	0.89	
	10^4k_A/mol^{-1} dm^3 s^{-1}	0.60	0.89	1.08	1.26	1.48	1.59	
(6)	[Py] 0.48M							
	[PIP]/M	0.10	0.24	0.40	0.59	0.72	0.79	
	10^4k_A/mol^{-1} dm^3 s^{-1}	0.46	0.86	1.30	1.45	1.76	1.66	
(7)	[Py] 0.76M							
	[PIP]/M	0.10	0.20	0.30	0.40	0.50	0.59	
	10^4k_A/mol^{-1} dm^3 s^{-1}	0.57	1.01	1.21	1.45	1.62	1.75	

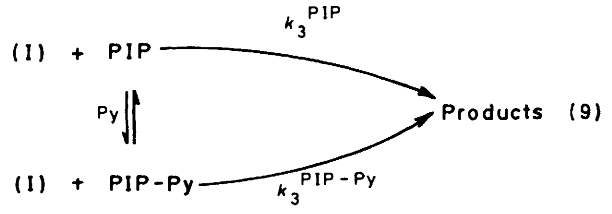
Table 5. Regression analysis of k_A for the reaction between 1,2-DNB and PIP in n-hexane [by equation (8)]

System[a]	10^4a	10^4b	c	10^3C.V.[b]
(1)	0.304	2.572	0.534	2.19
(2)	1.123	2.480	1.081	1.73
(3)	7.417	2.442	4.490	3.01
(4)	0	3.811	1.524	2.05
(5)	0	3.110	0.832	1.66
(6)	0	2.849	0.513	0.95
(7)	0	3.009	0.423	2.00

[a] Number corresponds to those in Table 4. [b] Coefficient of variability.

observed in Figure 2. By considering equation (9) we can deduce that, at low [PIP], the preferred mode of the decomposition of intermediate (I) would involve $k_3^{\text{PIP-Py}}$, while at high [PIP] it would involve k_3^{PIP}.

Behaviour similar to that depicted in Figure 2 was found previously for the Py-catalysed reaction of 1-fluoro-2,4-dinitrobenzene with n-butylamine in benzene,[20] and was explained by considering that at low nucleophile concentration the intermediate complex is captured preferentially by the catalyst present in excess. This explanation does not exactly fit all our results, since in such a case the effect should be observed at constant [Py] when the PIP concentration is varied. As already discussed for Figure 3, this is not so. Therefore our proposal of two competitive processes [equation (9)] for proton abstraction from the intermediate (I) seems more adequate to explain our whole set of data. Moreover, the fact that there are no significant changes of k_A with [Py] when the constant concentration of PIP is high (Figure 2) may be taken as evidence that PIP is a better catalyst than PIP–Py.



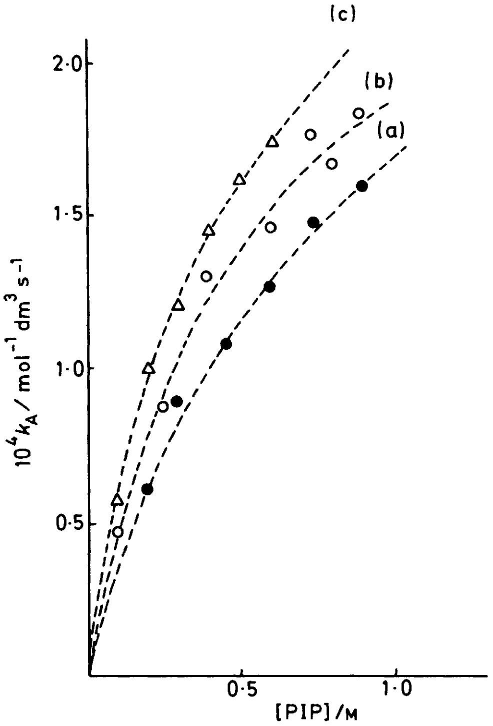


Figure 3. Plots of k_A for the reaction of 1,2-DNB with piperidine in n-hexane in the presence of pyridine against [piperidine]; T 27.0 °C; [Py]/M (a) 0.251, (b) 0.485, (c) 0.761; dashed lines are the theoretical lines obtained from the kinetic parameters in Table 5

From an analysis of the kinetic parameters in Table 5 it can be shown that a plot (not shown) of b *vs.* [Py] gives a limiting value of b when [Py] approaches zero; this is the value of b for system (4). Thus the parameters b seems to be a rather complex combination of two terms, one including the catalytic rate constants for PIP and the other corresponding to catalysis by PIP–Py. Since b decreases when the Py concentration increases, we can presume that PIP–Py is less efficient than PIP as catalyst, in agreement with the previous conclusion.

The values of the parameter c for the systems (4)—(7) (Table 5) also increase regularly with decrease of [Py] and tend to the value of c in system (4) at [Py] = 0. This explains the fact that k_A increases at low [PIP] for the systems with increasing constant [Py].

Conclusions.—The S_NAr reaction of 1,2-DNB with PIP in n-hexane is wholly base-catalysed by the nucleophile. This is expected in view of the almost non-existent ionizing power of the solvent. Although PIP is a secondary amine, it is much more reactive than acyclic homologues; this gives some idea of the steric requirements of this reaction.

The curvilinear dependence of k_A on [PIP] can be rationalized in terms of the proposal of formation of an EDA complex from 1,2-DNB and PIP previous to the formation of the intermediate (I). Although this proposal is kinetically indistinguishable from that in equation (7), the fact that K calculated from kinetic data agrees quite well with that from spectroscopic measurements is encouraging.

Finally the catalytic behaviour of Py seems to be best explained in terms of an association with PIP in an effect that could be described as catalysis of catalysis. This type of effect can only be detected if a study is performed by varying concentrations not only of the nucleophile but also of the non-nucleophilic base, such as was carried out in this work.

Experimental

Spectra were obtained for samples in thermostatically controlled cells in a Cary 17 spectrophotometer. ^{1}H N.m.r. spectra were obtained with a Bruker X (60 MHz) instrument and mass spectra with a Finnigan 3300 spectrometer. Data processing was performed with a Digital PDP 11/34 computer [programs are from the author (J. J. S.)].

Synthesis and Purification of Materials.—n-Hexane and 1,2-DBN (Fluka) were purified by methods described previously.[1]

Piperidine (Carlo Erba) was kept over sodium wire, then refluxed and fractionated over sodium; the fraction of b.p. 105—106 °C was used.

Pyridine (Merck) was kept over sodium hydroxide for several days and distilled immediately after use. The purity of the amines was estimated by g.l.c. and u.v. spectroscopy.

1-Nitro-2-piperidinobenzene was prepared by reaction of 1,2-DNB (100 mg, 0.6 mmol) with neat PIP (6 ml, 60 mmol) at room temperature. Reaction was completed within 20 min as established by following the disappearance of 1,2-DNB by t.l.c. [silica gel F_{254} with benzene–light petroleum (1:1) as solvent]. From the solution a bright reddish solid was separated by column chromatography in 90% yield. This solid was then sublimed under vacuum; m.p. 78.5 °C (lit.,[24] 78 °C); $\lambda_{max.}$(n-hexane) 380 nm (log ε 3.17); δ_H (CCl_4; standard Me_4Si) 1.97 (4 H, m), 3.16 (4 H, t), 6.73 (2 H, m), 7.23 (1 H, m), and 7.58 (1 H, m); m/z 206 (30%, M^+), 189 (100, $M - OH$), 175 (17, $M - CH_2 - OH$), 160 (9, $M - NO_2$), 159 (69, $M - NO - OH$), 158 (73, $M - NO - H_2O$), and 130 (28, $M - NO_2 - C_2H_4$).

If the reaction just described is performed in the presence of an excess of Py, it gives the same organic product in the same yield as in absence of the additive.

Kinetic Procedures.—The concentration range of 1,2-DNB was 1—9 × 10^{-4}M, and at least a 100-fold concentrations of PIP were used. The reaction was followed spectrophotometrically, by measuring optical densities at 380 nm during at least half-lives. In all cases pseudo-first-order kinetics were observed; k_{obs}(s^{-1}) reproducibility was ±3%. When the reaction was slow enough, the whole u.v.–visible spectrum was recorded at various times; two isosbestic points (at 325 and 305 nm) were detected. The same behaviour was observed when the reaction was carried out with addition of Py. The occurrence of isosbestic points is good evidence that competing or sequential reactions are absent.[25]

The optical densities at infinite time were identical with those of solutions prepared with standard 1-nitro-2-piperidinobenzene on the basis of complete consumption of 1,2-DNB.

Determination of EDA Complex Formation Constants.—A u.v. spectrophotometric method described previously[1,19] was used. The solutions were prepared in the concentration ranges shown in Table 3. The absorbances of the mixtures were measured at 300 nm (ref. 19) by extrapolating to zero time of reaction except in the case where the amine was Py, in which case the solution was completely stable. The enhanced absorbances of the mixtures at 300 nm with respect to the components alone is interpreted as due to the EDA complex; K is then calculated by an iterative procedure developed by us.

Acknowledgements

Financial support from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Consejo de Investigaciones Científicas y Tecnolóicas de la Provincia de Córdoba (CONICOR) is gratefully acknowledged. R. I. C. thanks CONICOR for a research fellowship. We are also grateful to Professors J. E. Bunnett and N. S. Nudelman for discussions.

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Received 19*th February* 1986; *Paper* 6/360