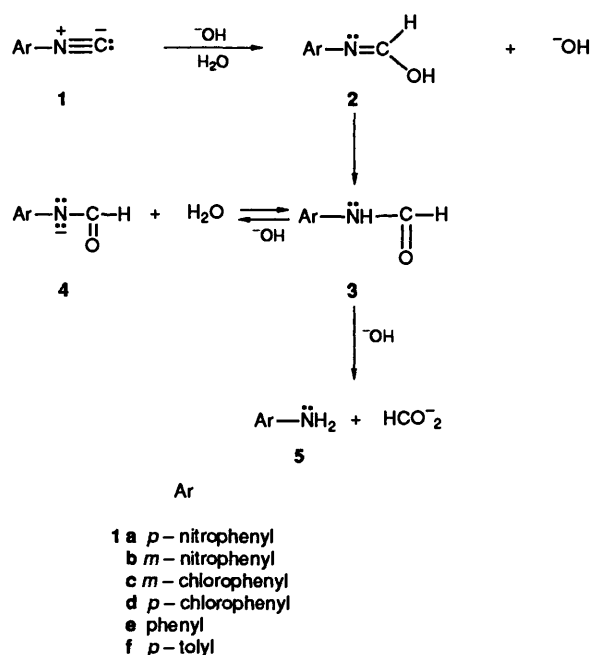


Chemistry of Isocyanides. Part 2.¹ Nucleophilic Addition of Hydroxide to Aromatic Isocyanides in Aqueous Dimethyl Sulphoxide. Correlations of Rate with a Nucleophilicity Function

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A range of aromatic isocyanides has been found to undergo nucleophilic addition of hydroxide in aqueous dimethyl sulphoxide (DMSO) over the composition range 0–98.67 mol% DMSO. The rate of reaction increases as the aqueous content of the solutions is decreased. At compositions low in DMSO correlations of $\log k_{\text{obs}}$ with $H_- + \log a_w$ are linear with slopes of 0.47–0.50, while at higher levels of DMSO correlations are also linear, but with slopes of 0.73–0.90. The results are discussed in terms of a solvent-induced switch from a concerted to a stepwise mechanism. An unusually enhanced reactivity of *m*-nitrophenyl isocyanide is observed and possible explanations for this are considered.

Recent studies^{1,2} have shown that isocyanides are susceptible to attack by nucleophiles. In particular, we have shown in an earlier paper¹ that aromatic isocyanides (1) in aqueous dioxane, are attacked by hydroxide, yielding the appropriate aniline 5 after hydrolysis of the *N*-aryl formamide 3, formed from 1, presumably *via* the imidic acid 2 (Scheme 1). In that work¹ a



Scheme 1

brief analysis of the effect of varying the aqueous content of the solvent showed that the rate of reaction was susceptible to such a solvent change, but no clear relationship with any solvent parameter was established. We therefore decided to study the reaction in aqueous dimethyl sulphoxide (DMSO) where rate-influencing factors which change with solvent aqueous content, such as hydroxide basicity³ and nucleophilicity,⁴ can be quantified in terms of an acidity function (H_-) and 'nucleophilicity function' (J_-), respectively. Following others⁴ we have used the function $H_- + \log a_w$, where a_w is the activity of water, as an approximation to J_- .

Experimental

Materials.—The isocyanides 1a–f and the formamides 3a–f were prepared as previously described.¹ The water used was de-ionised and distilled. DMSO was dried over calcium sulphate, fractionally distilled from calcium hydride and stored over molecular sieves; it was further distilled prior to use. Tetramethylammonium hydroxide (TMAH) was obtained as a 25% solution in water from BDH and was titrated using standard 0.1 mol dm⁻³ HCl prior to use.

Solutions.—Solutions of TMAH (0.011 mol dm⁻³) in aqueous DMSO were prepared in one of three ways. (a) A syringe was used to deliver into a pre-weighed 50 cm³ volumetric flask the volume of standardised '25%' aqueous TMAH required to yield a final solution 0.011 mol dm⁻³ in TMAH. After the flask had been weighed, sufficient water to give approximately the required mol% was added and the flask was weighed again. Finally, DMSO was added up to the mark and the flask was weighed again. The exact mole fraction of DMSO was then calculated from the known weights of DMSO and water, allowing for the water provided by the concentrated TMAH solution. (b) Solutions of mol% close to those solutions prepared by method (a) were obtained by adding a known weight of aqueous TMAH (0.011 mol dm⁻³) to a known weight of the solution prepared in (a) and recalculating the mol% of the solution. (c) Solutions of >98.5 mol% DMSO were obtained by using a syringe to deliver a quantity (typically 12 mm³) of '25%' aqueous TMAH into a weighed cuvette, reweighing, and then adding the volume of DMSO required to yield a solution 0.11 mol dm⁻³ in TMAH. Solvent compositions were estimated to be accurate to better than ±0.2% and reproducible to ca. ±0.2%.

Kinetics.—Reactions were initiated by injecting 2–6 mm³ of 0.02–0.15 mol dm⁻³ solutions of isocyanide in DMSO into 3 cm³ of the solvent in thermostatically controlled, stoppered, silica cuvettes. The rate in each case was measured, using a Pye Unicam SP1800 or Phillips 8700 spectrophotometer, by monitoring the UV absorbance change at a wavelength determined by a preliminary rescan; this wavelength usually corresponded to the λ_{max} of the conjugate base of the product formamide. The value of k_{obs} was determined from a least-squares plot of $\ln(A_{\text{inf}} - A)$ against time. The value of A_{inf} was determined after ca. ten half-lives, but for very slow reactions A_{inf} was calculated from the extinction coefficient for the product under identical conditions. Deviations from the mean

Table 1 Observed rate constants for the reaction of isocyanides **1a–f** in aqueous DMSO containing 0.011 mol dm⁻³ TMAH at 30 °C, and the nucleophilicity functions

mol% DMSO	$H_- + \log a_w$	$k_{\text{obs}}/10^{-4} \text{ s}^{-1}$	mol% DMSO	$H_- + \log a_w$	$k_{\text{obs}}/10^{-4} \text{ s}^{-1}$
<i>p</i> -Nitrophenyl isocyanide			<i>m</i> -Nitrophenyl isocyanide		
0.00	12.04	0.023	0.00	12.04	0.0070
10.55	13.13	0.069	9.88	13.04	0.0170
12.90	13.43	0.084	17.67	14.02	0.0664
17.30	13.98	0.161	28.00	15.04	0.176
22.50	14.56	0.248	38.12	15.90	0.498
26.61	15.01	0.393	45.42	16.49	1.11
31.52	15.34	0.694	55.68	17.42	3.16
37.49	15.84	1.37	60.06	17.78	6.47
46.20	16.64	2.88	65.02	18.19	13.1
50.52	16.95	4.13	70.28	18.63	34.1
57.12	17.48	7.20	73.74	18.90	57.8
59.72	17.69	9.23	79.01	19.32	157
64.96	18.13	16.4	84.60	19.78	320
70.94	18.64	30.3	92.20	20.67	2690
73.60	18.88	42.1			
78.76	19.30	77.0			
84.58	19.78	162			
92.20	20.67	774			
<i>m</i> -Chlorophenyl isocyanide			Phenyl isocyanide		
61.45	17.92	0.388	92.20	20.67	1.19
72.86	18.81	1.15	95.77	21.41	5.18
78.95	19.28	2.37	98.64	22.29	25.0
84.52	19.78	5.66			
92.20	20.67	22.1			
95.77	21.41	120			
98.64	22.29	630			
<i>p</i> -Chlorophenyl isocyanide			<i>p</i> -Tolyl isocyanide		
73.55	18.85	0.551	92.20	20.67	0.375
78.77	19.27	0.982	95.77	21.41	1.64
84.60	19.79	1.88	98.63	22.29	8.17
92.20	20.67	11.6			
95.77	21.41	44.4			
98.67	22.30	300			

over separate determinations of k_{obs} were within $\pm 12\%$ for slow reactions, where a calculated value of A_{inf} was used, and for reactions in solutions $>92 \text{ mol}\%$, but in general deviations were within $\pm 6\%$. A second-order rate constant k was obtained by dividing k_{obs} by the hydroxide ion concentration (0.011 mol dm⁻³). Activation parameters were calculated from plots of $\ln k$, measured at different fixed temperatures, against $1/T$, or from single runs in which the temperature was varied. In the case of a kinetic run where the temperature was varied a sigmoid plot of absorbance against time was obtained. Absorbance and temperature data at fixed time intervals were input directly from the spectrophotometer into a computer and a polynomial curve was fitted to the absorbance–time data. From the slope, at any time, of this curve, a value of k could be calculated and matched to the temperature corresponding to that time. A plot of $\log k$ determined in this way, against $1/T$, using 15–18 data points, yielded the activation parameters. Quoted errors are standard deviations.

Product Analysis.—Products were identified by comparison of the spectra obtained on completion with those of reference compounds. In some cases the contents of the cuvette were poured into *ca.* 20 cm³ of pH 7 buffer, extracted with chloroform, dried (Na₂SO₄), filtered, concentrated and analysed by TLC.

Results

The reactions of the isocyanides **1a–f** were studied under pseudo

first-order conditions at 30 °C in a range of water–DMSO mixtures containing 0.011 mol dm⁻³ TMAH. Isocyanides **1a** and **1b** were studied across the range 0–92.20 mol% DMSO, **1c** across the range 61.45–98.64 mol%, **1d** across the range 73.55–98.67 mol%, and **1e** and **1f** across the range 92.20–98.63 mol%. In almost all cases the only product found was the conjugate base **4** of the corresponding formamide **3**. For the *para*-nitro compound (**1a**), however, at composition $<38 \text{ mol}\%$ the product was found to be the aniline **5a**, formed by hydrolysis of the formamide **3a**. Hydrolysis of **3a** was generally faster than that of **1a** in this region so that k_{obs} for the overall reaction of **1a** to **5a** could be considered to relate only to the step **1a** to **3a**; where rates of isocyanide and formamide hydrolysis were comparable the reaction was monitored at the isosbestic point for conversion of **3a** to **5a** as in previous work.¹ No other products or isolable intermediates were detected by UV or TLC analysis.

The values of $H_- + \log a_w$ corresponding to the solvent compositions were interpolated graphically from those of Bowden *et al.*,^{4,5} which in turn were calculated using the measured values of H_- from Dolman and Stewart.⁶ Values of a_w were obtained from the equation $a_w = f_w x_w$ where x_w is the mole fraction of water and values of the activity coefficient f_w were interpolated graphically from those of Cox and McTigue.⁷

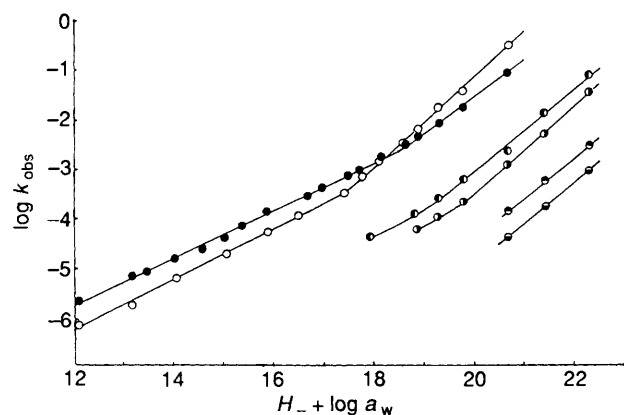
The values of $H_- + \log a_w$ and k_{obs} for reactions of the isocyanides in solutions of various mol% DMSO are shown for each isocyanide **1a–f** in Table 1. Plots of $\log k_{\text{obs}}$ against $H_- + \log a_w$ are shown for **1a–f** in Fig. 1. The plot for the *para*-nitro compound **1a** is linear with a slope of 0.47 up to $H_- +$

Table 2 Activation parameters for the reaction of isocyanides **1a**, **1b** and **1d** in aqueous DMSO solutions of 92.20 mol% DMSO containing 0.011 mol dm⁻³ TMAH, determined by the fixed temperature method, over the temperature range 27–38 °C

Compound	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	$k_{\text{obs}} \text{ range}/10^{-3} \text{ s}^{-1}$	Temperature range/°C	Number of points	r
1a	72 ± 1	+10 ± 4	57.2–140	27.20–36.43	8	0.999
1b	59 ± 2	-27 ± 6	192–373	27.06–35.21	11	0.994
1d	75 ± 4	-18 ± 14	1.02–2.51	27.95–36.77	10	0.987

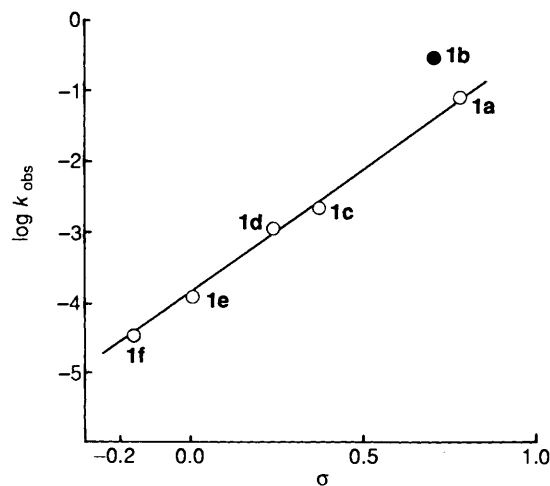
Table 3 Activation parameters for the reaction of isocyanide **1d** in aqueous DMSO solutions of 92.20 and 98.64 mol% DMSO containing 0.011 mol dm⁻³ TMAH, determined by the variable temperature method

mol% DMSO	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	Temperature range/°C	Number of runs
92.20	73 ± 1	-22 ± 3	27.17–34.56	3
98.64	43 ± 5	-97 ± 13	26.27–34.56	3

**Fig. 1** Plots of $\log k_{\text{obs}}$ for the reactions of isocyanides **1** in aqueous DMSO containing 0.011 mol dm⁻³ TMAH at 30 °C vs. $H_- + \log a_w$. **1a**, ●, **1b** ○, **1c** ◐, **1d** ◑, **1e** ◒ and **1f** ◓.

$\log a_w = ca. 18.15$, but then curves upward with a slope increasing to 0.73. The plot for the *meta*-nitro compound **1b** is linear with a slope of 0.50 up to $H_- + \log a_w 17.42$, but is linear again with a slope of 0.90 up to 20.67. Plots for compounds (**1c**–**1f**) cover the upper range of the nucleophilicity function ($H_- + \log a_w = 18$ –22.5) only and correlations are linear above 19.78 with slopes of 0.81 (**1c**), 0.87 (**1d**), 0.81 (**1e**) and 0.83 (**1f**). There appears, however, to be a slight upward curvature at the extreme lower end of the range for the *meta*-chloro (**1c**) and *para*-chloro (**1d**) compounds. All the slopes quoted have deviations of $< \pm 0.03$ and all correlation coefficients are > 0.998 .

The values of the activation parameters ΔH^\ddagger and ΔS^\ddagger are listed in Tables 2 and 3. In order to minimise the possible problems with temperature-induced changes in solvent properties, the activation parameters at 92.20 mol% DMSO were determined from 8–11 measurements of k_{obs} , each made at fixed temperature, over a relatively small temperature range, typically 27–37 °C. A series of trial experiments using the alkaline hydrolysis of substituted formanilides as a model reaction showed that values of activation parameters obtained in this way were at least as good as those obtained using fewer points, but a wider temperature range.⁸ Activation parameters, for the reaction of isocyanides **1a**, **1b** and **1d** at 92.20 mol% DMSO, obtained in this way are collected in Table 2. This method gave a very poor result for the reaction of **1d** in 98.64 mol% DMSO, since uncertainties in solvent composition ($\pm 0.2\%$) resulted in uncertainties in k_{obs} of the same order ($\pm 12\%$) as the variation in k_{obs} over 2–3 °C. Activation parameters at this composition were therefore determined from repeated single runs in which the temperature was varied over the range 26–35 °C during the run. Using this method, the uncertainties in solvent repro-

**Fig. 2** Plot of $\log k_{\text{obs}}$ for the reaction of isocyanides **1a** and **1c**–**f** in 92.20 mol% aqueous DMSO containing 0.011 mol dm⁻³ TMAH at 30 °C vs. σ . The filled circle (●) is the point for **1b**.

ducibility cause a scatter in the derived activation parameters obtained from different runs; this scatter is expressed as a standard deviation. By way of comparison, this variable temperature method was used to determine the activation parameters for **1d** at 92.20 mol% DMSO. Values obtained by the variable temperature method are collected in Table 3, and the values for **1d** at 92.20 mol% DMSO from the two methods agree within experimental error.

A Hammett plot (Fig. 2) has been constructed at composition 92.20 mol% DMSO ($H_- + \log a_w = 20.67$) where all compounds show a correlation of rate constant with $H_- + \log a_w$ of high (0.73–0.90) slope. Omitting the point for *m*-nitrophenyl isocyanide (**1b**), the plot shows a good correlation ($r = 0.998$) of $\log k_{\text{obs}}$ with σ and a ρ value of $+3.50 \pm 0.13$. Replacement of the point for **1a** by that for **1b**, or inclusion of both points, gives a much poorer fit. Standard values of σ were used.⁹

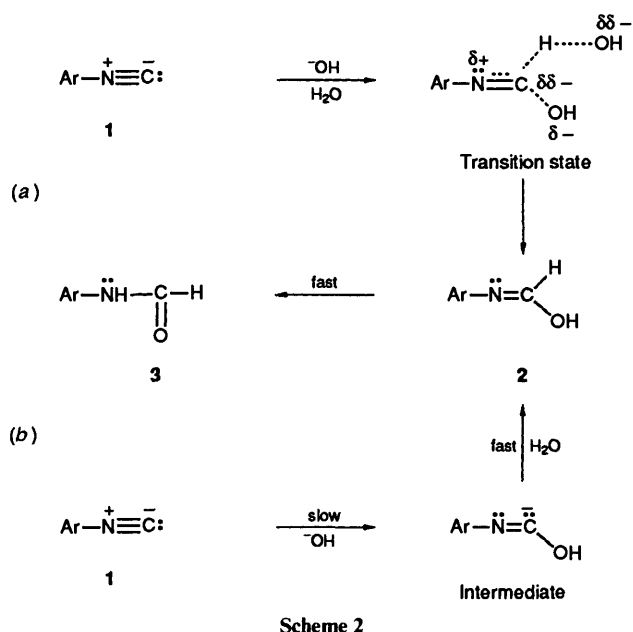
Discussion

In aqueous dioxane¹ the general reaction Scheme 1 was proposed and it appears that a similar scheme prevails in aqueous DMSO under all conditions tested in the current work, except that in most cases the conjugate base **4** of the amide **3** is formed, and that this conjugate base is relatively stable to further hydrolysis. Furthermore, it seems reasonable to assume that tautomerisation of the imidic acid **2** (or its conjugate base) to the amide **3** (or its conjugate base **4**) is very rapid and that the observed rate constant k_{obs} therefore relates to the reaction of the isocyanide **1** with hydroxide. At this point we note that there

is no evidence of a competing reaction leading to other products. Stirling has shown¹⁰ that the isocyano group can behave as a leaving group, and Bowden has shown^{4,5} that a good leaving group attached to an aromatic ring, particularly one containing nitro groups, can be displaced under the same conditions as in our experiments to yield phenoxides. No phenoxide formation was found in our work. Values of λ_{\max} for the phenoxide compounds might be expected to coincide with λ_{\max} values for the conjugate bases of the amides **4** and be hidden with respect to UV analysis, but phenols would have been easily detected by our TLC analysis.

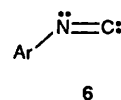
If the plots of $\log k_{\text{obs}}$ against $H_- + \log a_w$ are considered in two portions (the region where the slope is 0.47–0.50 and the region where the slope is 0.73–0.90), there is in each portion, for all compounds tested, a good linear correlation over 2–6 units of the scale. We interpret this as support for the proposal that $H_- + \log a_w$ is a suitable parameter for quantifying the nucleophilicity of hydroxide towards isocyanide in aqueous DMSO. The justification for seeking such relationships and for using the $H_- + \log a_w$ function has been examined in some detail by Bowden⁴ who has found extensive correlation between the rate of nucleophilic aromatic substitution by hydroxide and $H_- + \log a_w$. We like to consider such correlations as simple linear free energy relationships (LFERs), implying that a parameter which aptly describes the nucleophilicity of hydroxide in nucleophilic aromatic substitution, can also reflect the nucleophilicity of hydroxide in the reaction discussed here. As with other LFERs, the slopes, changes in slope and deviations can be interpreted in mechanistic terms.

In a reaction involving initial nucleophilic attack of hydroxide on the isocyanide carbon atom there appear to be only two reasonable mechanisms, and these are shown in Scheme 2. The first (a) involves concerted attack by hydroxide



and protonation by water, while the second (b) involves slow rate-limiting attack of hydroxide on the isocyanide carbon of the isocyanide to form an intermediate, followed by rapid protonation to give the imidic acid **2** (or its conjugate base). We believe that the 'high slope' region of the plots is the region in which the stepwise mechanism (b) is operative. Firstly we consider the magnitude of the slope (0.73–0.90). Other workers have interpreted the slopes of such correlations (usually against H_-) in terms of the 'advancement of transition states',¹¹ or in terms of how closely a transition state resembles the indicator

compounds used to set up the H_- scale,¹² or in terms of whether charge is localised or dispersed in the transition state.¹³ However, Johnson¹⁴ and Bowden^{4,5} have reviewed such interpretations and found little support for them. Bowden has suggested⁴ that the slope may depend to a large extent on the change in requirement for protic solvation on going from the initial to the transition state, while others¹⁵ relate the slope to the solvent structure-making ability of the transition state, implying that transition states in which negative charge is concentrated on a carbon atom cause less solvent structuring than those where the charge is concentrated on oxygen. Adopting this solvation based interpretation, we believe that the high slope reflects a loss of requirement for protic solvation as the charge on the hydroxide oxygen is lost on going to the transition state where, in effect, it is neutralised by the formal positive charge on the isocyano nitrogen. Therefore we believe that the high slope is consistent with a stepwise mechanism (b) rather than concerted. Secondly we consider the Hammett plot in this region. The high value of the Hammett ρ factor (+3.50) indicates a very high degree of positive charge destruction at the nitrogen adjacent to the aromatic ring. This shows that (i) the dipolar (**1**) rather than the carbene (**6**)

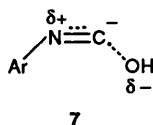


description of the isocyanide in such solutions is valid, and (ii) the transition state is advanced and intermediate-like. Thirdly we consider the activation parameters for *p*-chlorophenyl isocyanide (**1d**) (Tables 2 and 3). The value of ΔS^\ddagger changes quite substantially (by 75–79 J mol⁻¹ K⁻¹) on going from 98.67 to 92.20 mol% DMSO ($H_- + \log a_w = 22.30$ to 20.70). It is tempting to assume that the main solvation contribution to the entropy term is due to the loss in solvation of hydroxide on going to the transition state. However, in the absence of measured thermodynamic transfer entropies for hydroxide in aqueous DMSO such an assumption remains speculative. The change in ΔH^\ddagger is also large (+30–32 kJ mol⁻¹) over the same composition range. This change can be considered as a combination of the enthalpies of transfer of hydroxide, isocyanide and the transition state. The enthalpy of transfer of hydroxide can be estimated from published work^{16,17} to be no higher than 10 kJ mol⁻¹, suggesting that there is a significant contribution from the enthalpies of transfer of isocyanide and/or the transition state.

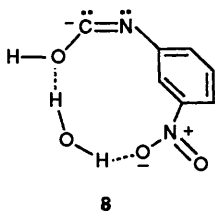
We propose that the low (0.47–0.50) slope of the correlation in the more aqueous region is consistent with a concerted mechanism (a). In this mechanism we envisage the charge on the hydroxide being dispersed rather than destroyed in the transition state, and indeed the concerted protonation by water would result in the formation of a 'new' hydroxide with the net result being that charge is still found on the oxygen atoms. Other workers¹⁵ have interpreted the very low slopes found for correlations of rates of detritiation of ketones with the H_- function in terms of charge being located on the oxygen atom of the enolate in the transition state rather than being exclusively localised on the carbon atom. Applying this interpretation to our results we propose, therefore, that the transition state for mechanism (a) would have an appreciable effect on solvent structuring (*vide supra*), leading to a lower correlation slope than for mechanism (b). The fact that the correlation extends to aqueous solution (0 mol% DMSO) suggests a continuity of mechanism between the reaction in low mol% DMSO and that in the essentially aqueous conditions studied in the earlier work,¹ in which the evidence supported a concerted mechanism.

A most unusual aspect of this study is the anomalous

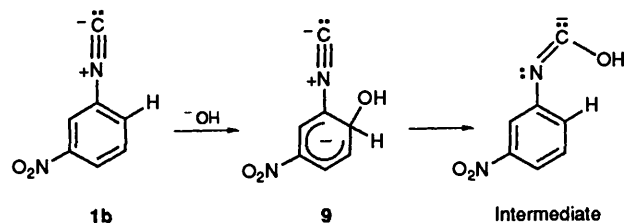
behaviour of the nitro compounds at high mol% DMSO. The Hammett plot (at 92.20 mol% DMSO and $H_{-} + \log a_w = 20.67$) (Fig. 2) shows that this anomaly is due to an enhanced reactivity of the *meta*-nitro isocyanide (**1b**) rather than a reduced reactivity of the *para*-nitro isocyanide (**1a**), and that the remaining compounds follow the expected pattern of reactivity. We have considered several possible explanations for this unusual reactivity. Firstly, it is well known that the electron-withdrawing ability of the nitro group can change as solvent is altered from protic to aprotic.¹⁸ However, we are aware of no evidence in the literature of an effect as pronounced as in this work. Secondly, we have considered the possibility of a mechanism involving rate-limiting initial transfer of an electron from hydroxide to isocyanide prior to formation of the intermediate in Scheme 2. Such an electron transfer would be likely to occur with some loss in solvation, particularly of the hydroxide, and the negative value of ΔS^\ddagger for the reaction of **1b** (particularly relative to the positive value found for **1a**) seems inconsistent with this. Thirdly, it is possible that the less symmetrical *meta*-nitro isocyanide causes less solvent disruption than does the *para*-nitro isocyanide on going to the non-linear transition state, reflected in a more negative entropy term, but a lower solvent reorganisation contribution to the enthalpy term. However, the enhancement seems rather large to be explained in this way, and no similar enhancement is observed for the *meta*-chloro compound (**1c**). Fourthly, we note that Hegarty¹⁹ has, on the basis of *ab initio* calculations, proposed that the transition state for stepwise nucleophilic addition preferentially adopts a structure **7** in which the incoming nucleophile is *cis* to



the nitrogen substituent. We suggest that the '*cis*' bending of the *meta*-nitro compound (**1b**) is favoured by a 'solvent (water) bridge' between the nitro group and the incoming hydroxide (**8**);



again however, we feel that this may be too small an effect to explain the observed difference in reactivity. Finally, there is the possibility of nucleophilic attack at the 6-position of the ring followed by intramolecular attack on the isocyanide carbon (Scheme 3). Bowden²⁰ has suggested that such an attack can occur at a hydrogen-bearing ring carbon when nitro groups are present *ortho* and *para*, and although **1b** has an isocyanide group rather than a nitro group, such an attack does not seem



Scheme 3

unreasonable. However, since we see no evidence for build-up of a coloured intermediate²⁰ such as **9**, we believe that the second step would have to be fast. Given the fact that the linear isocyanide group points away from the hydroxy group, and the fact that the aryl ring would now be relatively electron-rich, we are not certain that the proposed second step would be fast.

Acknowledgements

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