The Effect of a Hydrogen Bond Acceptor Catalyst on the Dimer Mechanism in Aromatic Nucleophilic Substitution

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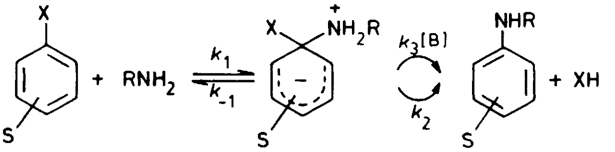
The reaction of 2,6-dinitroanisole with cyclohexylamine in toluene–dimethyl sulphoxide (DMSO) mixtures was studied at several amine concentrations. In pure toluene and toluene–DMSO mixtures of low DMSO content ($\leqslant$ 1%) third-order kinetics with respect to the amine are observed. These results are interpreted as a consequence of the aggregation of the nucleophile (dimer) in low-polarity solvents. Association of DMSO with the amine ('mixed dimer') in a solute–solvent hydrogen-bond interaction can be responsible for the observed catalytic effect of DMSO. At higher DMSO contents behaviour typical for amine catalysis was found which is related to considerable additional stabilization of the intermediate complex through solvation by DMSO.

The occurrence of base catalysis in aromatic nucleophilic substitution (ANS) has been taken as one of the most important pieces of evidence for the S_NAr mechanism in ANS[1] [equation



(1)

(1)]. Although it has been extensively studied since its discovery in 1958[2,3] the mechanism(s) by which it operates in aprotic solvents is (are) still unclear.[4] If the zwitterionic σ-intermediate does not accumulate to an appreciable extent during the course of reaction (1) the overall second-order rate constant, k_A, derived by standard steady-state approximation has the form of equation (2). According to equation (2) if $k_{-1} \gg (k_2 + k_3[B])$ the reaction is base-catalysed and k_A depends linearly on base concentration. If k_2 is relatively small and $k_{-1} \approx k_3[B]$, k_A depends on base concentration in curvilinear fashion (downward curvature): the linear dependence at low [B] changes to a plateau at high [B].

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

We have recently reported an unusual k_A dependence on [B]: in reactions of dinitroanisoles[5,6] and of dinitrofluorobenzene[7] with amines in aprotic solvents k_A is of third order in amine, and the plot of k_A *versus* [B] exhibits an upward curvature. Examination of the literature reveals some other 'unusual' findings for ANS in benzene,[8–10] toluene,[11] cyclohexane,[12] and iso-octane.[13] These abnormalities were usually interpreted as an unspecific 'medium' effect.[9,12–14] Nevertheless, we have presented evidence for the participation of a dimer of the amine in the first step to explain the kinetic results in aprotic solvents[5–7] and in benzene–methanol mixtures of low methanol content.[15] In those mixtures methanol acts as a strong hydrogen-bond donor (h.b.d.) solvent competing with the amine molecules to form the aggregates. It was therefore of interest to find out if the addition of a strong hydrogen-bond acceptor (h.b.a.) entity has the reverse effect. The present paper describes the reaction of 2,6-dinitroanisole (DNA) with cyclohexylamine in toluene–dimethyl sulphoxide (DMSO) mixtures.

Results

The reaction of DNA with cyclohexylamine (CHA) in toluene–DMSO mixtures proceeds straightforwardly to give the expected *N*-(2,6-dinitrophenyl)cyclohexylamine. The S_N2 demethylation that was observed in the reactions of the same substrate with piperidine[16] does not occur in the present system at a detectable extent, and a quantitative yield of the substitution product was obtained in all the present reactions. The reactions were studied kinetically in the pure solvents and in the following mixtures: 0.4, 0.6, 1.0, 2.0, 5.0, 10, 20, 30, 40, 50, 60, 70, 80, and 90% v/v DMSO–toluene, and were carried out at 35.0 °C.

The effects of varying excess of nucleophile (in the range 0.05—0.8M) were investigated under pseudo-first-order conditions. The reactions proved to be first order in substrate, and on division of the pseudo-first-order rate coefficients k_ψ by the appropriate concentration of cyclohexylamine, the second-order rate coefficients k_A were calculated and the data are gathered in Table 1.

It can be observed from Table 1 that the change of toluene to DMSO produces an increase in the reaction rate of almost two orders of magnitude at [CHA] 0.300M. Figure 1 shows that the increase in rate is proportional to the the DMSO content in solvents from 20 to 100% DMSO, but at lower % DMSO the rate increases more rapidly than expected. When k_A is plotted against % DMSO for reactions carried out at % DMSO $\leqslant$ 2 linear dependence is also observed at various amine concentrations (Figure 2). But the most interesting findings were obtained when the dependence of k_A on amine concentration was studied. In pure toluene and toluene–DMSO mixtures of low DMSO content (< 2%) curved lines of upward curvature are obtained in the plot of k_A *versus* [CHA] (Figure 3) which indicates kinetics of order higher than two with respect to the amine; while in 10, 30, and 100% DMSO the lines exhibit downward curvature indicating orders equal to or smaller than two (Figure 4).

Discussion

Reactions in 10, 30, *and* 100% *DMSO*.—It has been recently shown[17] that the solvent effects in ANS free of complications can be satisfactorily predicted by the $E_T(30)$ solvent polarity parameter[18] if h.b.d. solvents are excluded. In particular, correlation with the h.b.a. solvents is remarkably successful and DMSO is not an exception among the 13 solvents studied: a

Table 1. Kinetics of the reaction of 2,6-dinitroanisole with cyclohexylamine (CHA) in toluene–DMSO mixtures at 35 °C[a]

DMSO (%)	[CHA]/M	10 k_A/l mol^{-1} s^{-1}	10 k_A[B]/l^2 mol^{-2} s^{-1}
0	0.300	3.18	1.06
	0.400	5.14	1.29
	0.450	6.53	1.45
	0.500	7.52	1.50
	0.600	10.00	1.67
	0.700	13.60	1.94
0.4	0.300	6.37	2.12
	0.400	9.48	2.37
	0.500	13.20	2.62
	0.600	16.70	2.78
0.6	0.200	4.63	2.32
	0.300	7.41	2.47
	0.400	11.20	2.80
	0.500	15.60	3.12
	0.600	20.10	3.35
1.0	0.200	6.94	3.47
	0.300	11.10	3.70
	0.400	15.90	3.98
	0.500	21.70	4.34
	0.600	26.60	4.46
2.0	0.100	5.36	5.96
	0.200	12.10	6.05
	0.300	18.10	6.06
	0.400	26.60	6.65
	0.500	32.60	6.52
5.0	0.300	3.85	
10.0	0.100	22.60	
	0.200	43.30	
	0.300	57.30	
	0.400	79.40	
	0.500	63.40	
	0.600	108.00	
	0.800	132.00	
20.0	0.300	82.10	
30.0	0.050	25.30	
	0.100	45.50	
	0.200	78.10	
	0.250	93.40	
	0.300	100.10	
	0.400	123.00	
	0.500	135.00	
	0.600	151.00	
	0.800	174.00	
40.0	0.300	110.00	
50.0	0.300	125.00	
60.0	0.300	139.00	
70.0	0.300	151.00	
80.0	0.300	170.00	
90.0	0.300	189.00	
100.0	0.050	90.10	
	0.075	120.00	
	0.100	142.00	
	0.150	159.00	
	0.200	174.00	
	0.250	201.00	
	0.300	204.00	

[a] [2,6-Dinitroanisole] *ca.* 1.7—2.2 10^{-4}M.

change in k_A of almost two orders of magnitude was found when passing from cyclohexane to DMSO in the reaction of 2,4-dinitrochlorobenzene with piperidine.[17] Therefore, the observed increase in rate in the present reactions was expected.

The dependence with the amine concentration depicted in Figure 4 is characteristic of a base-catalysed departure of the nucleofugue as shown in equation (1) and represented by the general equation (2). Previous studies of base catalysis in ANS carried out in DMSO show interesting results. In the reaction of 2,4-dinitrochlorobenzene with aniline, Hirst *et al.*[19] did not find base catalysis, which is in agreement with the good nucleofugacity of the chlorine atom $\{k_{-1} < (k_2 + k_3[B])\}$, and similar results were observed in the reactions of X = OPh with primary amines.[20] Nevertheless, in the case of a poor nucleofugue such as X = F base catalysis was neither found in the reactions with primary[19,21] nor with secondary amines.[22,23] In contrast, for X = OPh, Hirst *et al.*[20] found base catalysis in the reactions with secondary amines. Specific base catalysis was observed by Bunnett *et al.* in the reactions of 2,4-dinitro-1-naphthyl ethyl ether with primary[24] and secondary[25] amines, for which a specific base–general acid (SB–GA) catalysis mechanism is proposed. In the present case with a poor nucleofugue, X = OCH_3, 'base catalysis' was even observed with a primary amine; it is worth mentioning that in this system the Meisenheimer complex is not stabilized enough to be detected.[26]

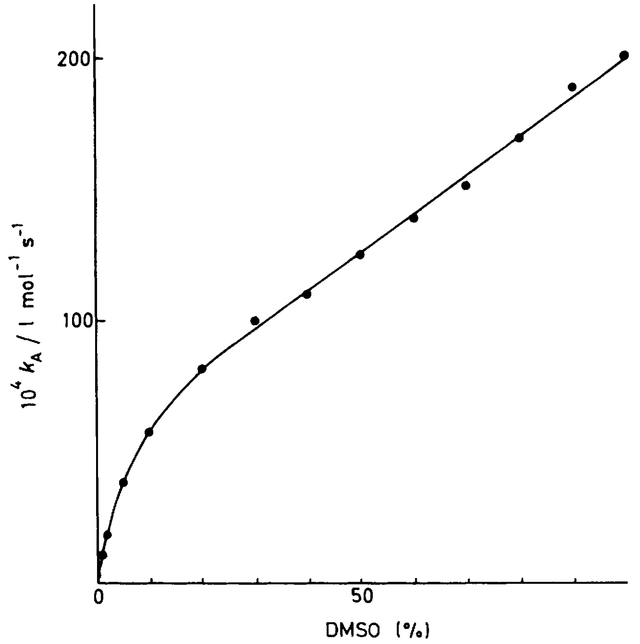


Figure 1. Second-order rate coefficients, k_A, for the reaction of 2,6-dinitrochlorobenzene with cyclohexylamine (0.300M) in toluene–DMSO mixtures as a function of the % DMSO, at 35 °C

The curvilinear dependence of k_A *versus* [CHA] shown in Figure 4 allows the determination of k_1 as the inverse of the intercept in the plot of $1/k_A$ *versus* $1/[B]$ [equation (3)].[27] Since k_2 is practically nil for reactions carried out in 10 and 30% DMSO, and it should be negligible for reactions in pure DMSO, the ratio k_3/k_{-1} can be calculated from the slope of the same plot and the data are gathered in Table 2. It can be observed that the rate of formation of the intermediate complex, k_1, is almost independent of the solvent, while the ratio k_3/k_{-1} increases considerably with the DMSO content.

$$\frac{1}{k_A} = \frac{k_{-1}}{k_1(k_2 + k_3[B])} + \frac{1}{k_1} \qquad (3)$$

The intermediate complex shown in equation (1) is expected to be more stabilized in DMSO which is known to be a good solvent for large cations and dipolar structures.[28] Then, diminutions in k_{-1} and k_3 are expected on increasing DMSO content. This type of zwitterionic intermediate are strong h.b.d.s,[29] although it has been recently found[30] that the N–H protons of *o*-nitroanisoles derivatives remain intramolecularly hydrogen bonded in h.b.a. solvents. Among all the current scales of h.b.a. basicities the β scale developed by Taft *et al.*[31]

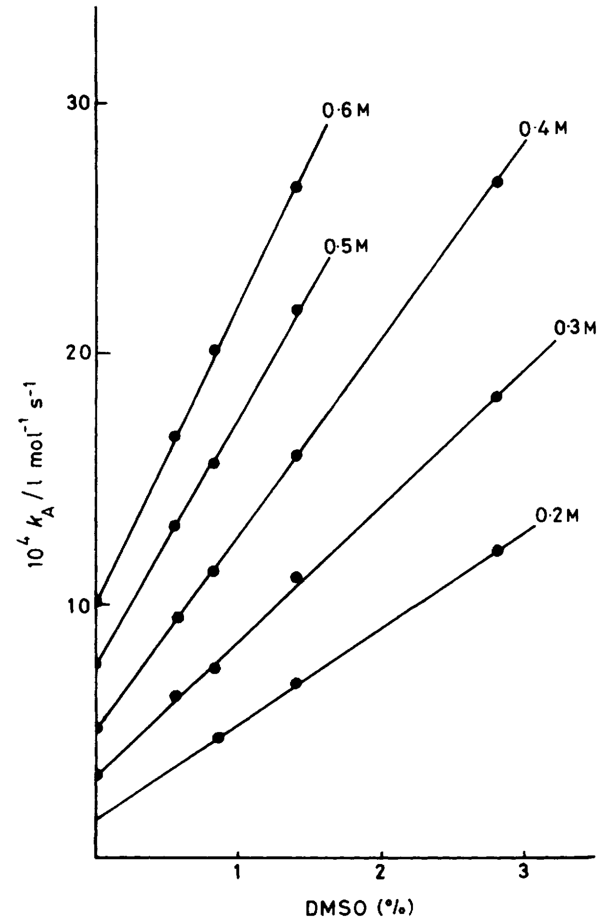


Figure 2. Second-order rate coefficients, k_A, for the reaction of 2,6-dinitrochlorobenzene at several cyclohexylamine (CHA) concentrations in toluene–DMSO mixtures, at 35 °C

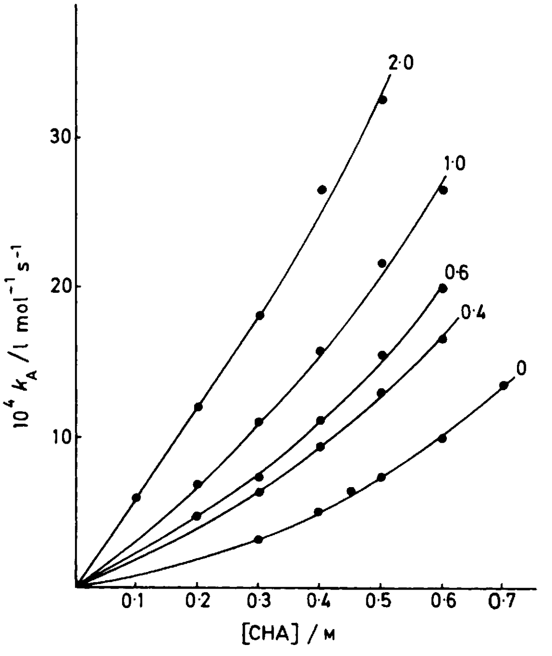


Figure 3. Second-order rate coefficients, k_A, for the reaction of 2,6-dinitrochlorobenzene with cyclohexylamine (CHA), in toluene–DMSO mixtures of low DMSO content, as a function of [CHA], at 35 °C

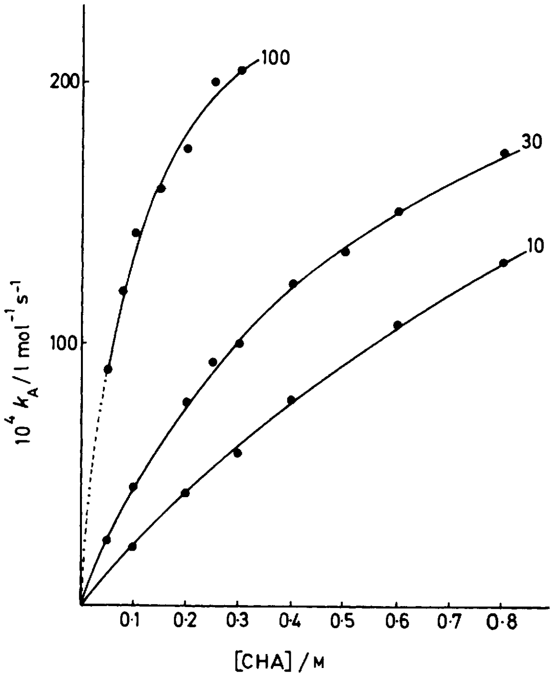


Figure 4. Second-order rate coefficients, k_A, for the reaction of 2,6-dinitrochlorobenzene with cyclohexylamine (CHA) in toluene–DMSO mixtures of high DMSO content, as a function of [CHA], at 35 °C

Table 2. Partial rate coefficients for the reaction of 2,6-dinitroanisole with cyclohexylamine in toluene–DMSO mixtures of high DMSO

DMSO (%)	$10^2 k_1$/l mol^{-1} s^{-1}	k_3k_{-1}/l mol^{-1}	k_2	r
10	3.99	0.60	~0	0.9992
30	2.69	2.07	~0	0.9998
100	2.70	10.1		0.995

provides a good measure of the solvent's ability to accept a proton in a solute–solvent hydrogen bond. DMSO has a β value (0.76) bigger than the β value of *NN*-dimethylcyclohexylamine (0.71),[32] the most closely related amine whose β value has been reported. Therefore, the increasing basicity of the solvent should exert an additional levelling effect on k_3.

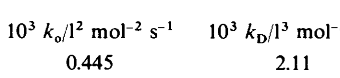
Reactions in Pure Toluene.—When the rate of the reaction was examined under different [CHA] a complex dependence was observed. The plot of the second-order rate constant, k_A, *versus* [CHA] (Figure 3) is curvilinear (upward curvature) and extrapolation to zero [CHA] gives an intercept which is practically zero. Thus, no term of overall second order (first order in CHA) plays a significant role in the rate law. When third-order rate constants (second order in CHA) were plotted against [CHA] (not shown) a straight line was obtained. An analytical expression consistent with such behaviour is equation (4) where B symbolizes CHA in the present case.

$$k_A = k_o[B] + k_D[B]^2 \qquad (4)$$

These results are similar to those reported previously for reactions in benzene[6] which were interpreted as a consequence of a dimer of the amine (B:B) acting as the nucleophile in the first step, producing an intermediate complex, SB_2, whose decomposition to products may be spontaneous or base-catalysed [equation (5)].

Table 3. Partial rate coefficients for the reaction of 2,6-dinitroanisole with cyclohexylamine in toluene–DMSO mixtures of low DMSO

DMSO (%)	$10^3\ k_0/l^2\ mol^{-2}\ s^{-1}$	$10^3\ k_D/l^3\ mol^{-3}\ s^{-1}$	r
0	0.445	2.11	0.994
0.4	1.47	2.23	0.995
0.6	1.73	2.71	0.994
1.0	2.96	2.56	0.989



$$S + B{:}B \rightleftharpoons [SB_2] \xrightarrow[B]{} P \qquad (5)$$

Reasons why the amine dimer should be a better nucleophilic species than the monomer have already been given[6] and dimers of amines has been postulated as probable reactive species in an aprotic solvent for other systems.[33]

Comparing the values for k_0 and k_D in pure toluene given in Table 3 with those found in benzene ($4.57 \times 10^{-4}\ l^2\ mol^{-2}\ s^{-1}$ and $2.00 \times 10^{-3}\ l^3\ s^{-1}\ mol^{-3}$, respectively)[6] it is clear that there is no significant difference between these solvents and all the considerations regarding amine association in benzene previously given[6] are straightforwardly applicable to the reactions in toluene.

Reactions in Mixtures of Low DMSO Content.—We have found only two previous studies of ANS carried out in DMSO solvent-mixtures. Bernasconi *et al.*[34] studied the reaction of 2,4-dinitrochloro- and 2,4-dinitrofluoro-benzene, and Suhr studied the reaction of *p*-fluoronitrobenzene,[35] all three with piperidine in benzene–DMSO mixtures.

In both studies a considerable increase in rate was found for small additions of DMSO to benzene, which in both cases is considered to exceed that expected based uniquely on considerations of the polarity of the medium. Nevertheless, although Bernasconi *et al.* recognise that the mechanism of catalysis by DMSO is not easy to explain they disregard a base-catalysis effect based on the fact that the pK_A of DMSO in water (*ca.* 0) is considerably smaller than the pK_A of DABCO (8.19) and pyridine (pK_A 5.23), while the observed catalytic effects are DABCO ~ DMSO > pyridine. They also take into account the equilibrium constant for picric acid in DMSO (*ca.* 1) and pyridine (*ca.* 3 000) and conclude that the catalytic effect of DMSO is a specific medium effect. Suhr, on the other hand, interprets the increase in rate observed in the reaction of *p*-fluoronitrobenzene as a sort of base catalysis based on the basic properties of DMSO.

In the reactions of 2,6-dinitroanisole with CHA third-order kinetics in amine [equation (4)] are observed for reactions carried out in mixtures of DMSO content smaller than 2% (Figure 3). The third-order rate coefficients, k_A/[CHA], plotted against [CHA] give good linear correlations whose intercepts and slopes are gathered in Table 3 and, therefore, the dimer mechanism represented by equation (5) is still operating.

Although addition of DMSO should affect the amine-dimer equilibrium, since the amounts of DMSO present are very low ([DMSO] < 0.14M), k_D is less affected than k_0. There is a linear correlation between k_0 and [DMSO] which is expressed by equation (6). k_D can be calculated as the average of the values in

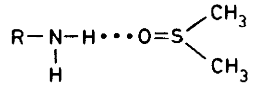
$$k_0[B] = k_\alpha[B] + k_\beta[DMSO][B] \qquad (6)$$

Table 3 (k_D $2.40 \times 10^{-3}\ l^3\ s^{-1}\ mol^{-3}$) and the coefficients k_α and k_β can be obtained from equation (6) ($k_\alpha = 4.19 \times 10^{-4}\ l^2\ mol^{-2}\ s^{-1}$ and $k_\beta = 1.75 \times 10^{-2}\ l^3\ mol^{-3}\ s^{-1}$). Equations (4) and (6) are valid in the whole range of [CHA] studied and in solvents of DMSO content <2% (0.282M).

Two points are worthy of notice: (a) the observation of a quadratic dependence of k_A on [B] even in 1% DMSO and (b) the catalytic effect of DMSO measured by k_β, which exceeds considerably that expected on the basis of polarity or dipolarity of the medium.

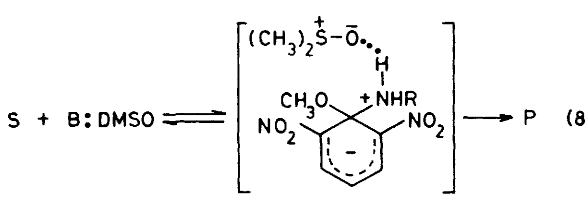
Taking into account the known tendency of CHA to form aggregates in non-polar aprotic solvents and the greater nucleophilicity of the dimer in these reactions[5–7] the catalytic effect of DMSO may be interpreted as a result of an association between the amine and DMSO molecules in a solute–solvent hydrogen-bond interaction of the type depicted by complex (7).

Besides measurements that allow determination of the h.b.a. properties of DMSO there are i.r. data that indicate that the association constants between amines and DMSO in CCl_4 are 2.5—35 for aromatic amines[36] and 1—4 for aliphatic amines.[37]



(7)

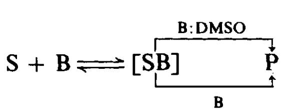
An enhancement in the amine basicity is derived from this aggregation[37] and for the case of aniline it has been found that it is related to the electronic effects of the substituents.[38] Since it has been shown that association with DMSO reduces amine self-association[37] we propose that the catalytic effect of DMSO is due to its participation in the first step of the reaction forming a mixed dimer with the amine molecules and producing the intermediate complex shown in equation (8). B:DMSO



(8)

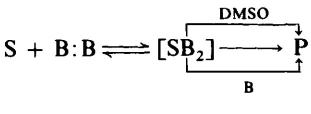
should have the structure depicted in (7). This kind of coordination of the amine proton should produce greater nucleophilicity of the amine owing to the greater electron density on the nitrogen atom,[39] and therefore, explains the catalytic effect of DMSO (β_{DABCO} 0.73; $\beta_{Pyridine}$ 0.64).[29b]

Two other reaction schemes are consistent with the observed kinetic results. In equation (9) an amine molecule and a DMSO molecule (probably in the form of a B:DMSO complex) assist the decomposition of intermediate complex, SB. This sequence should occur simultaneously with the sequence shown in equation (5) where the nucleophile is the dimer of the amine.



$$S + B \rightleftharpoons [SB] \xrightarrow[B]{B:DMSO} P \qquad (9)$$

In a second mechanism the dimer of the amine is the nucleophile and the DMSO catalyses the decomposition of the intermediate complex, SB_2, [equation (10)].



$$S + B{:}B \rightleftharpoons [SB_2] \xrightarrow[B]{DMSO} P \qquad (10)$$

Although the three mechanisms (8)—(10) for the DMSO catalytic effects are compatible with the present kinetic results only the first [equation (8)] should show catalysis by DMSO when the first step is rate determining, as is the case for a good nucleofugue. In the reaction of 2,4-dinitrochlorobenzene with piperidine in benzene a linear dependence between k_A and

[DMSO] is found for small additions of DMSO (< 0.2M)[35] which can be explained by equation (8).

Taking into account the evidence, *i.e.* (i) the ability of DMSO to associate to amines by a solute–solvent hydrogen-bond interaction and (ii) catalysis by DMSO even in reactions where the first step is rate controlling, it is reasonable to conclude that the mechanism of the catalytic effect of DMSO observed in the present reactions can be represented by equation (8). When the DMSO content is $> 2\%$ the mechanism represented by equation (5) is not observable. This is probably due to the known ability of DMSO to interfere with amine–amine aggregation in non-polar aprotic solvents.[37] The concentration of the dimer is too low and the whole reaction can be represented by equation (1). The present kinetic results seem to indicate that the change in mechanism occurs at *ca.* 2% DMSO in toluene.

Two additional points are worthy of notice to confirm that the catalytic effect of DMSO is not a classical medium effect. In the reactions of *p*-fluoronitrobenzene studied by Suhr[34] a plot (not shown) of the observed k_A *versus* the classical function of the dielectric constant, D $[(D - 1)/(2D + 1)]$; or *versus* the DMSO content in benzene is linear in the range 11—100% DMSO but the point for benzene is considerably below the line and the complete curve resembles Figure 1 quite closely. Secondly, when the effect of small additions of another solvent of dielectric property relative to toluene similar to those of DMSO, *e.g.* methanol, was studied in the present system completely different behaviour was observed. A marked decrease in rate was found in 4% methanol, and the rate continued decreasing to *ca.* 30% methanol after which it began to increase as expected for an increased solvent polarity effect. Methanol has a β value similar to that of DMSO but it is also a very strong h.b.d. (α 0.86) molecule, and in the presence of CHA there is no doubt that a solvent–solute hydrogen-bond interaction must occur. This interaction reduces the nucleophilicity of CHA, and also reduces, by competition, the concentration of the self-associated amine (dimer) which is a better nucleophile than monomeric amine, thus leading to a decrease in rate. A similar association, but now in a solute–solvent hydrogen-bond interaction, is responsible for the observed increase in rate in DMSO–toluene mixtures.

Conclusions.—The present results offer further support to the dimer mechanism previously proposed for ANS for aprotic non-polar solvents.[5-7] They also show the ability of DMSO to form complexes with amines which may be better nucleophiles than the monomeric amines. These complexes compete with the amine-dimer in the nucleophilic attack on the substrate, producing, in this way, catalysis of the first step. These effects are observable for DMSO contents $< 2\%$. The finding of amine catalysis in pure DMSO even with a primary amine is related to a considerable stabilization of the intermediate complex through solvation by DMSO and the known poor nucleofugacity of the methoxy group.

Experimental

Reagents and Solvents.—2,6-Dinitroanisole and cyclohexylamine (CHA) were purified as previously described.[6] *N*-(2,6-Dinitrophenyl)cyclohexylamine, m.p. 77.5—78 °C (methanol) (lit.,[41] 78.5 °C), was prepared by standard procedure. Toluene was kept over sodium strings for several days, refluxed, and then fractionated. DMSO was refluxed over calcium hydride, then distilled twice under reduced pressure, the first fraction (20%) being discarded.

Kinetic Procedures.—The reactions were followed spectrophotometrically. A Gilford 260 spectrophotometer with automatic cuvette positioner was used with 1.00 cm silica cells provided with ground-glass stoppers. The cuvette compartment was maintained at 35.0 ± 0.2 °C and the optical densities were recorded at the absorption maximum of the *N*-(2,6-dinitrophenyl)cyclohexylamine, λ 428 nm. Two different procedures were followed depending on the overall reaction rate: whenever possible the reactions were measured by both procedures and identical results were found. For the slower reactions a portion of a solution of 2,6-dinitroanisole in toluene was mixed with a measured volume of DMSO in a 10.0 ml volumetric flask, diluted with toluene, mixed with a portion of CHA in toluene, and the volume made up with toluene. All the solutions were at 35.0 °C, the reaction mixture was shaken, dropped into the cuvette, and the optical density registered. The first points were discarded until the temperature of the reaction mixture reached exactly 35.0 °C.

For rapid reactions portions of an amine solution in toluene was mixed with a measured volume of DMSO in a 10.0 ml volumetric flask and made up to volume with toluene. This solution (3 ml) was dropped into the cuvette and maintained at 35.0 °C. 20 μl of a solution of 2,6-dinitroanisole in toluene were added and the mixture vigorously shaken with a small glass helix. For the reactions in pure DMSO standard solutions of 2,6-dinitroanisole and of CHA in DMSO were used.

In all cases the absorption spectrum of the reaction mixture at infinite time corresponded within 2% to the 'mock' infinity prepared by using *N*-(2,6-dinitrophenyl)cyclohexylamine. The kinetics were determined under conditions of excess of nucleophile over substrate, and, in all cases, excellent pseudo-first-order plots were obtained. The second-order rate constants, k_A, were obtained by dividing the pseudo-first-order rate constants by the amine concentration. All experiments were run at least in duplicate and the rate constants are accurate to within ± 2%.

Acknowledgements

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