Solvent-induced changes in nitrosation mechanisms. Part 3.[1,2] The effects of tetrahydrofuran–water and dimethyl sulfoxide–water mixtures on the nitrosation of ureas

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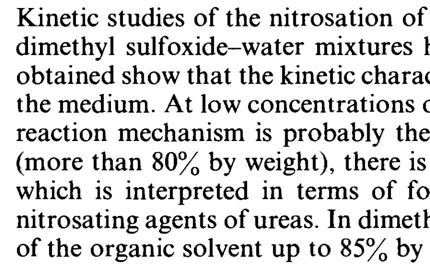
Kinetic studies of the nitrosation of 1,3-dimethylurea and 2-imidazolidone† in tetrahydrofuran–water and dimethyl sulfoxide–water mixtures have been carried out. In tetrahydrofuran–water mixtures, the results obtained show that the kinetic characteristics of the reaction depend on the proportion of tetrahydrofuran in the medium. At low concentrations of organic solvent, the reaction is not catalysed by chloride ions and the reaction mechanism is probably the same as in pure water. At very high proportions of tetrahydrofuran (more than 80% by weight), there is a change in the reaction mechanism. Halide ions catalyse the process, which is interpreted in terms of formation of the corresponding nitrosyl halides which act as efficient nitrosating agents of ureas. In dimethyl sulfoxide–water mixtures the results obtained show that the addition of the organic solvent up to 85% by weight of dimethyl sulfoxide inhibits the reaction rate, which increases slightly upon further increasing the proportion of dimethyl sulfoxide. However, unlike other organic solvents, in dimethyl sulfoxide–water mixtures we did not observe catalysis by halide ions. The reaction mechanism seems to be the same as in pure water, with the proton transfer from the protonated nitroso compound to the medium being the rate limiting step.

The mechanism of the nitrosation of amides and ureas in water is now well established.[3–6] Three aspects characterizing the kinetics of these reactions (general basic catalysis, primary solvent isotope effect and the absence of catalysis by nucleophiles such as Cl^-, Br^- or SCN^-) together show that their rate-controlling step is the transfer of a proton to the medium. It is now known that the complete mechanism is in fact as shown in Scheme 1: attack by the nitrosating agent on the carbonyl oxygen atom, which is probably the most nucleophilic site,[7] is followed by the slow proton transfer step and then by an internal rearrangement in which the NO group is transferred from the oxygen to a nitrogen atom to afford the thermodynamically stable *N*-nitroso compound. This mechanism follows from application of the theories of Marcus and Eigen to results obtained in our laboratory for a variety of different amides and bases,[3] and has been confirmed[2] by kinetic experiments carried out in acetonitrile–water at high H^+ or X^- concentration; under these conditions the slow step is the internal transfer of the NO group from the oxygen to the nitrogen atom, which proves conclusively that the nitrosation of amides and ureas, like their alkylation[8] and protonation,[9] occurs *via* an initial attack on the oxygen atom.



Scheme 1

Kinetic experiments in mixtures of water and an organic solvent have also settled the question of whether amides and ureas are directly nitrosated by XNO species. The question arises because XNO species are only weakly electrophilic,[10] and amides are deactivated towards electrophilic attack, largely because of the electron-withdrawing ability of the CO group. The mechanism described in the previous paragraph means that kinetic experiments in water can throw no light on this issue, since the reaction rate depends on the equilibrium concentration of the protonated *O*-nitroso compound, which is independent of the route by which this intermediate is formed. In 9:1 (w/w) dioxane–water, however, the step controlling the rate of nitrosation of dimethylurea by XNO is the attack on the substrate by the nitrosating agent and the finding that under these conditions nucleophiles catalyse the reaction clearly shows that XNO species do indeed perform direct nitrosation.

The above examples corroborate results from other kinds of reactions[11,12] in showing that by altering the relative rates of the various steps involved in a reaction, a change in the medium in which the reaction is carried out can afford valuable information about its mechanism. In this work we extended our studies of solvent-induced changes in nitrosation mechanisms to the nitrosation of two ureas (1,3-dimethylurea and 2-imidazolidone) in THF–water and DMSO–water mixtures.

Experimental

All reagents were supplied by Merck. 1,3-Dimethylurea (DMU) was purified by recrystallization from ethanol, and all others were used as supplied. The composition of solvent mixtures is indicated by the weight percentage of the organic component.

Kinetic data were obtained with a Kontrol Uvikon 930 spectrophotometer at 25 °C by recording the absorbance at 270 nm (in THF–water) or 275 nm (in DMSO–water) due to the formation of the *N*-nitroso compound. All reactions were

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† IUPAC preferred name: imidazolidin-2-one.

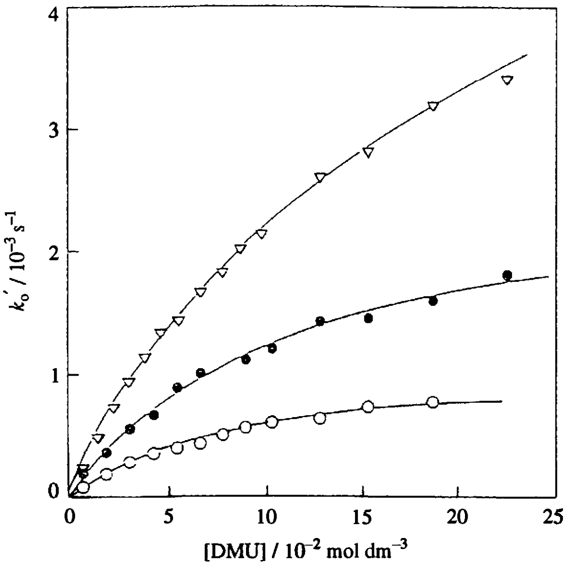


Fig. 1 Influence of DMU concentration on the pseudo-first-order rate constant of the nitrosation of DMU by HNO_2 in 90% THF. $[HClO_4]$ = 0.0071 (○), 0.0142 (●) or 0.026 mol dm^{-3} (△).

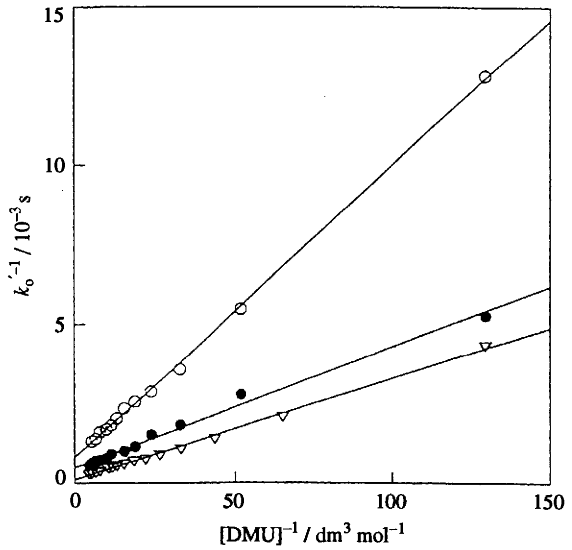


Fig. 2 Plot of $1/k'_o$ *vs.* 1/[DMU] for the data of Fig. 1. $[HClO_4]$ = 0.0071 (●), 0.0142 (○), 0.026 mol dm^{-3} (△).

carried out with nitrous acid concentrations of the order of 10^{-4} mol dm^{-3} and all other reagents in large excess. All reactions were of first-order with respect to nitrous acid, and the values of the pseudo-first-order rate constant, k_o, were always reproducible to within ±5%.

Nitrous acid was found to be stable for several hours in DMSO–water mixtures under the working conditions, but in THF-rich THF–water mixtures it underwent a slow decomposition process that competed with the nitrosation reaction at low urea concentrations. The decomposition process was almost first-order with respect to nitrous acid and was catalysed by X^- and H^+. Its rate constant, k_{dec}, was determined under all the experimental conditions involving 90% THF–water mixtures. Since the simultaneous occurrence of a first-order process (nitrosation) and a quasi-first-order (decomposition) in the nitrosation experiments led to overall kinetics that were satisfactorily fitted by first-order integrated equations, we calculated the pseudo-first-order rate constant of the nitrosation reaction in 90% THF as $k'_o = k_o - k_{dec}$.

Results and discussion

Results in THF–water

Regardless of the presence or absence of halide ion in the medium (8.0 × 10^{-3} mol dm^{-3} NaCl), increasing the percentage of THF in the solvent from 0% to *ca.* 80% while maintaining fixed concentrations of DMU (4.2 × 10^{-3} mol dm^{-3}) and $HClO_4$ (1.3 × 10^{-2} mol dm^{-3}) progressively diminished the reaction rate, but which increased slightly upon further increasing the proportion of THF (Table 1). For THF concentrations less than *ca.* 60%, the value of k_o obtained in the presence of halide differed from the value obtained in its absence by only 0–15%; and since a difference of this order can be attributed to a saline effect, the reaction mechanism operating at these THF concentrations seems likely to be the same as in pure water. However, at higher THF concentrations the effect of the halide is more marked, causing, for example, a six-fold increase in k_o in 90% THF. This catalysis by nucleophiles at high THF concentrations suggests that under these conditions the reaction mechanism either differs from that obtained in pure water or undergoes a significant change in the relative rates of its various steps.

Table 1 Influence of THF concentration (%) on the pseudo-first-order rate constant of the nitrosation of DMU by HNO_2 in the presence and absence of NaCl

	$k_o/10^{-3}$ s^{-1}	
THF (%)	[NaCl] = 0 mol dm^{-3}	[NaCl] = 8.0 × 10^{-3} mol dm^{-3}
0	12.4	13.0
10.1	10.7	12.4
17.7	8.1	8.4
25.5	3.9	4.5
31.8	2.0	2.3
35.0	1.6	1.7
38.3	1.0	1.0
53.2	0.31	0.41
61.7	0.18	0.30
70.4	0.12	0.23
79.3	0.09	0.23
90.3	0.12	0.73
94.0	0.23	—

The nitrosation mechanism in THF-rich media was studied in greater detail using 90% THF. For any fixed concentration of $HClO_4$, a plot of k'_o *vs.* DMU concentration passes through the origin (indicating an irreversible process) and is non-linear (Fig. 1; the same kind of behaviour was also observed at higher $HClO_4$ concentrations). As in earlier work on the nitrosation of DMU in dioxane–water[1] and the *S*-nitrosation of thiourea in alcoholic media,[13] this non-linearity can be attributed to partial protonation of the substrate at the working acidity, which would mean that an increase in DMU concentration would reduce the effective acidity of the medium. For free DMU very much in excess of protonated DMU, this hypothesis leads to eqn. (1), where K_a is the acidity constant of protonated DMU

$$k'_o = \frac{kK_a[DMU][HClO_4]}{K_a + [DMU]} \qquad (1)$$

and k is the rate constant for the nitrosation of free DMU. Plotting $1/k'_o$ *vs.* 1/[DMU] shows the linear relationship predicted by eqn. 1 (Fig. 2), and the slopes and intersects of these lines afford values of 0.12 mol dm^{-3} for K_a and 1.65 dm^6 mol^{-2} s^{-1} for k.

An alternative explanation of the curvature shown in Fig. 1 (or the fact that the value of k'_o tends to a limit that increases

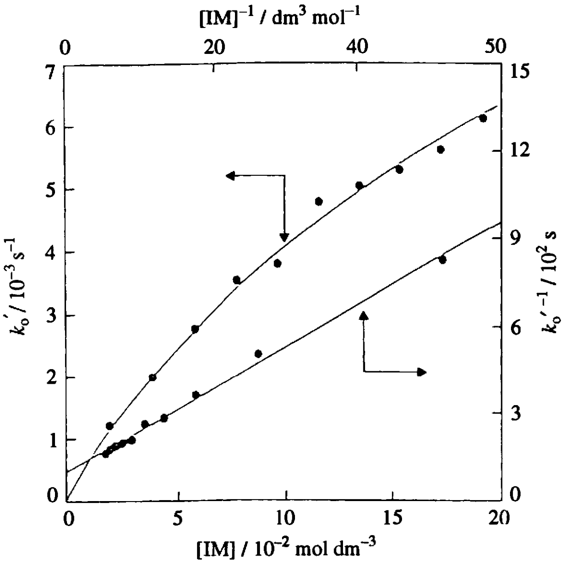


Fig. 3 Influence of 2-imidazolidone (IM) concentration on the pseudo-first-order rate constant of the nitrosation of IM by HNO_2 in 90% THF. $[HClO_4] = 0.0142$ mol dm^{-3}.

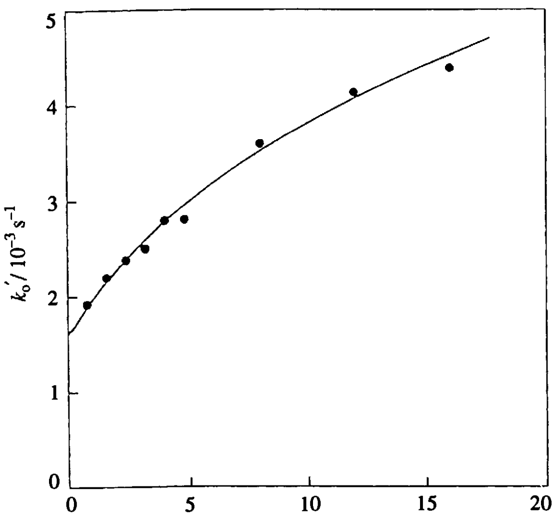


Fig. 4 Influence of NaCl concentration on the pseudo-first-order rate constant of the nitrosation of DMU by HNO_2 in 90% THF. [DMU] = 0.067, $[HClO_4] = 0.026$ mol dm^{-3}.

linearly with $[HClO_4]$) is that at higher DMU concentrations the slow step of the reaction might be the formation of the effective nitrosating agent. For under this hypothesis, increasing the substrate concentration must result in k'_o reaching a limiting value that depends only on $[H^+]$ and $[HNO_2]$. Since this hypothesis also implies that the limiting values of k'_o ought not to depend on the identity of the substrate, it was investigated by carrying out similar experiments with a different substrate, 2-imidazolidone (IM). It was found that for a given $[HClO_4]$ and $[HNO_2]$, the limiting value of k'_o was considerably higher for IM than for DMU (Fig. 3), which rules out the hypothesis that the formation of the effective nitrosating agent is the rate-limiting step at high substrate concentration. This finding lends further support to eqn. (1), from which the slope and intersect of a line fitted to a plot of k'^{-1}_o *vs.* $[IM]^{-1}$ (Fig. 3) afford values of 0.15 mol dm^{-3} for the acidity constant of protonated IM and 5.10 dm^6 mol^{-2} for the rate constant for the nitrosation of free IM.

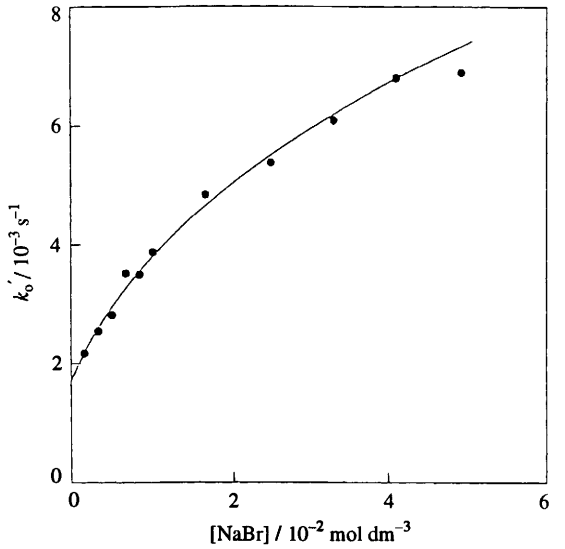


Fig. 5 Influence of NaBr concentration on the pseudo-first-order rate constant of the nitrosation of DMU by HNO_2 in 90% THF. [DMU] = 0.067, $[HClO_4] = 0.027$ mol dm^{-3}.

The nucleophile catalysis at high THF concentrations that is suggested by the data of Table 1 was investigated in more detail in a series of experiments in which the concentration of NaCl was varied from 0 to 0.016 mol dm^{-3}, or the concentration of NaBr was varied from 0 to 0.049 mol dm^{-3}, while $[HClO_4]$ and [DMU] remained constant. The observed non-linear dependence of k'_o on the NaX concentration is shown in Figs. 4 and 5. The catalysis of the nitrosation reaction by halides at high organic solvent concentrations, which was also observed in dioxane–water[1] and acetonitrile–water,[2] means (*i*) that under these conditions the reaction rate is limited, at least partially, by the rate of the step in which the effective nitrosating agent attacks the substrate and (*ii*) the introduction of a reaction path in which the effective nitrosating agent is the XNO species. We previously explained [1] nucleophile catalysis of the nitrosation of DMU in dioxane–water in terms of a mechanism that assumes that ion pairs predominate over free ions and that electrolytes and strong acids are only partially dissociated. The same assumptions can be made for THF–water as solvent, since the predominance of ion pairs is in general favoured in solvents with low donating ability and low relative permittivity ($\varepsilon_r = 12$ for 90% THF),[14] and has been confirmed experimentally for pure THF.[15-17] For the reactions studied in this work, we accordingly propose the mechanism shown in Scheme 2.

$$DMU^+HClO_4^- \xrightleftharpoons{K_a} DMU + HClO_4 \qquad (2)$$

$$XNa + HClO_4 \xrightleftharpoons{K_1} HX + NaClO_4 \qquad (3)$$

$$HX + HNO_2 \xrightleftharpoons{K_2} XNO + H_2O \qquad (4)$$

$$HClO_4 + HNO_2 \xrightleftharpoons{K_3} ClO_4^-NO^+ + H_2O \qquad (5)$$

$$ClO_4^-NO^+ + DMU \xrightarrow{k_4} \text{Products} \qquad (6)$$

$$XNO + DMU \xrightarrow{k_5} \text{Products} \qquad (7)$$

Scheme 2

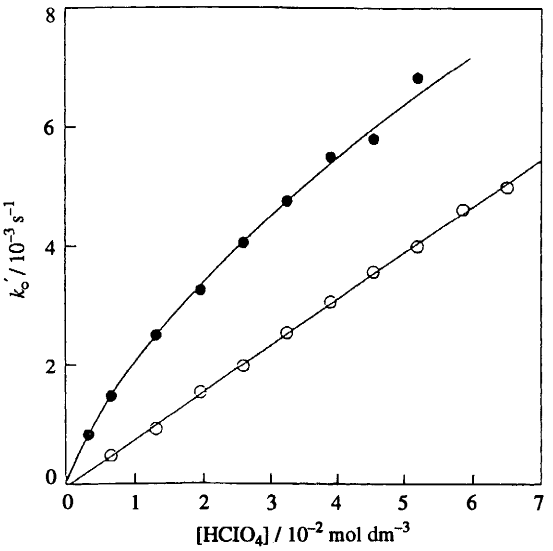


Fig. 6 Influence of $HClO_4$ concentration on the pseudo-first-order rate constant of the nitrosation of DMU by HNO_2 in 90% THF, in the presence (●) or absence (○) of 0.008 mol dm^{-3} NaCl. [DMU] = 0.0857 mol dm^{-3}.

Table 2 Influence of DMSO concentration (%) on the pseudo-first-order rate constant of the nitrosation of DMU by HNO_2 in the presence and absence of NaCl

	$k_o/10^{-3}$ s^{-1}		
DMSO (%)	[NaCl] = 0 mol dm^{-3}	[NaCl] = 0.0081 mol dm^{-3}	[NaCl] = 0.021 mol dm^{-3}
0	13.5	13.5	—
8.6	12.1	11.7	—
24.6	7.2	6.9	—
38.4	3.3	3.5	—
62.3	0.43	0.43	—
69.9	0.19	0.20	0.19
77.9	0.11	0.11	0.10
85.7	0.10	0.10	—
91.9	0.17	0.18	0.18
95.0	0.27	0.33	0.33
96.5	0.45	0.51	0.54
98.0	0.82	—	—
99.6	2.77	—	—

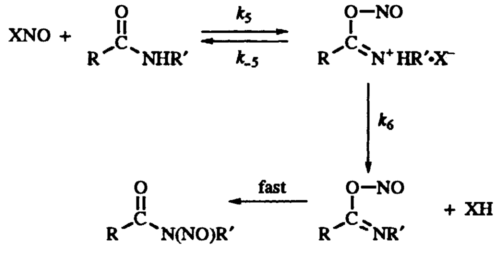
In the absence of X^-, Scheme 2 reduces to eqns. (2), (5) and (6), which satisfactorily explain the kinetic behaviour observed under these conditions. The rate-limiting step is the attack on the urea by the nitrosating agent, which to stress the importance of ionic association in THF-rich THF–water has been written in Scheme 2 as the ion pair $NO^+ClO_4^-$, even though the observed kinetics would also be explained if the effective nitrosating agent were free NO^+. In the presence of NaX the reaction also occurs *via* steps (3), (4) and (7), and since the rate-limiting step is again the attack by the nitrosating agent, the rate equation for the two simultaneous processes is given by eqn. (8).

$$k'_o = k_4K_3[HClO_4][DMU] + k_5K_2[HX][DMU] \quad (8)$$

The curvature of the plots of k'_o *vs.* [NaX] (Figs. 4 and 5) can be attributed to the formation of HX in step (3) being limited by the constant initial concentration of $HClO_4$ and by the value of K_1. Eqn. (8), and hence the mechanism of Scheme 2, is further supported by the results of studying the influence of $HClO_4$ concentration on k'_o for DMU in the presence and absence of a constant concentration of NaCl, [DMU] being kept fixed (Fig. 6). In the absence of NaCl, k'_o depends linearly on $[HClO_4]$, as predicted by eqn. (8), the right-hand side of which reduces to its first term under these conditions; while the concave $[HClO_4]$-dependence of k'_o that is observed in the presence of NaCl is attributable, according to Scheme 2, to the formation of HX in step (3) being limited by the constant concentration of chloride. The possibility that the non-linear $[HClO_4]$-dependence observed in the presence of NaCl might be due to protonation of DMU is ruled out by the observation of linear behaviour under experimental conditions that are identical except for the absence of NaCl.

Fitting eqn. (8) to the experimental data obtained in the absence of halide (using the values of K_a reported above to calculate $[HClO_4]$ and [urea]) afforded values of K_4k_3 of 1.65 dm^6 mol^{-2} s^{-1} for DMU and 5.10 dm^6 mol^{-2} s^{-1} for IM. Eqn. (8) was then fitted to the data obtained for the reaction with DMU in the presence of each halide by means of an optimization procedure involving trial-and-error on K_1, tentative values of which allowed, together with the value of K_a reported above, calculation of $[HClO_4]$, [DMU] and [HX]. The results were K_1 = 0.94 and K_2k_5 = 7.25 dm^6 mol^{-2} s^{-1} for the Cl^--catalysed reaction, and K_1 = 0,44 and K_2k_5 = 9.10 dm^6 mol^{-2} s^{-1} for the Br^--catalysed reaction. The curves shown in Figs. 4–6 were calculated from eqn. (8) using the above values of K_a, K_1, K_4k_3 and K_2k_5. The slopes of the curves in Figs. 4 and 5 at the origin show catalytic efficiencies of 0.44 dm^3 mol^{-1} s^{-1} for Cl^- and 0.35 dm^3 mol^{-1} s^{-1} for Br^-. The fact that the order of these efficiencies, $Cl^- > Br^-$, is the reverse of that usually found in water in other kinds of reaction is due to the catalytic capacity of halides depending on their nucleophilicity: in water and other solvents in which the nucleophile is deactivated by solvation, the degree of nucleophilicity decreases in the order $I^- > Br^- > Cl^-$, but in solvents with scant solvating power the 'natural' order found in the gas phase, pure acetone or pure acetonitrile holds, *i.e.* $Cl^- > Br^- > I^-$.[18] Finally, note that the optimized values of K_1, which are both of the order of unity, show that HCl and $HClO_4$ have very similar pK_a values in 90% THF (as in dioxane–water),[1,19] that the same holds for HBr and $HClO_4$, and that the pK_a values of HCl and HBr are therefore also similar in 90% THF, even though NBr is, as in water,[20] rather more acidic.

We would like to stress that it is kinetically impossible to distinguish whether the slow step in the process is the reaction between the urea and the nitrosating agent, as we have assumed for simplicity, or a further proton transfer reaction within the ion-pair thus formed (*i.e.* rate constants k_5 or k_6 in Scheme 3).



Scheme 3

Results in DMSO–water

The effect of DMSO on k_o was similar to that of THF: regardless of the presence or absence of 8.1 × 10^{-3} mol dm^{-3} NaCl in the medium, increasing the percentage of DMSO from 0% to *ca.* 85% while maintaining fixed concentrations of DMU (4.77 × 10^{-3} mol dm^{-3}) and $HClO_4$ (0.013 mol dm^{-3}) caused a 70-fold reduction in the reaction rate, which increased slightly upon further increasing the proportion of DMSO (although the

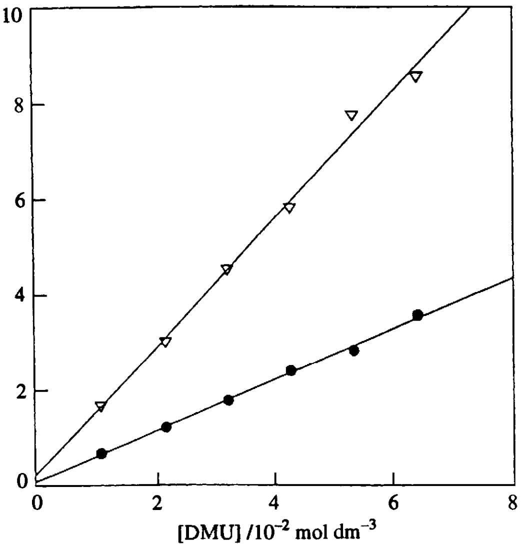


Fig. 7 Influence of DMU concentration on the pseudo-first-order rate constant of the nitrosation of DMU by HNO_2 in 95% DMSO. [$HClO_4$] = 0.013 (●) or 0.039 mol dm^{-3} (○).

Table 3 Slopes of plots of k_o *vs.* [DMU] in the presence and absence of NaCl, where k_o is the pseudo-first-order rate constant of the nitrosation of DMU by HNO_2 in 95% DMSO, for various fixed concentrations of $HClO_4$

	Slopes	
[$HClO_4$]/mol dm^{-3}	[NaCl] = 0 mol dm^{-3}	[NaCl] = 0.008 mol dm^{-3}
0.013	0.053	0.046
0.039	0.133	0.130
0.059	0.221	—
0.177	0.452	—

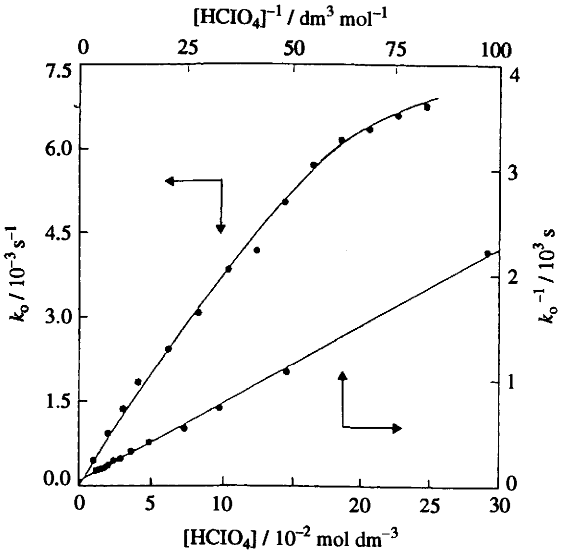


Fig. 8 Influence of $HClO_4$ concentration on the pseudo-first-order rate constant of the nitrosation of DMU by HNO_2 in 95% DMSO. [DMU] = 0.011 mol dm^{-3}.

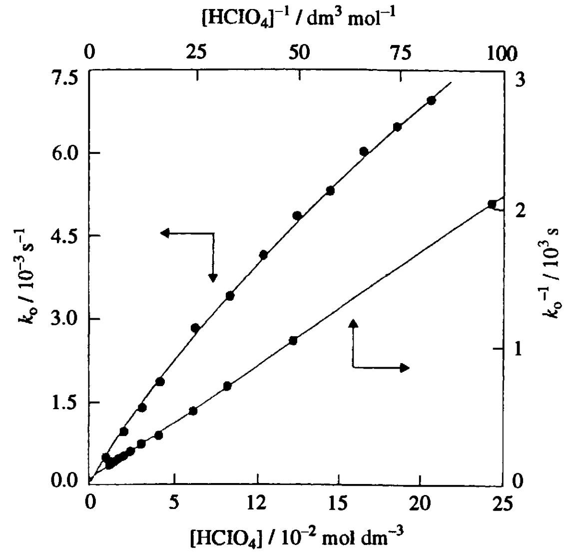


Fig. 9 Influence of $HClO_4$ concentration on the pseudo-first-order rate constant of the nitrosation of IM by HNO_2 in 95% DMSO. [IM] = 0.0032 mol dm^{-3}.

increase was only substantial when DMSO concentration exceeded 96%); see Table 2. However, unlike other organic solvents in whose mixtures with water we have studied this reaction (dioxane,[1] acetonitrile[2] and THF), DMSO did not facilitate catalysis by chloride. The slight increase in k_o caused by the presence of 8.1 × 10^{-3} mol dm^{-3} NaCl at DMSO concentrations greater than 95% is insufficient to be deemed to show nucleophile catalysis, and may be attributed to the saline effect, as was confirmed by the results of repeating experiments using a higher concentration of NaCl (Table 2).

The nitrosation mechanism in DMSO-rich media was studied in greater detail using 95% DMSO. Experiments to determine the effect of DMU concentration on k_o at four different acidities (Fig. 7 shows the results for $HClO_4$ concentrations of 0.013 and 0.039 mol dm^{-3}) showed that the reaction was of first-order with respect to DMU in all cases and that the slopes of the plots of k_o against [DMU] increased with $HClO_4$ concentration, suggesting acid catalysis (Table 3). The fact that adding 0.008 mol dm^{-3} NaCl to the medium did not alter these slopes (Table 3) confirmed that Cl^- does not catalyse the reaction in DMSO-rich media.

Experiments in which $HClO_4$ concentration was varied from 0 to 0.25 mol dm^{-3} while DMU concentration remained constant at 0.011 mol dm^{-3} led to a plot of k_o *vs.* [$HClO_4$] that was linear for low [$HClO_4$] (and passed through the origin), but non-linear at high [$HClO_4$] (Fig. 8). This behaviour may be attributed to the concentration of free DMU being reduced at high acidity by partial protonation. For [$HClO_4$] ≫ [$DMUH^+$], this assumption implies the following rate equation where, as in eqn. (1), K_a is the acidity constant of protonated DMU and k is the rate constant for the nitrosation of free DMU. Agreement of the experimental data with eqn. (9)

$$k_o = \frac{kK_a[\text{DMU}]_T[\text{HClO}_4]}{K_a + [\text{HClO}_4]} \tag{9}$$

is corroborated by the linearity of a plot of $1/k_o$ *vs.* [$HClO_4$]$^{-1}$ (Fig. 8), and the slope and intercept of the line fitted to this plot afford values of 0.40 mol dm^{-3} for K_a and 4.30 dm^6 mol^{-2} s^{-1} for k.

Similar [$HClO_4$]-dependence was observed for IM (Fig. 9), for which the values obtained for K_a and k were respectively 0.46 mol dm^{-3} and 15.3 dm^6 mol^{-2} s^{-1}.

The fact that halide ions do not catalyse the nitrosation of DMU in 95% DMSO rules out the possibility that the rate-limiting step of the reaction might be the attack by the nitrosating agent. Furthermore, the high relative permittivity and high donating ability of this medium ($\varepsilon_r = 51$, DN = 30) do not favour the formation of ion pairs; in fact, sulfuric acid[21] and perchlorates[17] are known to be strong electrolytes in pure DMSO and no evidence for the formation of ion pairs in this medium has been forthcoming. We therefore hypothesized that the mechanism of the nitrosation of ureas and amides in DMSO-rich DMSO–water mixtures is the same as in pure water, with proton transfer from the protonated *O*-nitroso compound to the medium as the rate-limiting step (Scheme 1). This mechanism is in keeping with eqn. (9).

The values of k obtained for DMU and IM (4.30 and 15.3 dm^6 mol^{-2} s^{-1}, respectively) are some 50 times smaller than those measured by Castro *et al.*[3] in pure water (280 and 680 dm^6 mol^{-2} s^{-1}, respectively). This may be attributed to the combined effects of two factors. First, the low concentration of water in 95% DMSO means that the effective concentration of the base withdrawing the proton from the protonated *O*-nitroso compound in the rate-controlling step is much lower than in water. Secondly, protons are more readily solvated by DMSO than by water (the free energy for transfer of a proton from water to DMSO is −4.5 kcal mol^{-1}), so that in 95% DMSO the proton to be removed from the protonated *O*-nitroso compound must be assumed to be stabilized by hydrogen bonding to DMSO.

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