An Indirect Method for the Determination of the Reactivity of Amines and Other Compounds Towards Nitrosyl Chloride

By D. LYN H. WILLIAMS

(*Department of Chemistry, Durham University, Durham* DH1 3LE)

Summary By noting the variation of the observed rate coefficient with added *N*-methylaniline, for the de-nitrosation of *N*-methyl-*N*-nitrosoaniline in the presence of added X (amines, *etc.*), it is possible to determine the relative reactivities of any compound X towards nitrosyl chloride.

NITROSYL chloride is believed to be the effective nitrosating agent in aqueous solution of nitrous acid containing chloride ion.[1] It appears that in the chloride ion-catalysed diazotisation of aniline derivatives (where the first-step is *N*-nitrosation) the rate coefficients for attack by nitrosyl chloride approach the diffusion-controlled limit[2] so that it is not easy to obtain accurate values of these rate coefficients. We report here a method whereby the relative rate coefficients (in this case relative to the reaction with *N*-methylaniline, NMA) for the reaction of a number of nucleophilic species, X, have been obtained using a conventional kinetic technique.

We have shown[3] that the de-nitrosation of *N*-methyl-*N*-nitrosoaniline (I) in hydrochloric acid in the presence of added nucleophiles, X, can be represented by the Scheme. Rearrangement[4] of (I) to the *para*-nitroso-isomer (Fischer–Hepp rearrangement) can take place *concurrently* with de-nitrosation, but is unimportant (*ca.* 1%) in 3·05M-HCl and excess of X. The overall first-order rate-coefficient

$$\mathrm{PhN(Me)NO} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{Ph\overset{+}{N}H(Me)NO} \underset{k_{-1}}{\overset{\mathrm{Cl^-},\, k_1}{\rightleftharpoons}} \mathrm{PhNH(Me)} + \mathrm{NOCl}$$

$$\mathrm{NOCl} + \mathrm{X} \xrightarrow{k_2} \text{various products}$$

k_0 from such a scheme is given by equation (1). K is the

$$k_0 = \frac{k_1 K h_0[\mathrm{Cl^-}]k_2[\mathrm{X}]}{k_{-1}[\mathrm{NMA}] + k_2[\mathrm{X}]} \qquad (1)$$

equilibrium constant for N-protonation of (I) (assuming a Hammett acidity dependence). Clearly k_0 can become independent of the concentration and nature of X at high values of [X], as is observed experimentally.[3] Thus values for $k_1Kh_0[\mathrm{Cl^-}]$ have been obtained for each X of *ca.* $16{\cdot}0 \times 10^{-4}\ \mathrm{s^{-1}}$. The addition of NMA decreases k_0 as expected and good straight lines have been obtained for plots of $1/k_0$ *vs.* $[\mathrm{NMA}]_{\mathrm{total}}$ at constant [X] [from equation (2)]. The ratio k_{-1}/k_2 should be obtained from the slope of such a line and the intercept gives a good check for $k_1Kh_0[\mathrm{Cl^-}]$. However at this acidity (3·05M-HCl) NMA is extensively protonated and X may also exist in a protonated form. If we assume that the nitrosation of both occurs largely *via* the non-protonated form under these conditions,[5] then the slope of the line is given by equation (3), where K_{X} and K_{NMA} are the equilibrium constants for the protonation of

$$\frac{1}{k_0} = \frac{k_{-1}}{k_2}\,\frac{[\mathrm{NMA}]}{16{\cdot}0 \times 10^{-4}[\mathrm{X}]} + \frac{1}{16{\cdot}0 \times 10^{-4}} \qquad (2)$$

$$\text{Slope} = \frac{k_{-1}}{k_2}\,\frac{K_{\mathrm{X}}h_0 + 1}{K_{\mathrm{NMA}}h_0} \times \frac{1}{16{\cdot}0 \times 10^{-4}[\mathrm{X}]} \qquad (3)$$

X and NMA respectively. If X is extensively protonated then $K_{\mathrm{X}}h_0 >> 1$, whereas if X is a very weak base then $K_{\mathrm{X}}h_0 << 1$. ($K_{\mathrm{NMA}}h_0$ is of course $>> 1$). Values of both the slopes of the lines and k_{-1}/k_2 are given in the Table for a number of X compounds.

Clearly the overall rate of reaction of nitrosyl chloride with hydrazoic acid is greatest, and with urea is least, *i.e.*, the order of efficiency of X as 'nitrite traps' under these conditions decreases $\mathrm{HN_3} > \mathrm{NH_2SO_3H} > \mathrm{PhNH_2} > \mathrm{NH_2OH} > \mathrm{CO(NH_2)_2}$. Urea has been widely used as a 'nitrite trap' but it can be seen from these figures that it competes rather poorly with N-methylaniline; sulphamic acid is rather better by a factor of 5×10^2. These reactivities as expressed by the slope are, in part, due to the varying degree of protonation of X. When this is taken into account it is found that the true k_2 values decrease in the order $\mathrm{NH_2OH} > \mathrm{PhNH_2} > \mathrm{NH_3} > \mathrm{CO(NH_2)_2}$, more as expected. The 2·7 factor for aniline represents the activating effect of the N-methyl group towards N-nitrosation.

Table

X	$k_1Kh_0[\mathrm{Cl^-}]$ [X] × slope	pK_a	k_{-1}/k_2
Hydrazoic acid . .	*ca.* 5×10^{-3}	−6·21[6]	*ca.* 4×10^3
Sulphamic acid . .	0·44	—	—
Aniline	1·5	4·60[7]	2·7
Hydroxylamine . .	8·5	5·95[8]	0·68
Urea	255; 284[a]	0·13[9]	13×10^6; 14×10^6[a]
(NMA)		4·85[10]	

[a] Value obtained from the variation of k_0 with [X] at constant [NMA].

There is no evidence, under these conditions, of a direct nitrosation of X by the protonated form of (I), such as has been proposed recently for the reversible reaction of N-nitrosodiphenylamine with NMA.[11] The limiting value of k_0 at high [X] (for all X) is subject to both halide ion and hydrogen ion catalysis and shows a normal solvent isotope effect, $k(\mathrm{D_2O}):k(\mathrm{H_2O})$ of 2·8 thus ruling out a rate-determining proton transfer. There is no reason to invoke a rate-determining intramolecular rearrangement of the protonated form of (I) to some sort of tetrahedral form.

This system, of course, can be used to determine the relative reactivity of any nucleophilic species X towards a variety of possible nitrosating agents. Already we have obtained similar results for reactions in sulphuric acid solution where the nitrosating agent is probably the nitrous acidium ion $\mathrm{H_2NO_2^+}$.

Values of k_0 were obtained spectrophotometrically at 31 °C by noting the decrease in the absorbance at 275 nm.

We thank The Royal Society for financial support.

(*Received*, 21*st February* 1974; *Com.* 225.)

---

[1] J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.

[2] H. Schmid and E. Hallana, *Monatsh.*, 1956, **87**, 560; H. Schmid and M. G. Fouad, *ibid.*, 1957, **88**, 631; H. Schmid and C. Essler, *ibid.*, p. 1110.

[3] D. L. H. Williams and J. A. Wilson, *J.C.S. Perkin II*, 1974, 13.

[4] T. D. B. Morgan, D. L. H. Williams, and J. A. Wilson, *J.C.S. Perkin II*, 1973, 473.

[5] B. C. Challis and J. H. Ridd, *Proc. Chem. Soc.*, 1961, 173.

[6] T. A. Bak and E. L. Praestgaard, *Acta Chem. Scand.*, 1957, **11**, 901.

[7] A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 1961, 388.

[8] P. Lumme, P. Lahermo, and J. Tummavnori, *Acta Chem. Scand.*, 1965, **19**, 2175.

[9] Mean value from D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution', Butterworths, 1965.

[10] A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, *J. Org. Chem.*, 1955, **20**, 747.

[11] B. C. Challis and M. R. Osborne, *J.C.S. Perkin II*, 1973, 1526.