Kinetic Study of the Nitrosation Reaction of 1,3-Dimethylurea in Dioxane–Water Mixtures

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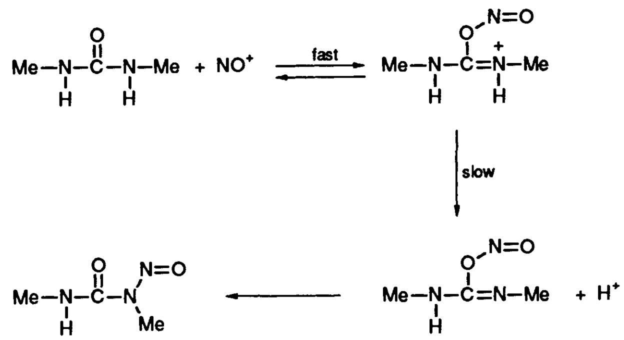
The nitrosation of dimethylurea has been studied in dioxane–water mixtures showing that the kinetic characteristics of the reaction depend on the proportion of dioxane in the medium. Adding dioxane to pure water causes the reaction rate to decrease, and pass through a minimum as a certain concentration of dioxane is reached. The further addition of dioxane increases the reaction rate steadily. At low concentrations of dioxane the system shows the behaviour seen in water, *i.e.* catalysis by bases and not by nucleophiles, suggesting proton transfer as the slow step. At very high proportions of dioxane, halides and thiocyanate catalyse the process, which is interpreted in terms of the formation of the corresponding nitrosyl halides which may act as efficient nitrosating agents towards the urea. The observed order of efficiency of the catalysts is the opposite to that seen in nitrosation or diazotization processes in water.

The nitrosation of 1,3-dimethylurea (DMU) in water has been studied in detail.[1] As for other amides and ureas,[1–4] this reaction is significantly different to that undergone by the secondary amines in three ways: (*i*) the nitrosation is not catalysed by nucleophiles (Cl^-, Br^-, SCN^-, thiourea) which form new nitrosating agents of general formula XNO that increase the rate of formation of the nitrosamines; (*ii*) the reaction is catalysed by bases, however; (*iii*) a primary kinetic solvent isotope effect is involved. These three characteristics suggest that the slow step of the nitrosation of DMU is proton transfer, rather than direct electrophilic attack on the substrate. Detailed studies of the Bronsted relation describing the catalyst bases for the reaction and of the inverse (denitrosation) reaction of *N*-nitroso-*N*,*N'*-dimethylurea (NDMU) have led to the proposal of a reaction mechanism (Scheme 1) where the nitrosating agent initially attacks the most nucleophilic centre of the molecule, the oxygen atom, and the proton transfer occurs later. This mechanism has been confirmed in other studies with phenylureas.[5]



Scheme 1.

Such a mechanism does not reveal the nature of the nitrosating agent and it cannot be known if only NO^+ will nitrosate amides, or if the nitrosyl halides or nitrosyl thiocyanate, which are less electrophilic species for amines,[6] are capable of this too. The kinetic elucidation of this point would only be possible if a change in the rate limiting step could be achieved. Recently, Crookes and Williams[7,8] reported a change in the rate-limiting step of the nitrosation of some substrates when acetonitrile was used instead of water as the solvent. We considered a kinetic study on the nitrosation of DMU in a reaction medium different from pure water to be relevant. We describe the results of experiments using dioxane–water mixtures as the solvent in the nitrosation of DMU.

Experimental

All reagents (Merck) were used without further purification. A Kontron-Unikon 820 spectrophotometer connected to a computer with thermostatted reaction cells was used to follow the increase in absorbance (at 270 nm), corresponding to formation of the product NDMU. All the experiments were carried out at 25 °C. Stopped-flow apparatus (Applied Photophysics) was used for the most rapid processes ($t_{\frac{1}{2}} < 20$ s). All kinetic experiments were performed with the stoicheiometric nitrite (nit) in large deficiency with respect to the other reagents. Reactions were always first order with respect to stoicheiometric nitrite and the observed pseudo first order rate constants k_0 were obtained from the corresponding integrated equation. Values of k_0 were reproducible to within $\pm 5\%$. The composition of the reaction mixtures is expressed as a percentage on a weight basis.

Results and Discussion

The Influence of Reaction Mixture Composition on the Rate of Nitrosation of DMU.—The rate at which DMU is nitrosated was studied for dioxane–water mixtures containing up to 95% dioxane. Other concentrations were fixed as follows: $[DMU] = 4.97 \times 10^{-3}$ mol dm^{-3}, $[nit] = 1.4 \times 10^{-4}$ mol dm^{-3}. In one set of experiments the medium was acidified by adding 4.28×10^{-3} mol dm^{-3} $HClO_4$, and in another the same concentration of HCl was added. The results are shown in Fig. 1. The reaction rate went down as more dioxane was present in the mixture, *e.g.* it was reduced by a factor of 19 on going from pure water to 64.5% dioxane. Above about 75% dioxane the reaction rate constant increased so that the whole curve describes a minimum. Two regions of behaviour were also seen when considering the influence upon the reactivity of the nature of the acid used ($HClO_4$ or HCl). In the first region (<75% dioxane) the

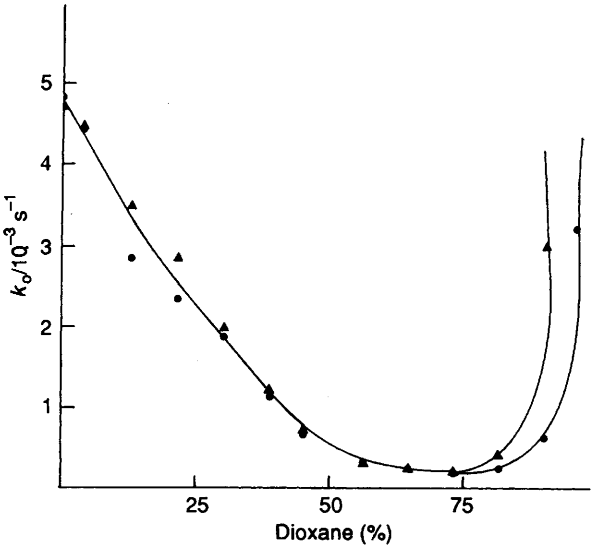


Fig. 1. Influence of the percentage of dioxane present in the medium upon the pseudo first order rate constant of nitrosation of DMU. $[DMU] = 4.97 \times 10^{-3}$ mol dm^{-3}, $[nit]_0 = 1.4 \times 10^{-4}$ mol dm^{-3}. (●) $[HClO_4] = 4.28 \times 10^{-3}$ mol dm^{-3}; (▲) $[HCl] = 4.28 \times 10^{-3}$ mol dm^{-3}.

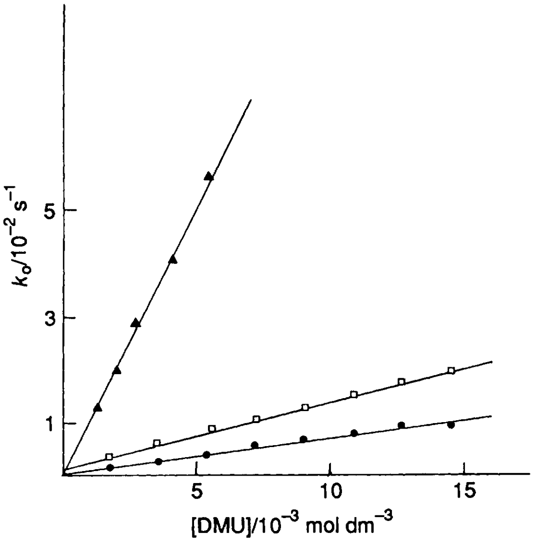


Fig. 2. Influence of the concentration of DMU upon the pseudo firs. order rate constant of its nitrosation in 31.8% dioxane. $[nit]_0 = 1.71 \times 10^{-4}$ mol dm^{-3}. (●) $[HClO_4] = 9.25 \times 10^{-3}$ mol dm^{-3}; (□) $[HClO_4] = 1.85 \times 10^{-2}$ mol dm^{-3}; (▲) $[HClO_4] = 0.11$ mol dm^{-3}.

reaction rate was the same for both acids, while the reaction was much faster with hydrochloric acid for higher percentages of dioxane (at 95% dioxane, the rate is 10 times higher, for example). We decided to analyse the nitrosation process in each region, using 30 and 90% dioxane in the mixture to represent the first and second regions respectively.

A Study of DMU Nitrosation with 30% *Dioxane.*—Initially, the influence of the concentration of DMU upon k_o was studied at three different acidities (Fig. 2). The acid here, and referred to in all general acidity studies, was perchloric acid. The reaction is first order in DMU. The change of k_o with acidity showed that the reaction was also first order in acid, so that the rate is given by eqn. (1), with $\alpha = 80.5$ dm^6 mol^{-2} s^{-1}. This value is notably lower than the value of 280 dm^6 mol^{-2} s^{-1} obtained for pure water.[1]

$$r = \alpha[HNO_2][DMU][H^+] \qquad (1)$$

Table 1. Influence of monochloroacetate buffers upon k_o in the nitrosation of DMU.[a]

[Buffer]/mol dm^{-3}	$k_o/10^{-4}$ s^{-1}
Buffer ratio = 1.48	
0.084	1.92
0.169	2.85
0.253	3.62
0.337	4.33
0.421	5.10
0.506	5.72
0.590	6.58
0.716	7.34
Buffer ratio = 0.46	
0.058	4.22
0.116	5.57
0.174	7.20
0.232	8.53
0.290	10.14
0.348	10.70
0.406	12.25
0.493	13.38

[a] $[DMU] = 4.97 \times 10^{-3}$ mol dm^{-3}, $[nit]_0 = 1.4 \times 10^{-4}$ mol dm^{-3}, 30.2% dioxane, buffer ratio = [monochloroacetate ion]/[monochloroacetic acid]

There was no halide catalysis in this region; substituting HCl for $HClO_4$ did not change the reaction rate. This behaviour is similar to that seen in water so we decided to check whether the system was subject to general base catalysis. Buffer solutions of monochloroacetic acid/monochloroacetate ion were added in different acid/base ratios and buffer concentrations. The other reagent concentrations were $[DMU] = 4.97 \times 10^{-3}$ mol dm^{-3} and $[nit] = 1.4 \times 10^{-4}$ mol dm^{-3}. Analysis of the results (Table 1) indicated that the percentage of catalysis brought about by the buffer increased upon increasing the base proportion in the buffer, suggesting general base catalysis, according to the general equation found in the case of other amides in water.[2,4]

The actual working acidity in these experiments could be estimated from the magnitudes of the intercepts at the origin, obtained from plotting the data in Table 1, by comparing them with values obtained in the absence of buffer. In this way it is possible to estimate the acidities at the different working conditions and these values together with the values of the ratio [monochloroacetate ion]/[monochloroacetic acid] allow the calculation of the pK_a of the acid at 30% dioxane. A pK_a value of about 3.4 was obtained, which is *ca.* 0.7 units higher than the pK_a in water. It is not surprising that the strength of the acid should decrease in a dioxane–water medium since the ions generated in the dissociation are less stabilized when the proportion of water in the medium is reduced.

A Study of DMU Nitrosation in Media containing 90% *Dioxane.*—At higher dioxane concentrations, the influence of DMU concentration on the reaction at different acidities was studied. Several sets of results are shown in Fig. 3. A linear relation between k_o and [DMU] was revealed, eqn. (2). A process obeying eqn. (2) suggests reversibility of the reaction, *i.e.* eqn. (3). The intercept at the origin [*a* in eqn. (2)] corresponds to the denitrosation reaction, while the slope [*b* in eqn. (2)]

$$k_o = a + b[DMU] \qquad (2)$$

$$HNO_2 + DMU \underset{}{\overset{K}{\rightleftharpoons}} NDMU \qquad (3)$$

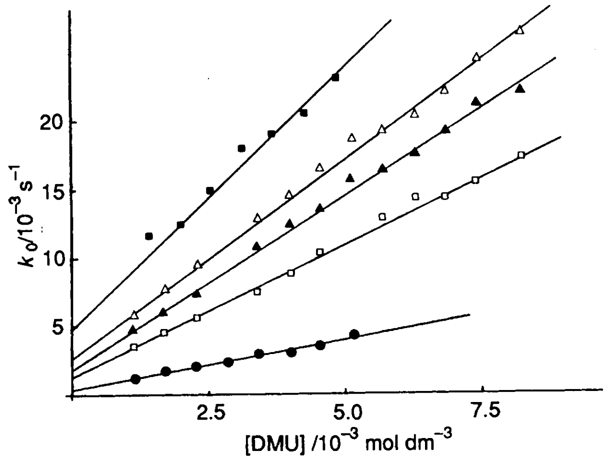


Fig. 3. Influence of the concentration of DMU upon the pseudo first order rate constant of its nitrosation in 90.1% dioxane. [$HClO_4$]: (■) 0.27 mol dm^{-3}; (△) 0.22 mol dm^{-3}; (▲) 0.18 mol dm^{-3}; (□) 0.14 mol dm^{-3}; (●) 0.034 mol dm^{-3}.

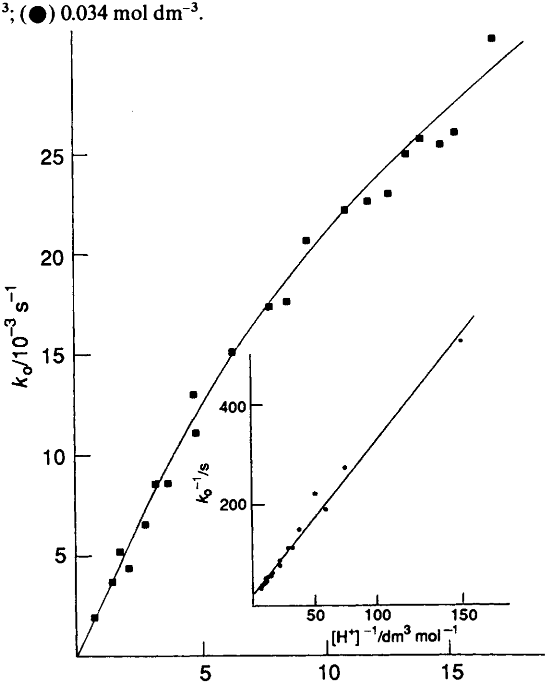


Fig. 4. Influence of the acidity upon the pseudo first order rate constant of nitrosation of DMU in 90% dioxane. [DMU] = 1.29 × 10^{-2} mol dm^{-3}, [nit]$_0$ = 1.46 × 10^{-4} mol dm^{-3}. Insert: linearization of the experimental data according to eqn. (4).

corresponds to nitrosation. It can be seen that both *a* and *b* are dependent on the acidity (forward and reverse reactions are acid-catalysed). The quotient *b*/*a* will give the value of the equilibrium constant *K*, defined as [NDMU]/[DMU][HNO_2]. The calculated value is uncertain as the values of the intercepts at the origin are difficult to determine accurately. A value of about $K = 1500$ dm^3 mol^{-1} seems likely. The reversibility of the process is unexpected and is not observed in water, which means that the equilibrium constant for the process in eqn. (3) decreases significantly when going from pure water to media containing 90% dioxane. The fact that the equilibrium constant for the nitrosation process is much lower in less polar solvents than in pure water is in agreement with the observations of Johal *et al.*[9] when studying the denitrosation of certain nitrosamines in ethanol.

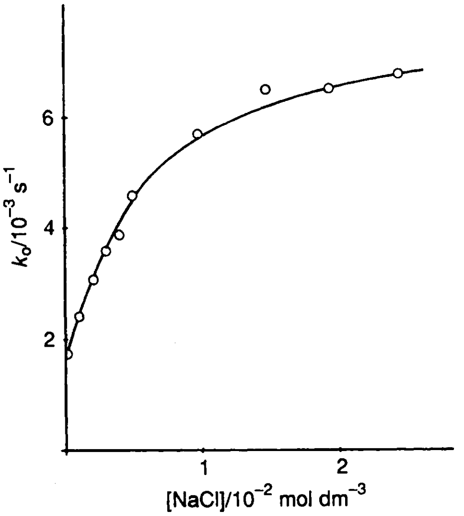


Fig. 5. Influence of chloride concentration upon the pseudo first order rate constant of nitrosation of DMU. [DMU] = 1.29 × 10^{-2} mol dm^{-3}, [nit]$_0$ = 1.46 × 10^{-4} mol dm^{-3}, [$HClO_4$] = 6.7 × 10^{-3} mol dm^{-3}, 90% dioxane. The solid line is the theoretical line resulting from the fitting of the experimental data to eqns. (6)–(10).

The effect of the acidity on the reaction was also studied in detail. Different amounts of perchloric acid were added to the medium and the change in the reaction rate observed. The results (Fig. 4) show that the plot of k_o *vs.* [$HClO_4$] passes through the origin and that the dependence deviates from linearity at high acidities. The DMU concentration used (1.29 × 10^{-2} mol dm^{-3}) was such that the reaction was practically irreversible and therefore the data only correspond to nitrosation and not the reverse reaction. This tendency can be explained in a way similar to that invoked by Crookes and Williams in a study of the *S*-nitrosation of thiourea in alcoholic solvents.[10] They assumed that protonation of thiourea could become significant at the higher acidities used. If an allowance is made in our case for DMU protonation, the effective nitrosatable DMU concentration will be lowered as the acidity is increased and the expression for k_o will be given by eqn. (4),

$$k_o = \frac{kK_a[HClO_4][DMU]_{total}}{K_a + [HClO_4]} \qquad (4)$$

which is only valid when [$HClO_4$] $\gg$ [protonated DMU], where *k* stands for the rate constant with free DMU and K_a is the acidity constant for protonated DMU. This hypothesis can be easily checked since eqn. (4) predicts that k_o^{-1} should be a linear function of [$HClO_4$]$^{-1}$. This double reciprocal plot is also shown in Fig. 4, yielding a good straight line from which values for K_a (0.3 mol dm^{-3}) and *k* (21 mol^{-2} dm^6 s^{-1}) can be obtained.

The reaction seemed to be catalysed when perchloric acid was replaced by hydrochloric acid (Fig. 1). A simple interpretation of this is to assume that hydrochloric acid forms a nitrosating agent with HNO_2, eqn. (5), that has an efficient and detectable kinetic activity. The process was analysed in detail by looking at the kinetic effects on the reaction rate of adding NaCl to a mixture containing [DMU] = 1.29 × 10^{-2} mol dm^{-3}, [$HClO_4$] = 6.7 × 10^{-3} mol dm^{-3} and [nit] = 1.46 × 10^{-4} mol dm^{-3} over the [NaCl] range 0–0.0243 mol dm^{-3} (Fig. 5). There is clearly a catalytic effect. The graph is non-linear with increasing chloride ion concentration showing a levelling-off effect at high [NaCl]. A similar study was performed adding bromide ions to the medium, with [NaBr] from 0 to 0.086 mol dm^{-3}, and the

$$HCl + HNO_2 \rightleftharpoons NOCl + H_2O \qquad (5)$$

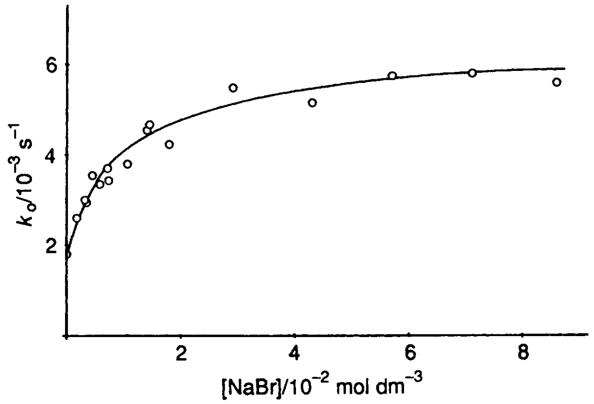


Fig. 6. Influence of the bromide concentration upon the pseudo first order rate constant of nitrosation of DMU. $[DMU] = 1.29 \times 10^{-2}$ mol dm^{-3}, $[nit]_0 = 1.46 \times 10^{-4}$ mol dm^{-3}, $[HClO_4] = 6.7 \times 10^{-3}$ mol dm^{-3}. The solid line is the theoretical line resulting from the fitting of the experimental data to eqns. (6)–(10).

Table 2. Influence of the concentration of NaSCN upon the pseudo first order rate constant for the nitrosation of DMU.[a]

$[SCN^-]/10^{-2}$ mol dm^{-3}	$k_o/10^{-3}$ s^{-1}
0	1.86
4.11	1.63
5.39	1.74
6.86	1.69
10.8	1.85
16.2	2.14
21.5	2.28
26.9	2.69
32.3	3.06

[a] $[DMU] = 1.29 \times 10^{-2}$ mol dm^{-3}, $[HClO_4] = 6.7 \times 10^{-3}$ mol dm^{-3}, $[nit]_0 = 1.46 \times 10^{-4}$ mol dm^{-3}, 90% dioxane.

same type of non-linear catalysis was seen (Fig. 6). A surprising feature is the greater catalytic capacity of NaCl with respect to NaBr, seen by the larger slope at the origin of the corresponding plots. This behaviour goes against the order of catalytic efficiency observed in water[6] for all types of nitrosation reactions.

In a similar experiment, using sodium thiocyanate, it was necessary to increase the concentration of NaSCN considerably to observe catalysis, which caused solubility problems. The [NaSCN] range 0–0.32 mol dm^{-3} was finally used, leading to the results shown in Table 2. In experiments with [NaSCN] < 0.1 mol dm^{-3} no catalysis was observed; at higher concentrations a slight increase in the reaction rate (*ca.* 60% at 0.32 mol dm^{-3}) is observed. This increase could even be attributed to a salt effect or a medium effect due to a slight reduction in the water content of the medium. Sodium thiocyanate is therefore a much less efficient nitrosation catalyst than the two halides considered, which indicates that the order of catalytic efficiency in mixtures containing 90% dioxane is the reverse of that seen in water.

This catalysis suggests that the reaction mechanism of the system may change with the percentage of dioxane. The efficient catalysis promoted by NaCl and NaBr suggests that the nitrosating species formed by them can be efficient nitrosating agents for amides and ureas (one of the aims of the study). It is now necessary to explain why the plots of k_o *vs.* [halide] are non-linear, tending towards a limiting value in the cases of NaCl and NaBr. Usually, in water, nitrosation by NOX is kinetically detected by the appearance of a term which is first order in X^- and curvatures are usually interpreted in terms of changes in the rate-limiting step when changing $[X^-]$.[6] However, our system (with a relative permittivity close to 6) presents a very different situation from that of pure water. In our reaction medium conventionally strong acids and electrolytes are only partially dissociated. As an example, NaCl in 70% dioxane–30% water has a very low dissociation constant (5×10^{-3}) and therefore will exist appreciably in the form of ion pairs; this value is quite close to the value measured for HCl.[11] The dissociation constant of HCl is reduced to 2×10^{-4} when the percentage of dioxane increases up to 82%[12] and 1.38×10^{-5} at 90% dioxane.[13] These data illustrate that the amount of free ions in the medium will be very low and that the formation of nitrosating agents should be expressed in terms of the stoicheiometrically predominant molecular species. Formation of the nitrosating agents NOX can therefore be explained in terms of the undissociated species as shown in eqns. (6) and (7). The proposed reaction mechanism is given by eqns. (6)–(10).

$$NaX + HClO_4 \xrightleftharpoons{K_1} HX + NaClO_4 \qquad (6)$$

$$HX + HNO_2 \xrightleftharpoons{K_2} NOX + H_2O \qquad (7)$$

$$HClO_4 + HNO_2 \xrightleftharpoons{K_3} ClO_4^-{\cdot}NO^+ + H_2O \qquad (8)$$

$$ClO_4^-{\cdot}NO^+ + DMU \xrightarrow{k_4} \text{Products} \qquad (9)$$

$$NOX + DMU \xrightarrow{k_5} \text{Products} \qquad (10)$$

Eqn. (9) represents the uncatalysed reaction in which NO^+ is arbitrarily associated in an ion-pair, since ion-pairing is extensive in this medium. Eqn. (10) represents the catalytic pathway due to the new nitrosating agent. The rate equation derived from eqns. (6)–(10) is given by eqn. (11).

$$k_o = k_4K_3[HClO_4][DMU] + k_5K_2[HX][DMU] \qquad (11)$$

The concentration of HCl available for reaction with HNO_2 to yield the nitrosating agent NOCl is determined by the initial concentrations of both NaCl and $HClO_4$ and by the value of K_1. This is the reason for the curvature in the k_o–[NaCl] plot. The amount of HCl in the medium is no longer a linear function of the initial concentration of NaCl, but will be determined by the equilibrium constant K_1. In the experiments shown in Figs. 5 and 6 the maximum concentration of HX in the medium is limited by the initial concentration of $HClO_4$ (6.7×10^{-3} mol dm^{-3} in both cases), so that the limiting value of k_o corresponds to the reaction of DMU in the presence of this concentration of HX, therefore allowing an estimate of the product k_2K_5.

An alternative way to test our ideas would come from an investigation of the influence that $HClO_4$ exerts upon k_o in the presence of chloride or bromide. $HClO_4$ would facilitate the new catalytic pathway only to the extent that it will help to produce HX, that is, through equilibrium (6). Therefore the same pattern of behaviour will hold for both $HClO_4$ and NaX and non-linear plots of k_o *vs.* $[HClO_4]$ will be expected.

Fig. 7 shows the results of some experiments performed in the presence of a constant amount of NaBr, varying the concentration of $HClO_4$. The plot shows a marked non-linearity. Curvature occurs at much lower acidity and is much more pronounced than for the reaction in the absence of halides, so

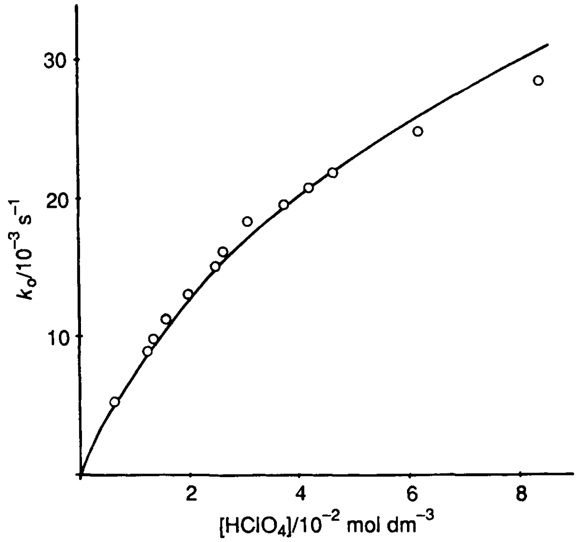


Fig. 7. Influence of the perchloric acid concentration upon the pseudo first order rate constant of nitrosation of DMU in the presence of sodium bromide in 90% dioxane. [DMU] = 1.29×10^{-2} mol dm^{-3}, [NaBr] = 4.3×10^{-2} mol dm^{-3}, $[nit]_0 = 1.46 \times 10^{-4}$ mol dm^{-3}. The solid line is the theoretical line resulting from the fitting of the experimental data to eqns. (6)–(10).

Table 3. The influence of the concentration of DMU upon the pseudo first order rate constant for its nitrosation in the presence of chloride.[a]

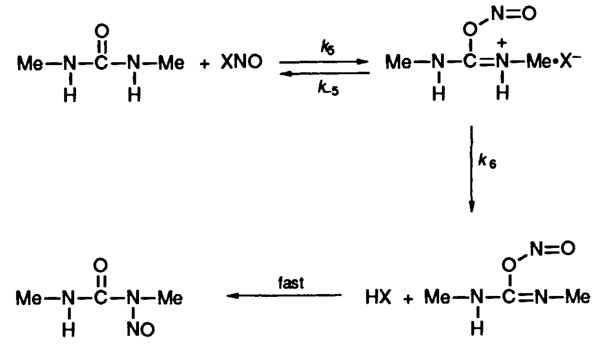
[DMU]/10^{-2} mol dm^{-3}	$k_o/10^{-2}\,s^{-1}$
0.33	0.53
0.66	1.10
0.99	1.93
1.32	2.48
1.65	2.88
1.98	3.69
2.31	3.90
2.80	4.70

[a] [NaCl] = 2.7×10^{-2} mol dm^{-3}, $[nit]_0 = 2.07 \times 10^{-4}$ mol dm^{-3}, $[HClO_4] = 6.13 \times 10^{-2}$ mol dm^{-3}, 89.7% dioxane.

that the source of curvature cannot be due to protonation of DMU but formation of HBr through equilibrium (6). Similar behaviour was also observed when different concentrations of perchloric acid were added to reaction mixtures with constant [NaCl]. Further confirmation of the mechanism outlined in eqns. (6)–(10) comes from the fact that the reaction remains first order in DMU even at the highest working concentrations of NaCl and $HClO_4$ (see Table 3).

All experimental results fit the mechanism proposed in eqns. (6)–(10) well and it is therefore possible to obtain experimental values for K_1 and for the product K_2k_5. There is, however, a problem in this estimation, since both magnitudes are correlated and several sets of values for K_1 and K_2k_5 fit the experimental data reasonably well. We therefore estimated K_2k_5 from the limiting value of k_o obtained in Figs. 5 and 6. Once this value is known it is easy to estimate the value of K_1 that would produce a better fit to the experimental data. The solid lines in Figs. 5, 6 and 7 are theoretical lines constructed assuming values of $K_1 = 0.38$ and $K_2k_5 = 77.5$ dm^6 mol^{-2} s^{-1} in the case of sodium bromide and values of $K_1 = 1.06$ and $K_2k_5 = 93$ dm^6 mol^{-2} s^{-1} in the case of sodium chloride. Allowance for DMU protonation has been made where necessary, eqn. (4). The fact that the values obtained for K_1 are close to unity in each case is satisfactory. We have already mentioned that NaCl and HCl show similar dissociation constants in media rich in dioxane; in addition, HCl and $HClO_4$ seem to show a similar acid strength at 90% dioxane.[14] Both facts support a value for K_1 close to unity.

We would like to stress that it is kinetically impossible to distinguish whether the rate determining step in the process is the reaction between DMU and the nitrosating agent—as we have assumed for simplicity—or a further proton transfer reaction within the ion-pair thus formed (*i.e.* steps of rate constant k_5 or k_6 in Scheme 2).



Scheme 2.

Finally, the surprising fact that the catalytic ability of the halides and of thiocyanate is the reverse of that found for the nitrosation of several substrates in water is difficult to rationalize since several constants will influence the final reactivity. The following catalytic efficiencies have been reported for aniline in water,[15,16,17] chloride:bromide:thiocyanate = 1:56:2130, which are associated with the nucleophilicity order of the anions. If nucleophilicity is still the driving force for catalysis under our conditions, the change in the efficiency detected is probably explained by the inversion of the nucleophilicity order when the solvent composition changes. It is known that the order $I^- > Br > Cl^-$ is only applicable when the nucleophile is deactivated by solvation (in water), whereas the 'natural' order of nucleophilicity $Cl^- > Br^- > I^-$ is observed in solvents such as acetonitrile, acetone, *etc.*[18] †

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† We have throughout considered that the amount of the different nitrosating agents formed during the reaction is negligible *vs.* the total concentration of HNO_2, as in water. This is probably the case, since the characteristic spectrum of HNO_2 (between 270 and 400 nm) is unaffected by the presence of significant amounts of sodium chloride in media with 90% dioxane.

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