

Solvent Effects on Aromatic Nucleophilic Substitutions. Part 4.¹ Kinetics of the Reaction of 1-Chloro-2,4-dinitrobenzene with Piperidine in Protic Solvents

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The kinetics of the reaction between 1-chloro-2,4-dinitrobenzene and piperidine were studied in 2-methylpropan-1-ol, propan-1-ol, propan-2-ol, butan-2-ol, benzyl alcohol, 2-phenoxyethanol, 2-methoxyethanol, and diethylene glycol at 15, 25, and 40 °C. The second-order rate coefficients, k_A , for the reaction in these solvents are not well correlated with the previously found relationship between the parameter $E_T(30)$ and the k_A values for reaction in aprotic non-hydrogen-bond donor solvents.¹ Inter- and intra-molecular hydrogen-bond interactions in the pure solvent and between the solvent and the amine are relevant in determining the reaction rate. The reactivity in hydroxylic solvents is inversely proportional to the hydrogen-bond-donating ability of the solvent. Fifteen (protic and aprotic) solvents are well correlated by Swain's parameters A and B , although caution is recommended when this linear free energy relationship is used.

The study of the highly specific properties of hydroxylic solvents, such as inter- or intra-molecular hydrogen-bonding,² acidity and basicity,³ and self-association,⁴ among others, has recently received new impetus. Such phenomena are frequently responsible for variations in relative rates and/or mechanisms.

In Part 3¹ we showed that solvent effects on the second-order rate coefficients, k_A , for the reactions of 1-chloro-2,4-dinitrobenzene with piperidine in thirteen aprotic solvents, with a range of 43 units in dielectric constant, are well correlated by the Reichardt⁵ solvent parameter $E_T(30)$. The correlation is remarkably good (r 0.981) if hydrogen-bond donor (HBD) solvents are excluded; conversely hydrogen-bond acceptor (HBA) solvents, including aliphatic, aromatic, and polychlorinated aliphatic systems, are successfully correlated.

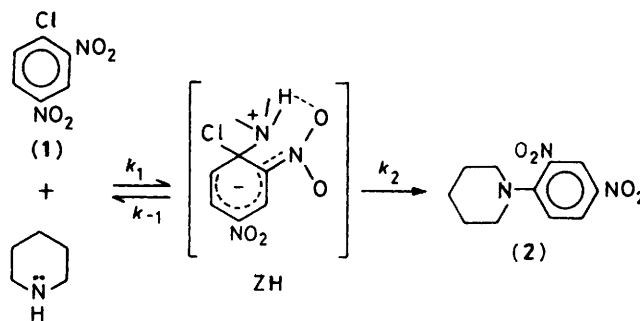
The mechanism of the title reaction is fully established, and is depicted in the Scheme. The transition state leading to the zwitterionic intermediate, ZH, is expected to be favoured by increasing solvent polarity; this was observed for a range of aprotic solvents spanning almost two orders of magnitude in k_A (cyclohexane to dimethyl sulphoxide).¹ However, previous studies of the reaction in methanol⁶ showed a reaction rate even smaller than that in cyclohexane (the slowest in the present series).

In addition to non-specific coulombic, inductive, and dispersion interactions, hydroxylic solvents exhibit the highly specific properties already mentioned. In order to identify and assess the relative influence of these factors in this simple model of aromatic nucleophilic substitution, we have studied the reaction in ten alcohols.

Results and Discussion

For aromatic nucleophilic substitution in protic solvents the breakdown of the zwitterionic intermediate with poor nucleofugues has been shown to occur by a rate-limiting proton transfer.⁷ Although *a priori* no base catalysis is expected for chloride expulsion, to confirm this the influence of amine concentration was studied in an aliphatic (propanol) and an aromatic (benzyl) alcohol.

Since the influence of temperature⁸ on the base-catalysis



Scheme.

Table 1. Reactions of 1-chloro-2,4-dinitrobenzene (1) with piperidine in propan-1-ol and in benzyl alcohol; search for amine catalysis at 15, 25, and 40 °C^a

[piperidine]/M	Propanol			Benzyl alcohol		
	15 °C	25 °C	40 °C	15 °C	25 °C	40 °C
0.0060		1.93	4.75			
0.0100		1.92	4.76			
0.0120					1.02	
0.0200		1.91	4.77		1.02	2.80
0.0300					1.01	2.76
0.0400	1.00	1.92		0.491	1.00	2.89
0.0800	1.02	1.89		0.497	1.02	2.87
0.1400	1.06	1.93		0.493	1.03	2.89

^a [(1)] = 10⁻⁴ M; values are of 10² k_A /l mol⁻¹ s.

coefficient has been recently demonstrated, the reaction was examined at three different temperatures. In all cases pseudo-first-order conditions were employed; the reactions yielded the expected *N*-(2,4-dinitrophenyl)piperidine (2) in quantitative yield, and proved to be first order in substrate. The second-order rate coefficients, k_A , calculated as in ref. 1, are collected in Table 1. As can be observed, no significant acceleration in rate

Table 2. Reaction of 1-chloro-2,4-dinitrobenzene (1) with piperidine in alcohols at 25 °C; search for amine catalysis^a

[piperidine]/M	2-Methylpropan-1-ol	Propan-2-ol	Butan-2-ol	2-Phenoxyethanol	2-Methoxyethanol	Diethylene glycol
0.0060	1.90	2.52				
0.0100	1.89	2.51				
0.0120			2.58	1.66	3.94	5.39
0.0200	1.88	2.50	2.55	1.66	3.94	5.35
0.0300			2.51	1.65	3.93	5.58
0.0400	1.90	2.51	2.59	1.71	4.02	5.59
0.0800	1.91	2.52	2.59	1.70	4.10	5.52
0.1400	1.91		2.62	1.69	4.14	5.56

^a [(1)] = 10⁻⁴ M; values are of 10²k_A/l mol⁻¹ s⁻¹.**Table 3.** Second-order reaction rate coefficients, k_A, at 15, 25, and 40 °C, and activation parameters for the reactions of 1-chloro-2,4-dinitrobenzene (1) with piperidine in hydroxylic solvent.^a Solvent parameters are included

No. ^f	Solvent	10 ² k _A /mol ⁻¹ s ⁻¹			ΔH [‡] kJ mol ⁻¹	ΔS [‡] J K ⁻¹ mol ⁻¹	E _T (30) ^b	α ^c	δ _{SA} ^d	β ^e
		15 °C	25 °C	40 °C						
14	Methanol	0.801	1.41	2.80	39.0	151.7	55.5	0.98	3.0	0.62
15	Ethanol		1.80				51.9	0.83	2.1	0.77
16	2-Methylpropan-1-ol	1.05	1.90	4.61	41.9	145.3	49.0			
17	Propan-1-ol	1.03	1.92	4.76	43.5	140.3	50.7	0.77	1.8	
18	Propan-2-ol	1.40	2.51	6.25	42.7	141.1	48.6	0.70	1.5	0.92
19	Butan-2-ol	1.48	2.57	6.04	39.9	150.3	47.1			
20	Benzyl alcohol	0.494	1.02	2.84	49.8	123.5	50.8	0.60		0.56
21	2-Phenoxyethanol	0.836	1.68	4.53	48.1	125.6	52.0			
22	2-Methoxyethanol	2.34	4.01	9.09	38.4	151.6	52.3			
23	Diethylene glycol	3.00	5.50	13.0	41.5	138.2	53.8			

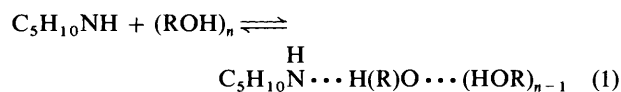
^a [(1)] = 10⁻⁴ M. ^b Ref. 5. ^c Ref. 12. ^d Ref. 4. ^e Ref. 6. ^f Solvents are numbered consecutively from solvents in Table 4 of ref. 1.

occurs with increasing amounts of amine at 15, 25, and 40 °C. Therefore, the influence of amine concentration was examined at only one temperature (25 °C) for the reactions in the other alcohols, and the absence of base catalysis was confirmed in all cases (Table 2).

The strikingly low reactivity previously observed for reaction in methanol⁶ was again found for reactions in other hydroxylic solvents. Table 3 lists the second-order rate coefficients, k_A, at 15, 25, and 40 °C, and the calculated activation parameters. In classical solvent theory an increase in rate would be expected with increasing solvent polarity, as observed in the reactions of 1-fluoro-2,4-dinitrobenzene with primary⁹ and secondary¹⁰ amines in going from benzene to methanol. A roughly similar dependence of k_A on solvent dipolarity as measured by E_T(30) was found for the present reaction in aprotic solvents.¹ Nevertheless, the reactions are not strictly comparable since the former are known to be subject to base catalysis in benzene⁷ although not in methanol.¹¹ The diminution in rate observed in alkanols (Table 3) must be associated with a specific hydroxylic solvent effect on this system, which is not recognised by the E_T(30) parameter. Table 3 shows the reported values, from which it is clear that the trend in rate does not follow the order of the E_T(30) values. The line defined by log k_A vs. E_T(30) for the alkanols is of a much smaller slope than the line for aprotic solvents (0.029 cf. 0.119). In Reichardt's paper^{5b} the correlation between E_T(30) and the differences between the transition energies of sodium 4-nitrophenolate and 4-nitroanisole shows two different straight lines with opposing slopes for protic and aprotic solvents, indicative of different solvation mechanisms in the two solvent series.

In the present work, all the reactions have lower rates than the slowest reaction studied in aprotic solvents (k_A for cyclohexane at 25 °C is 3.84 × 10⁻² l mol⁻¹ s⁻¹).¹ They exhibit higher enthalpy and entropy of activation than the reactions in aprotic solvents (average values 25 kJ mol⁻¹ and -180 J K⁻¹ mol⁻¹, respectively). Hydroxylic solvents are known to form strong

hydrogen bonds, being able to act as donors as well as acceptors. Taft and his co-workers¹² have recently developed and extensively used an empirical scale of hydrogen-bonding acidities and basicities, defining parameters α and β as a measure of HBD and HBA capabilities, respectively, to modify their solvatochromic parameter π* which measures solvent dipolarity when hydrogen-bonding interactions are absent. Table 3 shows that the present solvents exhibit high values for α and β. Because of these properties alkanols are regarded as highly 'polymerized'; Jorgensen¹³ has given new insights into the structure of methanol and ethanol, reproducing some of their thermodynamic properties by means of *ab initio* and Monte Carlo calculations. In the presence of piperidine, alcohols are known to act as hydrogen-bond donors, and there exists abundant evidence of strong hydrogen-bonding interactions between piperidine and alkanols.¹⁴ The pure oligomers (ROH)_n are modified to include piperidine molecules [equation (1)]. In recent studies performed with pyridine *N*-oxide and



several alkanols it has been found that self-association enhances both acidity and basicity relative to the same molecule acting only as acceptor or donor:^{4b} thus, the dimers of the alcohols are, on average, one order of magnitude more acidic towards pyridine *N*-oxide (in cyclohexane) than the corresponding monomers. This confirms Kamlet's¹⁵ earlier contentions based on more indirect evidence.

Quantitative estimates of the self-association energies, δ_{SA}, of various alkanols have been recently reported;^{4a} these values are also listed in Table 3. Methanol exhibits the largest δ_{SA} and α values, in an excellent correlation between the extent of oligomerization and HBD ability. As can be observed in the same Table the reactivity order is exactly the inverse of that of

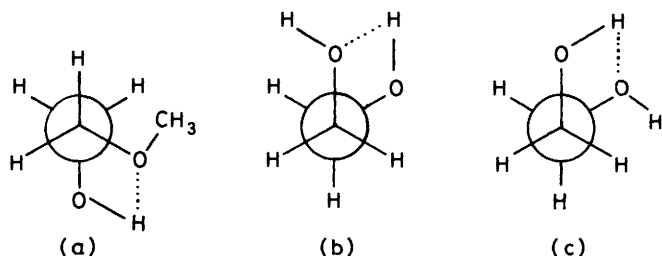


Figure. Preferred conformations postulated for (a) 2-methoxyethanol; (b) and (c) diethylene glycol

the δ_{SA} and α values, thus supporting the hypothesis that strong solvation of the piperidine molecule by protic solvents is responsible for the observed decrease in rate. This hypothesis is also supported by the activation parameters: the required desolvation of piperidine prior to the reaction causes the enthalpies of activation in the present cases to be *ca.* 12 kJ mol⁻¹ greater than those in aprotic solvents. Formation of the dipolar intermediate in those solvents produces a certain solvent organization from a random distribution of solute in the initial state, and therefore the activation entropies of those reactions are small (*ca.* -190 J K⁻¹ mol⁻¹). Conversely, reactions in protic solvents have a highly organized initial state [equation (1)]; the increase in 'freezing' of solvent molecules around the zwitterionic intermediate is then smaller and the reactions have higher entropies of activation than those in aprotic solvents.

Although the trend in reactivity follows the structural features of the alkanols, the variation in rate is relatively slight, and other hydroxylic solvents were examined to confirm the hypothesis based on the relevance of hydrogen bonding in these systems. Solvents expected to have lower and higher HBD abilities were studied, and the results are listed in Table 3. Benzyl alcohol can be considered as a methanol derivative in which a hydrogen atom has been replaced by an electron-acceptor group; an increase in its HBD ability is then expected, and its magnitude could be reflected in the value of the σ^* Taft's¹⁶ polar substituent constant σ^* (0.215 *cf.* 0 for methanol).^{*} The activation parameters are also consistent with the rationale of hydrogen-bonding causing the low rate: this reaction exhibits higher enthalpies and entropies of activation. When the phenyl group is isolated by an intermediate oxygen atom its effect is much attenuated; thus the reactivity in 2-phenoxyethanol is similar to that in the alkanols.

An alcohol of expected smaller HBD capacity was then examined. Gas-phase studies by electron-diffraction, microwave spectroscopy, and i.r. and Raman spectroscopy have shown that the 2-halogenoethanols all prefer the heavy atom *gauche* conformation with an intramolecular hydrogen bond.¹⁸ Microwave spectra and dipole moment investigations of 2,2-difluoroethanol have also shown that the molecule adopts a conformation where the intramolecular hydrogen bond is characterized by having the O-H and C-F bonds nearly parallel.¹⁹ A similar conformation can be written for 2-methoxyethanol as shown in the Figure (a). Such a conformation is very favourable for electrostatic stabilization between the O-H and C-OCH₃ dipoles, thus reducing the OH acidity, or, as shown by Shorter *et al.*,²⁰ increasing the Lewis basicity.

That the increase in rate is due to the diminution in hydrogen-bonding interactions with the piperidine molecule is supported

by the activation parameters: the smallest enthalpies and entropies of activation are observed for reactions in 2-methoxyethanol.

For the case of diethylene glycol, *a priori* a weaker intramolecular interaction would be expected than in the case of 2-methoxyethanol; however the existence of two hydroxy groups makes possible two different hydrogen-bonded conformations [Figure (b) and (c)]. Thus the statistical distribution of hydrogen-bonded molecules is higher and the reaction is the fastest observed in the hydroxylic solvents examined. The values of the activation parameters, compared with those for 2-methoxyethanol, are also consistent with a weaker hydrogen bond and a more abundant distribution.

Some Linear Free Energy Correlation Equations.—We have previously shown¹ that solvent effects in aprotic solvents can be satisfactorily correlated by $E_T(30)$ if HBD solvents are excluded. In the case of alkanols, σ^* values have been reported for all those listed in Table 3 and the correlation with the reaction rate is given by equation (2); the correlation coefficient (*r*) is 0.990

$$\log k_A = -1.863 - 1.293 \sigma^* \quad (2)$$

and the standard deviation (*s*) 0.0155. Application of Koppel and Palm's²¹ treatment showed the dielectric constant to be secondary in importance [equation (3)], although the cor-

$$\log k_A = -3.134 + 2.669 f(\epsilon) - 1.537 \sigma^* \quad (3)$$

relation is not very much improved (*r* 0.994, *s* 0.0131). The confidence level of this biparametric equation is 98.8%; the very poor confidence level for $f(\epsilon)$ (79%) as compared with σ^* (98%) shows that the inclusion of the second term is irrelevant, the confidence level of equation (2) being 98%. Equation (4) shows

$$\Delta \log k_A = 2.669 [f(\epsilon_1) - f(\epsilon_2)] - 1.537 (\sigma_1^* - \sigma_2^*) \quad (4)$$

that although there is an important difference in the dielectric constants of a pair of alkanols, their significance in $\log k_A$ is small in comparison with the strong dependence on σ^* . If the rest of the solvents in Table 3 are included, the resulting correlation is extremely poor, showing the importance of intramolecular hydrogen-bonding in these solvents. Only benzyl alcohol can be satisfactorily correlated, given equation (5) (*r* 0.977, *s* 0.0323).

$$\log k_A = -1.816 - 0.9473 \sigma^* \quad (5)$$

Attempts to correlate $\log k_A$ over the whole range of media studied (thirteen aprotic¹ and the present ten protic solvents) by only one equation were not successful for any of the solvent parameters examined in ref. 1. An original treatment of substituent and solvent effects has been recently proposed by Swain *et al.* (SSPA)³ and criticized by others.^{2,22-24} These authors assume that the most important solvent properties affecting chemical reactivity are anion-solvating tendency (measured by the parameter *A*) and cation-solvating tendency (measured by *B*). If the two-parameter equation is applied to the $\log k_A$ values of ref. 1 and the present work for the fifteen solvents for which parameters are recorded (all the aprotic solvents, except 1,1,1-trichloroethane and chlorobenzene, and the protic solvents methanol, ethanol, propan-1-ol and propan-2-ol), equation (6)

$$\log k_A = -1.884 - 1.353 A + 2.280 B \quad (6)$$

is obtained [*r* 0.940, *s* 0.250; confidence levels 99.9% (*A*) and 99.999% (*B*)] (If cyclohexane is excluded from the correlation, *r* is improved to 0.963.) If one takes into account the very

* Although some intramolecular hydrogen-bonding to its own π -electron system has been postulated for benzyl alcohol, it has been demonstrated¹⁷ that its relative strength is smaller than hydrogen bonding to amine nitrogen.

Table 4. Correlation of aprotic (1—13) and protic (14—23) solvents with the solvatochromic parameter π^* and α and β^a

Solvents ^b	<i>n</i>	Parameter(s)	log <i>k</i> ₀	<i>p</i>	<i>q</i>	<i>r</i> ^c
1—5, 8—19	17	π^*	-2.13	2.07		0.681
1—3, 5, 8—19	16	π^*	-2.13	2.07		0.681
14, 15, 18, 19, 20	5	π^*, α	-0.666	-0.942	-0.675	0.987
14, 15, 18, 19	4	π^*, α	-0.670	-3.38	0.913	0.9996
14, 15, 18, 20	4	π^*, β	-2.21	-0.137	0.711	0.9997
1—5, 8—15, 18, 19, 20	18	π^*, α	-1.38	1.27	-1.38	0.836
1—3, 5, 8—15, 18—20	17	π^*, α	-1.40	1.28	-1.40	0.841
1—3, 5, 8—15, 18, 19	16	π^*, α	-1.73	1.85	-1.17	0.929
1—5, 8—15, 17, 18	15	π^*, α	-1.74	1.91	-1.18	0.933 ^d
1—3, 5, 8—10, 12, 13	11	π^*, α	-1.74	1.87	-1.22	0.933
1—5, 8—15, 18, 20	17	π^*, β	-1.61	1.41	-0.47	0.468
1—3, 5, 8—15, 18—20	16	π^*, β	-1.59	1.43	-0.53	0.474
1—3, 5, 8—10, 11—15, 18, 19	14	π^*, β	-1.96	2.29	-0.62	0.715
1—5, 8—15, 17, 18	15	π^*, β	-2.06	2.40	-0.66	0.760

^a $\log k_A = \log k_0 + p\pi^* + q\alpha$ (or β). ^b Solvents are numbered as in Table 4 of ref. 1, and Table 3 of the present paper. ^c Correlation coefficient. ^d The confidence levels are 99.993% (π^*) and 99.994% (α). A three-parameter equation ($\log k_A = -1.74 + 1.86\pi^* - 1.21\alpha + 0.08\beta$) has *r* 0.934; the confidence levels 99.97% (π^*), 99.96% (α), and 22.66% (β) show the lack of relevance of the parameter β . The values for π^* , α , and β used in the present Table have been taken from M. J. Kamlet, J.-L. M. Abboud, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1981, 13, 485.

different solvating properties of the solvents involved in equation (6), this correlation could be considered satisfactory. This could, in principle, support the assumption³ that solvations involving hydrogen-bonding do not require treatment different from solvation involving other kinds of polar or polarizable solvent molecules. However, it is necessary to point out that if only the aprotic solvents are considered the correlation is very poor (*r* 0.88); this could show a weakness in the treatment of ref. 3.

Table 4 shows some of the different equations tested using the solvatochromic parameter π^* and the parameters α and β that account for the hydrogen-bond capabilities of the solvents. A single-parameter equation is insufficient to correlate the protic and aprotic solvents for which parameters have been given (ref. 2 and previous refs. therein). Correlations of the few protic solvents for which α or β have been parametrized in biparametric equations. (π^*, α or π^*, β) are very good, but when the aprotic solvents are included the correlation coefficient for π^*, α drops to 0.836, and when chloroform and benzyl alcohol are excluded it is improved to 0.929. If the solvents included in equation (6) are correlated, the coefficient (*r* 0.933) is slightly smaller than that of the treatment of ref. 3; if only the aprotic solvents are considered the correlation is still satisfactory which shows some supremacy over the ref. 3 treatment. Attempts to correlate protic and aprotic solvents by π^*, β were, as expected, unsuccessful, and cannot be improved by excluding some solvents.

Until a more critical definition is available of the subsidiary conditions under which each parameter must be used, and without entering into a discussion of which parameter is a better measure of general solvent properties, we can conclude that solvent effects in nucleophilic aromatic substitutions by amines free of complications are roughly correlated by the equation of ref. 3 (SSPA) or that of Taft *et al.*² If greater precision is required a very good prediction of solvent effects in non-HBD aprotic solvents can be obtained through Reichardt's parameter $E_T(30)$. HBD solvents form a separate series because of the relevance of hydrogen-bonding in amines, and the reactivity order is the inverse of the HBD ability of the solvents.

Experimental

Reagents and Solvents.—1-Chloro-2,4-dinitrobenzene and piperidine were purified as previously described.¹ *N*-(2,4-Di-

nitrophenyl)piperidine was prepared as previously reported;⁶ m.p. 92—93 °C. Anhydrous methanol and ethanol were prepared by Lund and Bjerrum's method.²⁵

Kinetic Procedures.—The kinetics of the reaction were studied spectrophotometrically, by running the reactions in the thermostatted cells of the spectrophotometer. Essentially the same procedure was followed as was used for the reactions in aprotic solvents.¹ All the kinetic runs were carried out at least in duplicate; the error in k_A is <2—3% for all the solvents examined. Values of ΔH^\ddagger are accurate to ca. ± 0.4 kJ mol⁻¹ and values of ΔS^\ddagger to ± 8 J mol⁻¹ K⁻¹.

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