Kinetics of the Reactions between 1,2-Dinitrobenzene and Aliphatic Primary Amines in Benzene. A Probable Mechanism for the Observed Mild Acceleration

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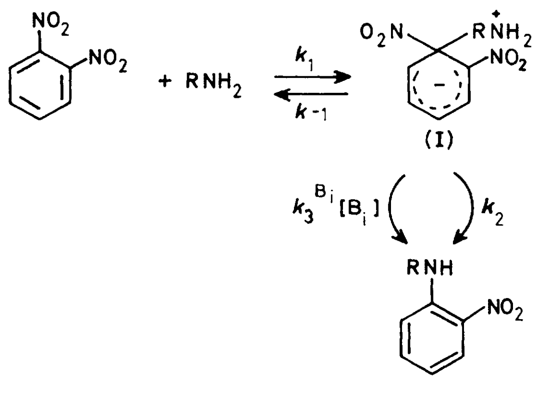
The kinetics of the aromatic nucleophilic substitution (S_NAr) between 1,2-dinitrobenzene (1,2-DNB) and n- (Bu^nNH_2) and s-butylamine (Bu^sNH_2) have been investigated in benzene and hexane–benzene. The second-order rate coefficient for these reactions varies linearly with the amine concentration. However, the ratio of the slope and intercept of the straight lines (k''/k') are in the range for Bunnett's mild acceleration of unclear origin. This is in contrast to the genuine catalysis previously observed for the same reactions in n-hexane. The effect of additives such as pyridine, triethylamine, α-pyridone, and dimethyl sulphoxide was examined. It was found that the catalytic power of the additives qualitatively correlates with Kamlet–Taft's π* and β parameters rather than with basicity constants of the additives in benzene. On other hand, when the steric requirements for the reactions of Bu_sNH_2 are compared with those for Bu^nNH_2, for the reaction with 1,2-DNB in benzene it seems that mild acceleration in benzene takes place for the decomposition of the S_NAr intermediate. Studies of the reaction of 1,2-DNB with Bu^nNH_2 in hexane–benzene give good evidence that benzene forms an electron-donor–acceptor (EDA) complex with 1,2-DNB. It is concluded that, in pure benzene, 1,2-DNB is preferentially solvated by EDA complex formation and consequently the proximity effects either of the nucleophile or any additive will be quite different than in n-hexane. Hence benzene cannot be considered a typical non-polar inert solvent for S_NAr reactions.

The mechanism of aromatic bimolecular nucleophilic substitution (S_NAr) reaction when primary or secondary amines[1] are the nucleophiles and 1,2-dinitrobenzene (1,2-DNB) is the aromatic substrate can be represented as in equation (1) where B is the nucleophile or any base added to the reaction medium.



(1)

Application of the steady-state hypothesis to this mechanism gives equation (2), where k_A is the second-order rate constant. It

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

is widely recognized that when $k_{-1} \ll k_2 + k_2{}^{B_i}[B_i]$ or more precisely $k_2 \gg k_{-1}$,[1] the formation of the intermediate (**I**) is rate limiting and consequently $k_A = k_1$.

On the other hand, if the decomposition of the intermediate is rate limiting, base catalysis may be expected. A linear response to base concentration such as depicted in equation (3) is characteristic of the majority of base-catalysed reactions. This can be rationalized for the mechanism in equation (1) by assuming that $k_3{}^{B_i}[B_i] \ll k_{-1}$ and $k_2 \ll k_{-1}$, which converts equation (2) into a linear expression of k_A with $[B_i]$ of the type (3).

$$k_A = k' + k_i''[B_i] \qquad (3)$$

It should be noted at this point, that according to Bunnett[2] genuine base catalysis occurs for reactions with the ratio $k_i''/k' \geq 50$. However, for many S_NAr reactions, the k''/k' ratios are smaller than this value and the interpretation of such ratios in terms of base catalysis is quite controversial. One criterion to resolve this matter is to discover in a given substrate–nucleophile system whether the accelerating effect bears a direct relationship with the base strength. If such a relationship is not found, it is usually accepted, in accord with Bunnett's criteria,[2] that the formation of the intermediate is rate limiting in these reactions and the mild acceleration is considered to be a medium effect, although its origin is still unclear.

In previous work on S_NAr of 1,2-DNB with several primary aliphatic amines[3,4] using n-hexane as solvent genuine base catalysis was found for every amine. Similar studies[5] of the reaction of piperidine [PIP] with 1,2-DNB in n-hexane showed that this is a wholly base-catalysed reaction (*i.e.* $k_3{}^B/k_2$ ∞). The fact that n-hexane is a non-polar solvent (π* −0.08)[6] could explain the appearance of base catalysis in these reactions.

On the other hand, Pietra and Vitali[7] found that the piperidinodenitration of 1,2-DNB in benzene as solvent is not base catalysed. This seems to be a rather surprising result since it may be expected than benzene should have solvation properties similar to those of n-hexane. Actually benzene is a little more polar (or polarizable) than n-hexane, and also it can behave as a weak hydrogen bond acceptor from the values of the Taft and Kamlet's parameters, *i.e.* π* 0.59 and β 0.10.[5]

The usual influence of solvent is to effect a change from non-catalysed to catalysed S_NAr when the solvent is changed from protic or dipolar aprotic to apolar.[8] Thus, benzene is a typical aprotic hydrophobic solvent unable to assist the decomposition

Table 1. Kinetic constants for the reaction of 1,2-DNB with Bu^nNH_2 and Bu^sNH_2 in benzene at various temperatures

T 18.0 ± 0.1 °C

$[Bu^nNH_2]$/M	0.13	0.25	0.38	0.51	0.63	0.76	0.88
10^5k_A/mol^{-1} dm^3 s^{-1}	1.98	2.65	3.32	4.07	4.49	5.61	6.02

T 27.5 ± 0.1 °C

$[Bu^nNH_2]$/M	0.15	0.20	0.30	0.40	0.55	0.60	0.65
10^5k_A/mol^{-1} dm^3 s^{-1}	4.25	4.97	5.80	6.54	7.85	8.32	8.83

T 44.5 ± 0.1 °C

$[Bu^nNH_2]$/M	0.10	0.30	0.40	0.50	0.60	0.70
10^5k_A/mol^{-1} dm^3 s^{-1}	11.50	15.28	17.18	19.86	21.00	23.80

T 27.5 ± 0.1 °C

$[Bu^sNH_2]$/M	0.20	0.40	0.55	0.70	0.80
10^5k_A/mol^{-1} dm^3 s^{-1}	0.30	0.48	0.51	0.57	0.78

Table 2. Second-order coefficient k_A for the reactions of 1,2-DNB with Bu^nNH_2, in benzene, in the presence of several additives

$[Bu^nNH_2]$ 0.60M; *T* 27.0 ± 0.1 °C

[DABCO]/M	0.00	0.03	0.07	0.10
10^5k_A/mol^{-1} dm^3 s^{-1}	8.32	9.06	10.17	10.36

$[Bu^nNH_2]$ 0.60M; *T* 27.0 ± 0.1 °C

[PONE]/M	0.00	0.10	0.25	0.30
10^5k_A/mol^{-1} dm^3 s^{-1}	8.32	8.88	10.03	10.65

$[Bu^nNH_2]$ 0.60M; *T* 27.0 ± 0.1 °C

[TEA]/M	0.00	0.10	0.20	0.40
10^5k_A/mol^{-1} dm^3 s^{-1}	8.32	8.31	8.69	9.06

$[Bu^nNH_2]$ 0.60M; *T* 27.0 ± 0.1 °C

[Py]/M	0.00	0.20	0.30	0.60	0.60	0.60
10^5k_A/mol^{-1} dm^3 s^{-1}	8.32	9.27	9.61	9.78	11.72	11.63

$[Bu^nNH_2]$ 0.30M; *T* 27.0 ± 0.1 °C

[Py]/M	0.00	0.20	0.30	0.40	0.50	0.60	0.60
10^5k_A/mol^{-1} dm^3 s^{-1}	5.80	6.73	7.33	7.73	8.26	9.21	9.10

$[Bu^nNH_2]$ 0.15M; *T* 27.0 ± 0.1 °C

[Py]/M	0.00	0.30	0.60	0.90
10^5k_A/mol^{-1} dm^3 s^{-1}	4.25	5.75	7.53	8.92

[Py] 0.3M; *T* 27.0 ± 0.1 °C

$[Bu^nNH_2]$/M	0.15	0.30	0.40	0.60	0.60
10^5k_A/mol^{-1} dm^3 s^{-1}	5.75	7.33	8.17	10.14	9.61

$[Bu^nNH_2]$ 0.60M; *T* 27.0 ± 0.1 °C

[DMSO]/M	0.00	0.28	0.58	0.97
10^5k_A/mol^{-1} dm^3 s^{-1}	8.32	23.30	38.00	49.90

of S_NAr intermediates in reactions with amines as the nucleophile with substrates containing leaving groups of low nucleofugacity such as fluoro, alkoxy, and phenoxy.[1,9,10] However examples for nitro group displacement by amines are scarce.[3–5,11]

Thus it seemed of interest to investigate denitration reactions previously studied in n-hexane by using benzene as solvent. This paper is concerned with reaction of 1,2-DNB with n-butylamine in benzene and binary mixtures of n-hexane–benzene. The effect of addition of diazabicyclo[2.2.2]octane (DABCO), pyridine (Py), triethylamine (TEA), α-pyridone (PONE), and dimethyl sulphoxide (DMSO) was examined. Since we found previously[4] that the catalytic power of primary aliphatic amines in the reaction with 1,2-DNB is strongly dependent on steric factors, the reaction of s-butylamine with 1,2-DNB in benzene was studied for comparison. Our results show that although n-hexane and benzene could be considered as typical non-polar solvents, their solvation properties are actually quite different at the least for the reaction under study.

Table 3. Kinetic parameters for the reaction between 1,2-DNB and Bu^nNH_2 in benzene in the presence of additives at 27.5 °C[a]

Base	10^5k/ mol^{-2} dm^3 s^{-1}	k''/k_o[b] mol^{-1} dm^3	π^*[c]	β[c]	K_b[d]
Bu^nNH_2	8.76	2.8	0.46[h]	0.72	101
DABCO	21.23	6.8		0.73	4 950
PONE[e]	7.65	2.5			
TEA	2.02	0.7	0.14	0.71	2 700
Py	5.75	1.9	0.87	0.64	1[i]
Py[f]	5.57	1.8			
Py[g]	5.26	1.7			
DMSO	43.00	13.9	1.00	0.76	

[a] $[Bu^nNH_2]$ 0.6M unless otherwise indicated. [b] k_o Refers to k' in the absence of additives. [c] Values from ref. 3. [d] Values from ref. 13. [e] The initial amount of PONE is calculating assuming monomeric species (M. H. Krackov, C. M. Lee, and H. G. Mautner, *J. Am. Chem. Soc.*, 1965, **87**, 892; F. Pietra and D. Vitali, *Tetrahedron Lett.*, 1966, 5701). [f] $[Bu^nNH_2]$ 0.30M. [g] $[Bu^nNH_2]$ 0.15M. [h] Value calculated by equation (24) in ref. 4. [i] Value estimated from refs. 13 and 14.

Results and Discussion

The reaction of 1,2-DNB either with Bu^nNH_2 or Bu^sNH_2 in benzene gives the corresponding *N*-alkyl-2-nitroaniline in quantitative yield as shown by t.l.c. and u.v.–visible spectroscopic analysis. The values of the apparent rate coefficients, k_A = rate/[1,2-DNB] [Amine], obtained for amine substitution of 1,2-DNB in benzene at different amine concentrations and temperatures are gathered in Table 1. It is observed that in accord with the general behaviour for S_NAr reactions with aliphatic amines as nucleophiles in non-polar solvents,[10,12] k_A varies linearly with amine concentrations following equation (3). For the reaction with Bu^nNH_2 at 27 °C k''/k' 2.8 mol^{-1} dm^3 is obtained and this value decreases slightly when the temperature is increased. In the reaction of Bu^sNH_2 k''/k' 1.5 mol^{-1} dm^3 is obtained.

The present results show that the values of k''/k' are much too low for both nucleophiles to indicate true base catalysis, being in the range of Bunnett's[2a] 'mild acceleration of unclear origin'.

It should be pointed out that these ratios are smaller than the values obtained for the same reactions in n-hexane[3,4] (*i.e.* for Bu^nNH_2 k''/k' ∞ and for Bu^sNH_2 16 at 27 °C) where it was proposed that true base catalysis takes place.

At first glance, the results in benzene are unexpected if benzene and n-hexane are typical non-polar solvents. These facts can either represent a different mechanism or at least a modification of the mechanism due to different solvation properties for each solvent.

In order to obtain information about a probable mechanism for catalysis, we have studied the reaction of 1,2-DNB with Bu^nNH_2 in benzene at 25 °C in the presence of various additives, most of which can be considered as non-nucleophilic bases. The results are shown in Table 2.

In general the data show that k_A varies linearly in the presence of the additives following equation (3). As a measure of the catalytic power of the additives the values of k''/k_o were

Table 4. Experimental and literature kinetic constants for S_NAr reactions of $\mathrm{Bu^nNH_2}$ and $\mathrm{Bu^sNH_2}$ with several substrates

		$\mathrm{Bu^nNH_2}$		$\mathrm{Bu^sNH_2}$				
Substrate	Solvent	k_o/dm^3 mol^{-1} s^{-1}	k''/dm^3 mol^{-1} s^{-1}	k_o/dm^3 mol^{-1} s^{-1}	k''/dm^3 mol^{-1} s^{-1}	$\frac{k'_{\mathrm{Bu^nNH_2}}}{k'_{\mathrm{Bu^sNH_2}}}$	$\frac{k''_{\mathrm{Bu^nNH_2}}}{k''_{\mathrm{Bu^sNH_2}}}$	Ref.
1,2-DNB	Hexane[a]	0.54×10^{-4}	6.10×10^{-4}	0.31×10^{-4}	0.23×10^{-4}	17	26.5	4
1,2-DNB	Benzene[b]	3.09×10^{-5}	8.76×10^{-4}	0.28×10^{-5}	0.41×10^{-5}	11	21.4	*c*
1-F-2,4-DNB	Benzene[d]	0.16	35.8	0.023	1.36	6.9	26.3	17
6-NO$_2$-2-Cl-benzothiazole	Benzene[d]	5.47×10^{-5}	1.11×10^{-3}	3.0×10^{-6}	5.28×10^{-5}	18.2	21.0	15
6-NO$_2$-2-Br-benzothiazole	Benzene[d]	5.13×10^{-5}	1.04×10^{-3}	1.0×10^{-6}	5.02×10^{-5}	51	20.7	15
6-NO$_2$-2-F-benzothiazole	Benzene[d]	1.20×10^{-2}	2.98	3.41×10^{-3}	1.90×10^{-1}	3.5	15.7	12

[a] *T* 37 °C. [b] *T* 27 °C. [c] This work. [d] *T* 25 °C.

calculated, where k_o is the value of k' when the base is the nucleophile itself. These values are collected in Table 3, together with the corresponding Taft–Kamlet π^* and β parameters[6] for the additives and basicity constant values of the bases in benzene.[13] The ratios k''/k_o are rather low and do not have any clear relation to the base strength K_b in benzene.[13] Thus k''/k_o for DABCO is *ca.* 3 times larger than for pyridine while K_b(DABCO) is 4 950 times greater than K_b(P$_y$.)[14] However, it should be pointed out that, due to the low solubility of DABCO in these media, the extent of addition is limited and this could make it very difficult to observe the catalytic effect.

On the other hand addition of a polar substance such as Py to benzene could affect the reaction rate by changing the properties of the medium. To obtain an indication of the sensitivity of the reaction to a change in the polar properties of the medium, and by considering that, in general, tertiary amines cannot be good catalysts due to their high steric requirements,[15] TEA was also used as an additive. As can be observed (Table 3) TEA practically does not exert even a small acceleration. It is worth mentioning that TEA for the same reaction in n-hexane produces a small inhibition.[5] In other cases where base catalysis is also proposed as for the reaction of piperidine and 2-chloro-6-nitrobenzothiazole [16] no effect on k_A is observed on adding TEA and this is taken as an indication that the reaction is not very sensitive to changes in the properties of the medium. The same can be argued for our case.

Since we found previously that the catalytic effect of Py in reactions of amines with 1,2-DNB[4] may depend on the concentration of nucleophile, the reaction in benzene was studied with different concentrations of $\mathrm{Bu^nNH_2}$ in the presence of constant concentration of Py and *vice versa* (Table 4). The ratio k''/k_o was independent of the nucleophile concentration, within experimental error. Thus, association with the nucleophile is precluded[4] as well as simply a medium effect, and the effect of Py may be attributed to some sort of catalytic effect.[17]

The values of k''/k_o for $\mathrm{Bu^nNH_2}$ and PONE are quite similar. However, as for DABCO, the addition of PONE was limited by its low solubility and it is difficult to derive conclusions from these results.

On the other hand, addition of DMSO exerts large acceleration relative to the other additives. This is expected since for base-catalysed S_NAr reactions with amines as nucleophiles and where addition of DMSO to benzene [18,19] or toluene[20] was performed, a considerable increase in the rates were found. Although it was recognized that the accelerations observed upon addition of DMSO exceed expectations based only on considerations of the polarity of the medium, the explanations are rather controversial.[18–20]

The properties of DMSO as a hydrogen-bond acceptor are well known.[21–23] As can be observed (Table 3) its β value is higher than for $\mathrm{Bu^nNH_2}$. It is also more polar.

From the results no definite conclusion can be drawn about what produces the small acceleration of this reaction in the presence either of nucleophile or additive. From inspection of Table 3 it seems that the catalytic power of the bases qualitatively correlates with the π^* and β values rather than K_b.

Since the intermediates in S_NAr are dipolar, increases in polarity (higher π^*) will stabilize them. Moreover zwitterionic-type transition states either for the formation of the intermediate (**I**) or for its decomposition, could be strong hydrogen-bond donors.[24] Thus either the nucleophile or an additive of high β value would stabilize them and in this sense DMSO seems to act as the most effective 'catalyst'. Nevertheless it is quite difficult to assess which transition state is preferentially stabilized.

In order to obtain some insight into which step of the mechanism [equation (1)] may be operating the small acceleration, the effect of changing the steric requirements of the nucleophile were analysed by comparing the kinetic parameters of the reaction of 1,2-DNB with $\mathrm{Bu^nNH_2}$ and $\mathrm{Bu^sNH_2}$ in benzene and hexane as solvent. Literature values for $\mathrm{Bu^nNH_2}$ and $\mathrm{Bu^sNH_2}$ displacement of other leaving groups (other than nitro) in benzene as solvent were also analysed and compared with our results.

Table 4 reports our studies and the literature values. As can be observed in Table 4 $\mathrm{Bu^sNH_2}$ exerts an important decrease in reactivity with respect to $\mathrm{Bu^nNH_2}$ for every substrate. For base-catalysed reactions it has been shown [12] that the α-branching in amines may retard the catalysed step a little more than the spontaneous decomposition of the σ-intermediate (**I**). The α-branching of amines decreases k_2/k_{-1} values probably by increasing k_{-1} *via* steric hindrance, and retardation is present despite the electronic effect of the methyl group. On the other hand, α-branching in the amine reduces k_3/k_{-1} by reducing the rate of proton transfer (k_3) and although it may be argued that there is also an increase in the rate of decomposition of the intermediate to reactants (k_{-1}) because of steric congestion, this effect was shown not to be very important.[25] Thus stronger influence of the steric effects is expected for k'' than for k'. For base-catalysed S_NAr reaction of $\mathrm{Bu^nNH_2}$ and $\mathrm{Bu^sNH_2}$ with 1-fluoro-2,4-dinitrobenzene[13] and the 6-nitro-2-halogenobenzothiazoles[12] in benzene as solvent and 1,2-DNB in hexane the ratios of the values of k_1k_2/k_{-1} ($k'_{\mathrm{Bu^nNH_2}}/k'_{\mathrm{Bu^sNH_2}}$) shown in Table 4 seem to depend on the substrate while the ratios of the values of k_1k_3/k_{-1} ($k''_{\mathrm{Bu^nNH_2}}/k''_{\mathrm{Bu^sNH_2}}$) for the same reactions are higher (stronger retardation effect) and similar, despite the nucleofugue.

Table 5. Pseudo-first-order rate constants for the reaction between 1,2-DNB and $\mathrm{Bu^nNH_2}$ in hexane–benzene at 27 °C[a]

[Benzene]/M	0.0	1.0	2.5	3.2	5.5	6.8	11.3
$10^5k_\psi/\mathrm{s^{-1}}$	7.5	5.5	4.2	4.0	3.3	3.1	2.6

[a] $[\mathrm{Bu^nNH_2}]$ 0.40M.

Note also that our reaction in benzene follows the same trend as these base-catalysed reactions.

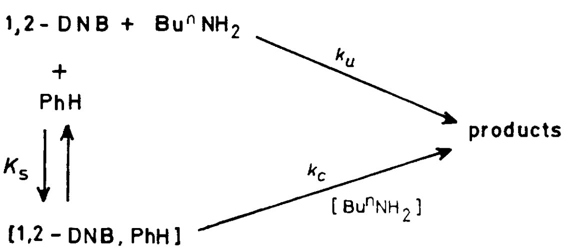
It seems that the steric effects on k' depend on the size of the leaving group and are in the order Br > $\mathrm{NO_2}$ ≥ Cl > F, while the ratios in k'' are almost constant. The latter could be taken as an indication that steric effects are related to the rate of proton transfer in k_3 which diminishes with the bulk of the amine and there is very little influence by the nucleofugue.

Although there are not enough examples in the literature, there is clear independence of the presence of an *o*-nitro group. Support for this idea comes from the S_NAr of *o*-fluoronitrobenzene by n-propyl- and isopropyl-amine in toluene,[25] which seems not to be base catalysed as the values of $k''_{\mathrm{Pr^nNH_2}}/k''_{\mathrm{Pr^iNH_2}}$ are very low (*ca.* 4). However, when the substrate is *p*-fluoronitrobenzene[25] the retardation produced by α-branching is similar to that shown for the other substrates with the butylamines.

On the other hand, primary steric effects on uncatalysed reactions, effects on k_1, are expected to be much lower[25] at least for fluorine as nucleofugue. Also, for the uncatalysed S_NAr of 1-chloro-2,4-dinitrobenzene in benzene $k_{1\mathrm{Bu^nNH_2}}/k_{1\mathrm{Bu^sNH_2}}$ is *ca.* 9.[17] Moreover, if we compare the reaction of 1,2-DNB with $\mathrm{Bu^nNH_2}$ and $\mathrm{Bu^sNH_2}$ in n-hexane with that in benzene, the ratios of k' and k'' are very similar. Therefore, and based on steric grounds, the 'mild acceleration' observed in benzene operates on the decomposition of intermediate (**I**).

A question which arises is why the catalytic effect of the nucleophile or the additives is so small in benzene relative to n-hexane. In order to obtain some insight into this question, we studied the kinetics of the reaction between 1,2-DNB and $\mathrm{Bu^nNH_2}$ in n-hexane–benzene. It is worth noting that the reaction between 1,2-DNB with $\mathrm{Bu^nNH_2}$ is benzene is slower that in n-hexane.[3,5] Thus, for example, at $[\mathrm{Bu^nNH_2}]$ 0.6M at 18 °C k_ψ $(\mathrm{C_6H_{14}})/k_\psi$ (PhH) is 4.4. However, the difference decreases below experimental error on increasing the temperature, and at 27 °C it is 2.1 and at 40 °C 1.9. The results for n-hexane–benzene are shown in Table 5. The plots (not shown) obtained for k_ψ *versus* benzene concentration gave us the idea that benzene may complex 1,2-DNB and then exert an inhibition effect. The formation of a molecular complex between benzene and 1-fluoro-2,4-dinitrobenzene has been postulated[26] to explain the kinetics features of the reaction between this substrate and aniline. The stability constant (K_s) of this complex has been calculated[19] to be 0.018 $\mathrm{dm^3\ mol^{-1}}$ in $\mathrm{CDCl_3}$.

In order to test the possible involvement of the complex between 1,2-DNB and benzene, we followed the treatment proposed by Nagy *et al.*,[27–29] to evaluate quantitatively the effect of solute–solvent interactions on reaction kinetics. Thus, for reactions in solvent mixtures they proposed that when an extra complexing agent is present in the reaction medium the substrate may undergo two parallel reactions. The first proceeds from the free substrate and the second from complexed substrate. The situation can be depicted by the Scheme, where k_u and k_c represent the pseudo-first-order rate coefficients for the reaction of free and complexed substrate, respectively.



It is assumed that 1,2-DNB can act as an electron acceptor and, in the presence of an electron donor such as benzene, form a 1 : 1 electron-donor–acceptor (EDA) complex.[30] The reaction with $\mathrm{Bu^nNH_2}$ can occur either with free 1,2-DNB (k_u) or through the EDA complex (k_c). It is also supposed that neither products nor $\mathrm{Bu^nNH_2}$ are significantly associated with benzene. Thus in pseudo-first-order conditions, *i.e.* $[\mathrm{Bu^nNH_2}]$ and [PhH] ≫ [1,2-DNB], the observed rate constant k_ψ can be expressed by equation (4). By rearrangement of equation (4), (5) is obtained.

$$k_\psi = \frac{k_\mathrm{u} + k_\mathrm{c}K_\mathrm{s}[\mathrm{PhH}]}{1 + K_\mathrm{s}[\mathrm{PhH}]} \tag{4}$$

$$\frac{k_\mathrm{u}}{k_\psi} = \frac{1 + K_\mathrm{s}[\mathrm{PhH}]}{1 + (k_\mathrm{c}K_\mathrm{s}/k_\mathrm{u})[\mathrm{PhH}]} \tag{5}$$

By plotting k_u/k_ψ against [PhH], the following four situations may be distinguished (see Figure 1 in ref. 27): (i) $k_\mathrm{c} = 0$, the reaction of the complexed substrate is totally inhibited; (ii) $k_\mathrm{c} < k_\mathrm{u}$, inhibition is only partial; (iii) $k_\mathrm{c} > k_\mathrm{u}$, there is a catalytic effect; (iv) $k_\mathrm{c} = k_\mathrm{u}$, the complex has no kinetic effect. The plot obtained from the data in Table 5 (not shown) is curvilinear with a concave downward dependence of k_u/k_ψ on the benzene concentration, which indicates that our system undergoes partial inhibition [case (ii)]. Thus equation (4) reduces to (6).

$$(k_\psi + k_\mathrm{u})/[\mathrm{PhH}] = k_\mathrm{c}K_\mathrm{s} - K_\mathrm{s}k_\psi \tag{6}$$

When the data of Table 5 are processed by equation (6), a linear plot is obtained (*r* 0.9979), given K_s 0.55 and k_c $1.85 \times 10^{-5}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$. Moreover, from these data one can easily obtain the complexing ability ($K^\ddagger$) of the activated complex since according to transition-state theory $K^\ddagger = K_\mathrm{s}(k_\mathrm{c}/k_\mathrm{u})$.[29] Therefore $K^\ddagger$ was calculated to be 0.14 $\mathrm{mol^{-1}\ dm^3}$.

These results show that benzene forms an EDA complex with 1,2-DNB. The value of K_s, obtained from kinetic data, gives a reasonable value for this type of complex.[30]

The competitive process proposed in the Scheme explains the observed temperature effect on k_ψ $(\mathrm{C_6H_{14}})/k_\psi$ (PhH), since an increase in temperature decreases K_s[30] and the complexing power of benzene diminishes.

These results indicate that when the reactions are performed in pure benzene, 1,2-DNB is preferentially solvated by the solvent through EDA complexation. Therefore proximity effects either of the nucleophile or any additive will be quite different from those in hexane. The preferential solvation of benzene could then explain the rather poor catalytic power observed by the added bases in these reactions. Moreover benzene, which has higher polarizability than hexane and through its hydrogen-bond acceptor properties, could better assist the spontaneous decomposition of the intermediate to products.

This work emphasizes that benzene cannot be considered as a typical non-polar 'inert' solvent in S_NAr reactions. Specific interactions with the S_NAr substrates (usually strong π acceptors) may introduce additional effects in the consideration of the stability of the rate-determining transition state and this may explain the different behaviour observed in the kinetics of these reactions in benzene by comparison with n-hexane.

Experimental

Materials.—Benzene (Carlo Erba) was washed several times with concentrated H_2SO_4 and then with dilute NaOH solutions and water until neutral. After drying ($CaCl_2$), it was refluxed three times over fresh P_2O_5 and fractionally distilled prior to use. 1,2-DNB (Fluka), Bu^nNH_2 (Aldrich), Bu^sNH_2 (Merck), TEA (Merck), n-hexane (Mallinckrodt), and pyridine (Sintorgan) were purified as previously described.[4,31] PONE (Fluka) and DABCO (Fluka) were recrystallised from benzene and then sublimed under vacuum prior to use. DMSO (Merck) was purified as described elsehwere.[32]

Kinetics Measurements.—The kinetics were followed spectroscopically as previously described.[5] The visible spectra of the aromatic products in benzene are *N*-n-butyl-2-nitroaniline, $\lambda_{max.}$ 425 nm (log ε 3.86); and *N*-s-butyl-2-nitroaniline, $\lambda_{max.}$ 428 nm (log ε 3.85). The reactions were run under pseudo-first-order conditions. The concentrations used for 1,2-DNB were of the order of 10^{-4} mol^{-1} dm^3 and those indicated in the Tables were used for the amines and additives. The observed pseudo-first-order coefficient is reported as k_ψ in the text.

Calculations.—Data processing was performing on a Digital PDP11/34 computer and on a Osborne microcomputer.

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