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COMPARATIVE KINETIC STUDY OF SOLVENT EFFECTS IN THE REACTIONS OF 1,2-DINITROBENZENE WITH BUTYLAMINE AND PIPERIDINE

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ABSTRACT

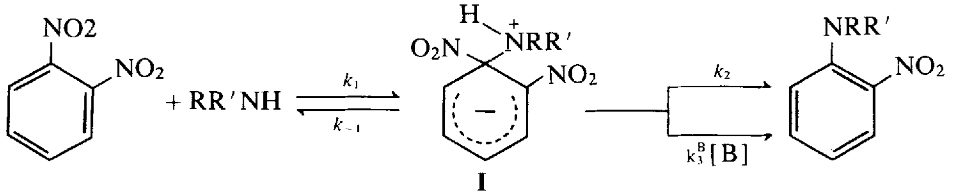
The kinetics of the aromatic nucleophilic substitution (S_NAr) reactions of 1,2-dinitrobenzene (1,2-DNB) with butylamine (BA) and piperidine (PIP) were investigated as a function of the amine concentration and temperature, in chloroform, ethyl acetate, tetrahydrofuran (THF), acetonitrile (ACN), dimethylformamide (DMF), dimethyl sulphoxide (DMSO), benzene, toluene, chlorobenzene and diisopropyl ether.

In the set of solvents consisting of ethyl acetate, THF, ACN, DMF and DMSO, neither reaction is catalysed ($k_A = k_1$). The sequence and range of reactivity for BA and PIP are similar in these solvents. These results indicate that reactions in which nitro in the leaving group behave differently from S_NAr reactions with other leaving groups, such as halogens or alkoxy groups, since an intramolecular hydrogen bond may be expected between the leaving nitro group and the ammonium H of the nucleophiles. The correlations of the rate coefficients obtained with Taft and Kamlet's solvatochromic method support these conclusions.

On the other hand, these reactions show mild acceleration with relatively non-polar solvents such as the aromatics and diisopropyl ether. The donor properties of these solvents and experiments with solvent mixtures suggest the formation of electron donor–acceptor complexes between them and 1,2-DNB. Hence the preferential solvation of 1,2-DNB by the donor solvent accounts for the mechanism observed.

INTRODUCTION

Our previous studies[1–4] have shown that the reactions between 1,2-dinitrobenzene (1,2-DNB) and primary or secondary aliphatic amines follow the generally accepted mechanism for aromatic nucleophilic substitution (S_NAr) given in equation (1), where B is the nucleophile or any base added to the reaction medium and R′ represents H and alkyl groups for primary and secondary amines, respectively.



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

$$k_A = (k_1k_2 + k_1k_3^B[B])/(k_{-1} + k_2 + k_3^B[B]) \qquad (2)$$

It is widely recognized that when $k_{-1} \ll (k_2 + k_3^B[B])$ or, more precisely, $k_{-1} \ll k_2$,[5] the formation of the intermediate **I** is rate limiting and consequently $k_A = k_1$. On the other hand, if $k_{-1} \gg k_2 + k_3^B[B]$, the decomposition of the intermediate is rate limiting and base catalysis may be expected. A linear response to base concentration such as depicted in equation (3) is characteristic of most of base-catalysed reactions.

$$k_A = k_0 + k''[B] \qquad (3)$$

If equation (2) cannot be simplified, a curvilinear concave downward dependence of k_A is found[5] and the decomposition of the intermediate is also rate determining.

Although S_NAr reactions between nitro-activated aromatic compounds, with a variety of leaving groups and amines as nucleophiles, have been extensively studied,[5-10] and the influence of the solvent has been recognized, there has been little systematic study of the way in which solvents may affect reaction rates.

More recently, several studies, in which different solvent properties allow an explanation of the differences observed in the catalysed steps when primary or secondary amines are used as nucleophiles, have been reported.[11-14] Systematic studies have also been performed using the reactions between amines and 1-halo-2,4-dinitrobenzenes, as model compounds,[15-17] in protic and aprotic solvents to identify and assess the relative importance of the various solvent effects observed.

The study of solvent effects on reactivity can give relevant information about the reaction mechanisms and the nature of the transition state in the rate-limiting step. In previous work, using 1,2-DNB as substrate, we found some unexpected solvent effects. Thus, the reaction between 1,2-DNB with several primary aliphatic amines[3] and with piperidine (PIP)[2] in hexane is wholly base catalysed. However, the same reaction for primary amines in benzene[4] gives only mild acceleration[7] even though this solvent is usually considered to be a typical non-polar solvent in S_NAr reactions. The difference in reactivity observed in hexane compared with benzene was explained by the specific solvent effect exerted by benzene, which solvates 1,2-DNB preferentially in view of its electron-donor properties.

In this work we have extended these studies in a series of aprotic solvents in order to obtain a deeper insight into the solvent effects exerted on amino denitration reactions by using 1,2-DNB as substrate. In order to identify the possible differences in reactivity between primary and secondary amines, butylamine BA and PIP were used as nucleophiles.

RESULTS AND DISCUSSION

The reactions of 1,2-DNB with PIP and BA in all the solvents studied proceed straightforwardly to give *N*-(2-nitrophenyl)piperidine and *N*-butyl-2-nitroaniline respectively, in quantitative yields as shown by thin-layer chromatographic and UV–visible spectroscopic analysis of the reaction mixtures.

The kinetics of the reactions were studied in the presence of various excess of amounts of nucleophile under pseudo-first-order conditions. The reactions proved to be first order in the substrate and on division of the pseudo-first-order coefficients, k_ψ, by the appropriate concentration of amine, the second-order rate coefficient, k_A, was calculated. Tables 1 and 2 summarize the data for the title reactions in chloroform, ethyl acetate, tetrahydrofuran (THF), acetonitrile (ACN), dimethylformamide (DMF), dimethyl sulphoxide (DMSO), benzene, toluene, chlorobenzene and diisopropyl ether, at several nucleophile concentrations and temperatures.

As can be observed two situations are clearly defined for both reaction systems: (i) for the set of solvents consisting of ethyl acetate, THF, ACN, DMF and DMSO, the k_A values are insensitive to the nucleophile concentration; (ii) in the other set of solvents, benzene, toluene, chlorobenzene and diisopropyl ether, k_A increases linearly with the amine concentration according to equation (3).

On the other hand, in the case of chloroform, the 1,2-DNB–PIP system behaves as the solvent set (i) whereas for the system 1,2-DNB–BA, a curvilinear downward dependence with a definite intercept is obtained for k_A vs nucleophile concentration.

The calculated values of k_1, k_0 and k'' for the corresponding reactions in all the solvents, including previous data obtained in hexane and benzene, are shown in Table 3, where the solvent parameters used in this study are also included.

For the purposes of discussion, the set of solvents which give situation (i) will henceforth be called set A and those which give situation (ii) will be called set B.

Reactions in solvent set A

In these solvents the reaction of 1,2-DNB with either PIP or BA is not base catalysed ($k_A = k_1$) and the formation of intermediate **I** is rate determining. When the amine reactivity is compared within this set of solvents, it is observed that in DMSO, DMF and ACN, PIP is slightly more reactive than BA, whereas in THF and ethyl acetate, the latter is more reactive than PIP. This is unexpected, considering that from the order of the overall rate constants observed for S_NAr reactions, in which the formation of the σ-adduct intermediate is rate determining, BA is usually an order of magnitude less reactive than PIP.[18,19] The superior reactivity of secondary over primary amines has been adduced to be due to favorable ion-induced dipole interactions in the transition state between partially positive charged amine nitrogen and the polarizable alkyl moieties attached to it.[19]

On the other hand, if we analyse the general solvent effect on k_1 using the dielectric constant (ε)[20] as a parameter of polarity, we observe that k_1 decreases from the more polar to the less polar solvent in a more or less regular fashion. The fastest reactions are in DMSO and DMF, as expected. It is well recognized[12,21] that when amines are the nucleophiles, the transition state for S_NAr reactions is a strong hydrogen-bond donor strongly solvated by basic solvents such as DMSO and DMF.

In addition, the sequences and ranges of reactivity in DMSO, DMF and ACN for PIP (5·93 : 2·08 : 1) and BA (8·58 : 3·78 : 1) are very similar.

In typical uncatalysed S_NAr reactions such as those of 1-chloro-2,4-dinitrobenzene with BA and secondary amines, although the order of reactivity for these solvents is similar, their range is much higher for primary amines.[13] In all these cases, the substrate contains an *o*-nitro group, 'built in' solvation[22,23] is involved and, since primary amines have two hydrogen atoms and secondary amines only one, the solvent leveling effect is expected to be higher for the secondary amine.[13] It is evident that no such effect is found for the reactions studied here.

This observation, added to the finding already discussed with respect to the apparent similar reactivity of PIP and BA, indicates that these reactions in which nitro is the leaving group behave differently from S_NAr reactions with other types of leaving groups, such as halogens or alkoxy.[12,13]

As stated before, 'built-in' solvation is a recognized feature of substrates with *o*-nitro groups

Table 1. Rate constants of reactions between 1,2-DNB (ca 10^{-4} M) and PIP in aprotic solvents at various temperatures

Solvent	Temperature (°C)	Parameter	Values
Chloroform	17·5 ± 0·1	[PIP] (M)	0·30 0·45 0·60 0·90
		10^4k_ψ (s^{-1})	0·12 0·17 0·23 0·36
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	0·39 ($r = 0·9986$)
	27·4 ± 0·1	[PIP] (M)	0·20 0·40 0·61 0·81 1·01
		10^4k_ψ (s^{-1})	0·15 0·30 0·45 0·60 0·75
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	0·74 ($r = 0·9999$)
	38·9 ± 0·1	[PIP] (M)	0·20 0·41 0·51 0·61
		10^4k_ψ (s^{-1})	0·30 0·60 0·76 0·90
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	1·49 ($r = 0·9989$)
Ethyl acetate	17·9 ± 0·1	[PIP] (M)	0·35 0·53 0·62 0·70
		10^4k_ψ (s^{-1})	0·24 0·35 0·42 0·47
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	0·68 ($r = 0·9999$)
	27·5 ± 0·1	[PIP] (M)	0·20 0·30 0·40 0·50 0·60
		10^4k_ψ (s^{-1})	0·24 0·36 0·45 0·58 0·72
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	1·17 ($r = 0·9996$)
	40·5 ± 0·1	[PIP] (M)	0·20 0·30 0·40 0·60
		10^4k_ψ (s^{-1})	0·50 0·76 1·01 1·52
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	2·52 ($r = 0·9999$)
THF	18·2 ± 0·1	[PIP] (M)	0·20 0·40 0·50 0·60
		10^4k_ψ (s^{-1})	0·26 0·51 0·65 0·78
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	1·29 ($r = 0·9999$)
	27·4 ± 0·1	[PIP] (M)	0·30 0·40 0·50 0·61 0·71
		10^4k_ψ (s^{-1})	0·63 0·83 1·02 1·26 1·50
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	2·08 ($r = 0·9998$)
	39·6 ± 0·1	[PIP] (M)	0·10 0·21 0·31 0·41
		10^4k_ψ (s^{-1})	0·42 0·82 1·27 1·71
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	4·11 ($r = 0·9999$)
ACN	18·1 ± 0·1	[PIP] (M)	0·21 0·41 0·62 0·82
		10^4k_ψ (s^{-1})	0·55 1·11 1·66 2·22
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	2·69 ($r = 0·9999$)
	27·0 ± 0·1	[PIP] (M)	0·21 0·41 0·62 0·82
		10^4k_ψ (s^{-1})	0·87 1·79 2·64 3·53
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	4·29 ($r = 0·9999$)
	40·7 ± 0·1	[PIP] (M)	0·21 0·41 0·62 0·82
		10^4k_ψ (s^{-1})	1·80 3·58 5·38 7·18
		10^4k_A ($mol^{-1} dm^3 s^{-1}$)	8·71 ($r = 0·9999$

DMF	17·6 ± 0·1	[PIP] (M)	0·12	0·24	0·36	0·48								
		10^4k_ψ (s^{-1})	0·62	1·24	1·87	2·48								
		10^4k_A (mol^{-1} dm^3 s^{-1})	5·20	($r = 0·9999$)										
	27·1 ± 0·1	[PIP] (M)	0·12	0·24	0·36	0·48								
		10^4k_ψ (s^{-1})	1·10	2·15	3·19	4·25								
		10^4k_A (mol^{-1} dm^3 s^{-1})	8·93	($r = 0·9999$)										
	37·5 ± 0·1	[PIP] (M)	0·06	0·12	0·24	0·36								
		10^4k_ψ (s^{-1})	0·92	1·81	3·64	5·46								
		10^4k_A (mol^{-1} dm^3 s^{-1})	15·24	($r = 0·9999$)										
DMSO	18·7 ± 0·1	[PIP] (M)	0·10	0·20	0·30	0·40								
		10^4k_ψ (s^{-1})	1·79	3·58	5·40	7·13								
		10^4k_A (mol^{-1} dm^3 s^{-1})	18·07	($r = 0·9999$)										
	27·2 ± 0·1	[PIP] (M)	0·08	0·13	0·16	0·19	0·24	0·29	0·32	0·40				
		10^4k_ψ (s^{-1})	2·13	3·35	4·02	5·04	6·17	8·00	8·13	9·79				
		10^4k_A (mol^{-1} dm^3 s^{-1})	25·45	($r = 0·9990$)										
	38·6 ± 0·1	[PIP] (M)	0·08	0·10	0·13	0·21								
		10^4k_ψ (s^{-1})	3·92	4·93	6·30	10·18								
		10^4k_A (mol^{-1} dm^3 s^{-1})	48·99	($r = 0·9999$)										
Diisopropyl ether	18·2 ± 0·1	[PIP] (M)	0·31	0·46	0·62	0·77	0·93							
		10^4k_A (mol^{-1} dm^3 s^{-1})	0·22	0·26	0·31	0·33	0·37							
	27·5 ± 0·1	[PIP] (M)	0·31	0·46	0·61	0·77	0·92							
		10^4k_A (mol^{-1} dm^3 s^{-1})	0·38	0·46	0·53	0·62	0·71							
	38·5 ± 0·1	[PIP] (M)	0·21	0·31	0·42	0·52	0·63							
		10^4k_A (mol^{-1} dm^3 s^{-1})	0·57	0·68	0·83	0·90	1·15							
Benzene	18·4 ± 0·1	[PIP] (M)	0·41	0·61	0·71	0·81	1·01							
		10^4k_A (mol^{-1} dm^3 s^{-1})	0·83	0·87	0·94	0·99	1·11							
	27·9 ± 0·1	[PIP] (M)	0·09	0·20	0·30	0·31	0·45	0·47	0·59	0·60	0·69	0·74	0·80	0·99
		10^4k_A (mol^{-1} dm^3 s^{-1})	1·05	1·22	1·26	1·30	1·43	1·38	1·48	1·56	1·56	1·74	1·75	1·89
	37·8 ± 0·1	[PIP] (M)	0·10	0·19	0·29	0·38	0·48	0·58						
		10^4k_A (mol^{-1} dm^3 s^{-1})	1·65	1·88	2·04	2·32	2·35	2·67						
Chlorobenzene	18·4 ± 0·1	[PIP] (M)	0·20	0·41	0·61	0·71	0·81							
		10^4k_A (mol^{-1} dm^3 s^{-1})	1·02	1·25	1·46	1·51	1·71							
	27·5 ± 0·1	[PIP] (M)	0·20	0·30	0·40	0·50	0·60							
		10^4k_A (mol^{-1} dm^3 s^{-1})	1·74	1·91	2·19	2·39	2·60							
	38·2 ± 0·1	[PIP] (M)	0·12	0·25	0·37	0·50	0·62							
		10^4k_A (mol^{-1} dm^3 s^{-1})	2·52	3·18	3·76	4·33	4·96							

Table 2. Rate constants of reactions between 1,2-DNB and BA in aprotic solvents at various temperatures[a]

Solvent	Parameter	Values								
Chloroform[b]	[BA] (M)	0·10	0·20	0·30	0·40	0·50	0·60	0·70		
	10^4k_A (mol^{-1} dm^3 s^{-1})	0·11	0·15	0·18	0·18	0·20	0·22	0·23		
Ethyl acetate[c]	[BA] (M)	0·20	0·28[d]	0·28[e]	0·30	0·40	0·49	0·50	0·60	
	10^4k_ψ (s^{-1})	0·32	0·29	0·92	0·52	0·86	1·01	0·95	1·19	
	10^4k_A (mol^{-1} dm^3 s^{-1})	1·97	($r = 0·9979$)							
THF[c]	[BA] (M)	0·10	0·11	0·20	0·30	0·40	0·50	0·60	0·30[d]	0·30[e]
	10^4k_ψ (s^{-1})	0·31	0·34	0·67	1·07	1·28	1·73	1·89	0·61	1·56
	10^4k_A (mol^{-1} dm^3 s^{-1})	3·29	($r = 0·9989$)							
ACN[c]	[BA] (M)	0·10	0·20	0·30	0·40	0·46	0·50	0·55	0·40[f]	0·40[g]
	10^4k_ψ (s^{-1})	0·23	0·45	0·63	0·81	0·91	1·12	1·29	0·52	1·56
	10^4k_a (mol^{-1} dm^3 s^{-1})	0·22	($r = 0·9979$)							
DMF[c]	[BA] (M)	0·20	0·30	0·40	0·50	0·60	0·40[d]	0·40[e]		
	10^4k_ψ (s^{-1})	0·16	0·24	0·34	0·39	0·52	0·29	0·55		
	10^4k_A (mol^{-1} dm^3 s^{-1})	0·83	($r = 0·9990$)							
DMSO[c]	[BA] (M)	0·10	0·20	0·30	0·40	0·50	0·30[h]	0·30[i]		
	10^4k_ψ (s^{-1})	0·24	0·35	0·64	0·77	0·90	0·84	1·16		
	10^4k_A (mol^{-1} dm^3 s^{-1})	18·89	($r = 0·9972$)							
Diisopropyl ether[b]	[BA] (M)	0·20	0·30	0·40	0·50	0·60				
	10^4k_A (mol^{-1} dm^3 s^{-1})	0·43	0·52	0·73	0·86	0·91				
Toluene[b]	[BA] (M)	0·10	0·20	0·30	0·40	0·50	0·70			
	10^4k_A (mol^{-1} dm^3 s^{-1})	0·38	0·51	0·63	0·71	0·81	1·00			
Chlorobenzene[b]	[BA] (M)	0·26	0·38	0·51	0·64	0·77	1·00	1·02		
	10^4k_A (mol^{-1} dm^3 s^{-1})	0·73	0·93	1·10	1·31	1·47	1·51	1·90		

[a] [1,2-DNB] ≈ 10^{-4} M.

[b] Reactions at 27·0 ± 0·1 °C unless stated otherwise.

[c] Reactions at 27·5 ± 0·1 °C unless stated otherwise.

[d] 17·0 ± 0·1 °C.

[e] 37·0 ± 0·1 °C.

[f] 16·3 ± 0·1 °C.

[g] 36·3 ± 0·1 °C.

[h] 34·5 ± 0·1 °C.

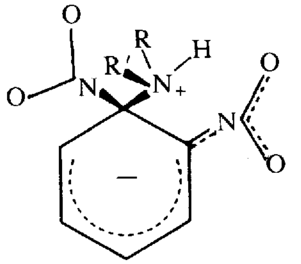
[i] 42·0 ± 0·1 °C.

Table 3. Calculated rate coefficients for the reactions of 1,2-DNB with piperidine and butylamine, and frequently used parameters for the aprotic solvents in this present study[a]

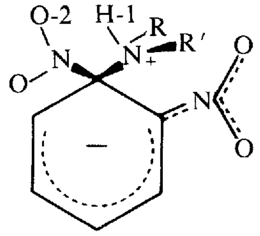
						PIP				BA			
Solvent	ε[b]	I_p[c]	π[d]	β[d]	$E_T(30)$	$10^5 k_1$ (s^{-1})	$10^5 k_0$ $(\mathrm{mol}^{-}\,\mathrm{dm}^3\,\mathrm{s}^{-1})$	$10^5 k''$ $(\mathrm{mol}^{-2}\,\mathrm{dm}^6\,\mathrm{s}^{-1})$	k''/k_0 $(\mathrm{mol}^{-1}\,\mathrm{dm}^3)$	$10^5 k_1$ (s^{-1})	$10^5 k_0$ $(\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{s}^{-1})$	$10^5 k''$ $(\mathrm{mol}^{-2}\,\mathrm{dm}^6\,\mathrm{s}^{-1})$	k''/k_0 $(\mathrm{mol}^{-1}\,\mathrm{dm}^3)$
Chloroform	4·8		0·58	0·00	39·1	7·4							
Ethyl acetate	6·0		0·55	0·45	38·1	11·7				19·7			
THF	7·6		0·58	0·55	37·4	20·8				32·9			
ACN	37·5		0·75	0·31	46·0	42·9				22·0			
DMF	36·7		0·88	0·69	43·8	89·3				83·2			
DMSO	46·7		1·00	0·76	45·0	254·5				188·9			
Diispropyl ether	3·88		0·27	0·49			2·2	5·2	2·3		2·1	11·9	5·5
Benzene	2·275	9·24	0·59	0·10	34·5		9·9	9·1	0·9		3·1[e]	8·8[e]	2·8[e]
Toluene	2·379	8·82	0·54	0·11	33·9						3·2	10·0	3·1
Chlorobenzene	5·621	9·07	0·70	0·07	37·5		12·9	22·1	1·8		3·1	15·3	4·8
Hexane[f]	1·879		−0·08	0·00	30·9		0·0	38·1			0·0	45·8	

[a] Temperature 27 °C.
[b] From Ref. 20.
[c] From Ref. 35.
[d] From Ref. 29.
[e] From Ref. 4.
[f] From Refs 1–3.

(**Ia**). However, in the case of 1,2-DNB (or the other substrates where nitro is the nucleofuge), another intramolecular hydrogen bond may be postulated for the intermediate *I*, such as depicted in **Ib**.



Ia



Ib

To a first approximation, molecular models and distances calculated by standard molecular geometry with the GELCA program[24] on structure **Ib** show that such a bond is possible, given a minimum distance between H-1 and O-2 of 2·07 Å. If the structure **Ib** makes a major contribution to the stability of the transition state, the usual reactivity and solvent effects found for other nucleofuges with these amines will not be the same as in our case. In fact, a structure such as **Ib** has been proposed for rationalizing the unexpected fast expulsion of the nitro group from the intermediate **I**[25] in the reactions of 1,2-DNB and 1,2,4-trinitrobenzene with PIP in benzene.

The next problem is to find which of the currently available parameters best reflect the experimentally observed solvent effects on the present reactions. This means obtaining the best measure of the solvent dipolarity[26] distinct from other possible specific effects.

The activation parameters calculated for these reactions (Table 4) show that the variation in rates due to a change of solvent cannot be attributed to a corresponding change in either the enthalpy or entropy of activation but rather to a random combination of both. Hence, solvent interactions are believed to be complex in nature.

By considering that, statistically, the multi-parametric equations are less significant than the single-parameter correlations, unless a sufficient number of data are available, we first performed single-parameter linear free-energy correlations with Dimroth and Reichardt's $E_T(30)$,[27] Gutman's DN[28] and the π^* values from Taft and co-workers' solvatochromic method.[26,29–31]

Table 4. Activation parameters for the reactions of 1,2-DNB with BA and PIP in solvent set at 25 °C

	PIP		BA	
Solvent	$\Delta H^{\ne}$ (kJ mol^{-1})	$\Delta S^{\ne}$ (J K^{-1}mol^{-1})	$\Delta H^{\ne}$ (kJ mol^{-1})	$\Delta S^{\ne}$ (J K^{-1}mol^{-1})
Chloroform	45 ± 4	− 160 ± 3		
Ethyl acetate	41 ± 2	− 167 ± 1	42 ± 1	− 195 ± 1
THF	39 ± 1	− 171 ± 5	41 ± 2	− 191 ± 8
AcN	37 ± 2	− 170 ± 4	30 ± 3	− 198 ± 4
DMF	37 ± 3	− 164 ± 2	38 ± 1	− 184 ± 2
DMSO	34 ± 1	− 165 ± 2	37 ± 4	− 198 ±

The correlation of log k_1 vs $E_T(30)$ with solvent set A gives the results shown in equations (4) and (5):

$$\log k_1^{PIP} = -6{\cdot}87 + 0{\cdot}08E_T(30) \qquad r = 0{\cdot}60;\ n = 5 \tag{4}$$

$$\log k_1^{BA} = -5{\cdot}34 + 0{\cdot}05E_T(30) \qquad r = 0{\cdot}45;\ n = 5 \tag{5}$$

where r is the correlation coefficient and n is the number of solvents. Chloroform was excluded from both correlations because, as was noticed before, it gives a different kinetic behaviour to the other solvents in the set with the 1,2-DNB–BA system (see below).

As can be observed, almost no correlation is found with this parameter. If ACN is excluded [equations (6) and (7)] the correlation is improved. However, we believe that still it is not satisfactory, particularly because there is no reason to exclude ACN as an anomalous solvent.

$$\log k_1^{PIP} = -9{\cdot}44 + 0{\cdot}15E_T(30) \qquad r = 0{\cdot}953;\ n = 4 \tag{6}$$

$$\log k_1^{BA} = -7{\cdot}52 + 0{\cdot}10E_T(30) \qquad r = 0{\cdot}935;\ n = 4 \tag{7}$$

$E_T(30)$ has been considered[15–17] as the single parameter that allows correlation with the rate when it is applied to the uncatalysed reaction between 1-chloro-2,4-dinitrobenzene and PIP in aprotic solvents. Further, it was expected to be similar for all S_NAr where no complications are present.[15] Since such complications are not observed in the reactions studied, the failure of these correlations may be attributed to the special characteristic of the nitro leaving group and its potential capability to form intermediate **Ib**.

Correlations of log k_1 with the DN parameter[28] were not satisfactory, as could be expected since this parameter accounts preferentially for the ability of the solvent to serve as an electron donor only for oxygen bases.[29]

The correlation between log k_1 and π^* gave the following results:

$$\log k_1^{PIP} = -5{\cdot}36 + 2{\cdot}70\pi^* \qquad n = 5;\ r = 0{\cdot}9880 \tag{8}$$

$$\log k_1^{BA} = -4{\cdot}77 + 1{\cdot}91\pi^* \qquad n = 5;\ r = 0{\cdot}8812 \tag{9}$$

As can be observed, the correlation for the 1,2-DNP–PIP system is much better than for the DNB–BA system. It should be pointed out that if chloroform is included in equation (8), similar results are obtained.

Although these correlations are more satisfactory than that with $E_T(30)$, they still do not fully account for the solvent effects observed, particularly for the 1,2-DNB–BA system.

It has been shown that a set of 'select' solvents can be chosen[26] for which the effects are well accounted for by π^* when solvent–solute hydrogen bonding interactions are absent. In fact, our set A (excluding chloroform) corresponds to this 'select' set. The rationale for the failure of correlations with π^* may be the hydrogen bonding ability of the transition state for the formation of intermediate **I**, which in the denitration reactions appears to be important. In order to account more quantitatively for these interactions, Taft and co-workers' β parameter, which measures the solvent hydrogen acceptor capability, was included in the correlations.

The results obtained are shown in equations (10) and (11), where F, F_1 and F_2 measure the whole and partial confidence levels.

$$\log k_1^{PIP} = -5{\cdot}47 + 2{\cdot}42\pi^* + 0{\cdot}57\beta \qquad r = 0{\cdot}9897;\ n = 6 \tag{10}$$

$$F = 71{\cdot}81;\ F_1 = 137{\cdot}421;\ F_2 = 6{\cdot}38$$

$$\log k_1^{BA} = -4{\cdot}89 + 1{\cdot}07\pi^* + 1{\cdot}39\beta \qquad r = 0{\cdot}9923;\ n = 5 \tag{11}$$

$$F = 63{\cdot}83;\ F_1 = 100{\cdot}67;\ F_2 = 26{\cdot}98$$

In the correlation in equation (10) we have included chloroform since for this system this solvent does not present kinetic complications. As can be observed, for the 1,2-DNB–PIP system, the inclusion of the parameter β does not have statistical significance. However, it becomes significant for the 1,2-DNB–BA system, as expected, owing to the 'extra' hydrogen on the amino group, which may be available for solvent interactions other than the intramolecular interactions with the nitro groups.

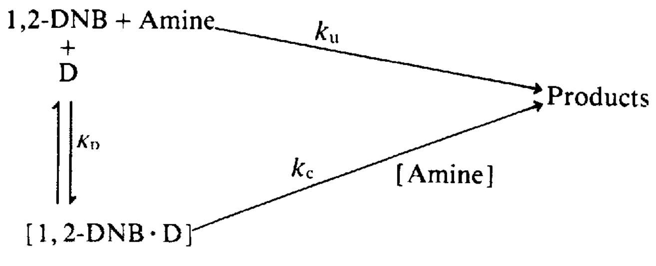
Reactions in solvent set B

In this solvent set, both reactions give, as stated before, a linear relationship between k_A and nucleophile concentration according to equation (3). However, the ratio k''/k_0 (Table 3), which can be taken as a measure of the extent of base catalysis, is too small to indicate true base catalysis and is in the range of Bunnett and Garst's[8] 'mild acceleration of unclear origin.'

Another fact that should be noted is that the reactions between 1,2-DNB and BA in this solvent set are slower than in hexane (Tables 2 and 3) for the same nucleophile concentration. However, for the system 1,2-DNB–PIP the reaction is faster in the aromatic solvents but slower in diisopropyl ether than in hexane. It becomes very difficult to rationalize this behavior in terms of solvent effects as we did with set A, and a more complex situation is immediately inferred.

These solvents have as common characteristic a low dielectric constant ($\varepsilon < 6$), and some of them, such as benzene, as considered typical non-polar solvents for S_NAr reactions. Another characteristic that seems to be important for our systems is that the aromatic solvents can act as π electron donors toward π electron acceptors such as 1,2-DNB.[4] Diisopropl ether could also act as an n electron donor.[32] A previous study on the kinetics of the 1,2-DNB–BA system[4] in hexane–benzene solvent mixtures revealed that the reaction can be partially inhibited by electron donor–acceptor (EDA) complex formation between 1,2-DNB and benzene. This study was acomplished by following the treatment proposed by Nagy and co-workers[33–36] and allowed us to evaluate quantitatively the effect of solute–solvent interactions on the reaction kinetics.

Thus we propose that for the reaction in a solvent mixture in which a complexing agent is present (i.e. benzene), the substrate may undergo two parallel reactions, the first proceeding from the free substrate and the second from the complexed substrate. The situation is depicted in Scheme 1, where k_u and k_c represent the pseudo-first-order rate coefficients for the free substrate (uncomplexed) and the complexed substrate, respectively, and D represents the complexing solvent. Moreover, it is assumed that 1,2-DNB forms a 1 : 1 EDA complex with the solvent D, and also that neither the products nor the amine are significantly associated with it.



Scheme 1

Accordingly, k_ψ can be expressed by

$$k_\psi = \frac{k_u + k_c K_D[D]}{1 + K_D[D]} \tag{12}$$

If $k_c < k_u$, the reaction is partially inhibited by complexation of the substrate by solvent D in the solvent mixture, and the plot of k_ψ vs [D] will be non-linear (downward curvature).[33] Equation (12) can be linearized to obtain

$$(k_\psi - k_u)/[D] = k_c K_D - K_D k_\psi \tag{13}$$

When data are processed using equation (13), a value of K_D for 1,2-DNB–benzene = 0·60 $mol^{-1}\,dm^3$ is obtained,[4] which is the expected value for this type of complex[32] in hexane. Hence it can be assumed that a stronger donor, such as mesitylene, will produce greater inhibition.[4,33,35]

Therefore, in order to obtain more evidence for the proposed mechanism, we studied the 1,2-DNB–BA system in mesitylene–hexane solvent mixtures. As can be observed in Figure 1, mesitylene exerts greater inhibition than benzene. From equation (13), the calculated value of K_D for 1,2-DNB–mesitylene = 0·90 $mol^{-1}\,dm^3$ seems reasonable.

Taking this evidence into account, it is believed that for the 1,2-DNB–BA system, 1,2-DNB will also be preferentially solvated for the other solvents in the set such as toluene, chlorobenzene and diisopropyl ether, through EDA complexation. Moreover, the inhibition exerted by these solvents in comparison with hexane should be correlated with the I_p of solvent D.[36] This is actually observed, since k_ψ (at the same nucleophile concentration) decreases as the I_p of D decreases.

The effects of the donor solvents on the 1,2-DNB–PIP system hitherto observed seem to be different from those on 1,2-DNB–BA since the aromatic solvents do not inhibit the reaction compared with hexane and only in diisopropyl ether does the reaction appears to be slower than in hexane.

In order to test the application of a reaction mechanism such as that in Scheme 1, the 1,2-DNB–PIP system was studied in benzene–hexane, diisopropyl ether–hexane and mesitylene–hexane. The results are shown in Figure 2. As can be inferred, only in the benzene–hexane mixture do the reaction rates increase with addition of the donor solvent.

At this point, it should be recalled that K_s for the 1,2-DNB–PIP EDA complex in hexane[2] (i.e. $K_s = 0{\cdot}55 \pm 0{\cdot}05\ dm^3\,mol^{-1}$) is higher than that for the complexes between 1,2-DNB and

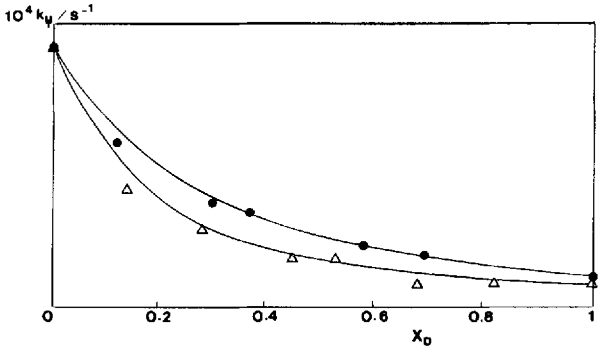


Figure 1. Plots of k_ψ against molar fraction (X_D) of the donor solvent for the reaction of 1,2-DNB with BA in hexane–donor solvent mixtures. (●) Benzene; (△) mesitylene. Temperature, 27 °C; [BA] = 0·4 M

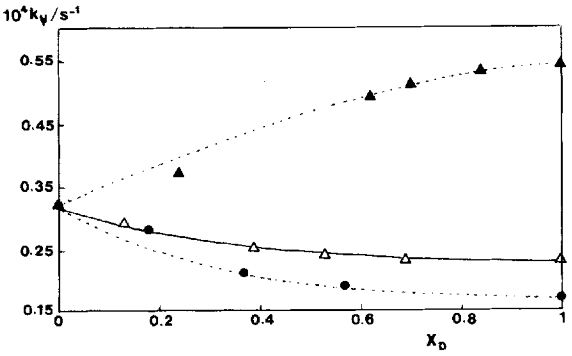
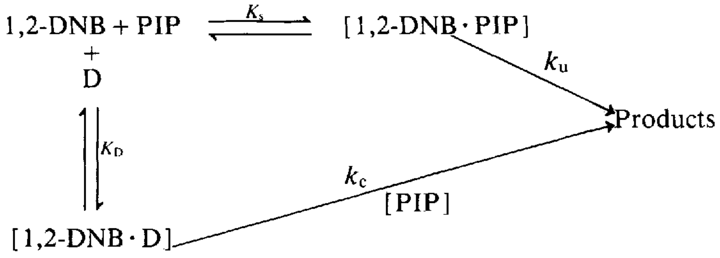


Figure 2. Plots of k_ψ against molar fraction (X_D) of donor solvent for the reaction of 1,2-DNB with PIP in hexane–donor solvent mixtures. (▲) Benzene; (△) mesitylene; (●) diisopropyl ether. Solid line, mathematical fit by equation (14). Temperature, 27 °C; [PIP] = 0·4 M

primary aliphatic amines.[3] Since this equilibrium is important for PIP, unlike that for the primary amines, a competition between the nucleophile and the donor solvent may be established in the solvent mixtures, as depicted in Scheme 2.



Scheme 2

The expression of k_ψ for such a scheme is given by

$$k_\psi = \frac{K_s k_c[\mathrm{PIP}] + K_D k_c[\mathrm{D}][\mathrm{PIP}]}{1 + K_s[\mathrm{PIP}] + K_D[\mathrm{D}]} \tag{14}$$

A satisfactory mathematical fit, shown by the full line in Figure 2, was obtained for the data for mesitylene–hexane mixtures with the values of K_s and K_D previously calculated in other systems.[2,4]

We believe that these results are in good agreement with the proposal of the effect of donor solvents in systems where K_D is greater than K_s.

Hence, in the 1,2-DNB–PIP system the inhibition effects will be observed only if $K_D > K_s$. Since this condition is not fulfilled for solvents such as benzene, toluene and chlorobenzene, the normal dipolarity solvent effect predominates.

Reaction of 1,2-DNB–BA in chloroform

The curvilinear dependence (downward curvature) of k_A with the nucleophile concentration for the 1,2-DNB–BA system in chloroform (Table 1) was adjusted by a non-linear regression analysis and equation (15) was obtained.

$$k_{\mathrm{A}} = \frac{(0{\cdot}552 \times 10^{-5}) + (8{\cdot}59 \times 10^{-6})[\mathrm{BA}]}{1 + 2{\cdot}62[\mathrm{BA}]} \tag{15}$$

The interpretation of equation (15) in terms of kinetic parameters is difficult. A possible explanation can be obtained by rearranging equation (2) to

$$k_{\mathrm{A}} = \frac{(k_1/k_{-1} + k_2) + (k_1 k_3^{\mathrm{B}}/k_{-1} + k_2)[\mathrm{BA}]}{1 + (k_3^{\mathrm{B}}/k_{-1} + k_2)[\mathrm{BA}]} \tag{16}$$

which actually implies that $k_{-1} \approx (k_2 + k_3^{\mathrm{B}}[\mathrm{BA}])$. However, considering the results obtained for this system in solvents of similar polarity (Table 2), this seems improbable.

A possible alternative is that chloroform exerts a special solvent effect due to its known hydrogen-bond donor ability.[37] Thus an association between the solvent and the nucleophile can be postulated as a side-reaction to the S_{N}Ar reaction.

Associations of chloroform with amines are known[38,39] and, for example, the association constant with triethylamine in cyclohexane is 0·58–0·59 $\mathrm{mol}^{-1}\,\mathrm{dm}^3$.[39] Association constants of the reactants of this order can produce downward curvature in the plots of k_{A} vs [amine] as for the 1,2-DNB–PIP system in hexane.[2]

Hence the assumption of a partial association between BA and chloroform as the cause of the curvature in these plots seems plausible.

CONCLUSIONS

When the solvent effects on the reaction of 1,2-DNB–BA and 1,2-DNB–PIP are compared in all the aprotic solvents studied, a similar reactivity in the kinetic behavior of the primary and the secondary amine is clearly observed. Both reactions are wholly base catalysed in hexane whereas a mild acceleration is observed in donor solvents. Neither reaction is catalysed at all in dipolar solvents of relatively high dipolarity ($\pi^* > 0{\cdot}55$).

The base-catalysed calculation in hexane can be clearly justified on the basis of its high non-polar character ($\pi^* = -0{\cdot}08$) and its consequently nonexistent ionizing power. However, the lack of apparent catalysis in solvents such as benzene and other aromatics is not as easily justifiable. Nevertheless, the preferential solvation exerted by these donor solvents through EDA complex formation with the substrate may provide evidence to explain why only a mild acceleration can be observed.

The fact that the substrate and even the intermediates may be solvated could mask the basic properties of the catalyst. In addition, the higher polarizability of these solvents with respect to hexane and through its hydrogen bond acceptor properties could better assist the spontaneous decomposition of the intermediate to products. In any case, the behavior of these reactions is not commonly observed when the substrate has a halogen as leaving group.

This leads us to propose that, when nitro is the leaving group, the possibility of a intramolecular hydrogen bond in the intermediate (**Ib**) may play an important role in the observed behaviour. This conclusion is supported by the evidence obtained when the reactions are performed in the solvent set A, where the spontaneous uncatalysed decomposition of this intermediate is best rationalized by this proposal. This may also explain the usually accepted high nucleofugacity of the nitro group.

EXPERIMENTAL

Reagents and solvents

1,2-DNB (Fluka), PIP (Carl Erba), BA (Aldrich) and benzene (Carlo Erba) were purified as described previously[2-4] and ACN[40] (Carlo Erba) and DMSO[41] (Merck) by reported procedures. THF (Merck) was dried for 2 days over calcium sulphate, then fractionally redistilled over sodium under a nitrogen atmosphere and used immediately. Ethyl acetate (Merck) was dried over calcium sulphate for several days and then distilled. The middle fraction of the distillate was distilled over P_2O_5 prior to use. DMF (BDH) was first dried over calcium sulphate and then over potasium hydroxide pellets; finally it was distilled over sodium before use. Chlorobenzene (Merck) was refluxed over P_2O_5 and then fractionally distilled. Toluene was purified by the same procedure as for benzene.[4] Diisopropyl ether (Fluka), free from peroxides, was dried over calcium chloride overnight, then treated with P_2O_5 for 1 h. After filtration it was distilled over sodium in a nitrogen atmosphere. Chloroform (Cicarelli) was purified by washing with concentrated sulphuric acid, then with dilute sodium hydroxide solution and finally with distilled water. It was dried over anhydrous potassium carbonate and stored in a dark flask until its use.

Kinetic procedures

The kinetics of the reaction were followed spectrometrically as described previously.[2,3]

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