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Direct Measurement of the Rate Constants in the Reaction of Nitrous Acid with Methanol

By S. ELAINE ALDRED and D. LYN H. WILLIAMS*
(*Department of Chemistry, Durham University, Durham* DH1 3LE)

Summary Rate constants have been determined by stopped-flow spectrophotometry, and mechanisms are deduced for the nitrosation of methanol by nitrous acid (and nitrosyl chloride in water) and for the reverse reaction, the hydrolysis (or denitrosation) of methyl nitrite.

IT is well known[1] that aqueous, acidified solutions of sodium nitrite readily form the corresponding alkyl nitrites when alcohols are added; indeed this is the method generally used for the preparation of alkyl nitrites.[2] Whilst the mechanism of the reverse reaction, the hydrolysis of alkyl nitrites, has received some attention,[3] the rapidity of the forward reaction has hitherto prevented a direct kinetic study of the system, although Schmid and Riedl[4] have calculated the rate constants for the nitrosation of alcohols by an indirect route involving the measurement of the nitrosation rates of phenol by nitrous acid in aqueous alcoholic solution.

The reaction was followed at 25 °C by noting the decrease in absorbance at 386 nm using a Canterbury SF-3A stopped-flow spectrophotometer. The change in absorbance at this (or any other available) wavelength was rather small and consequently the errors in the rate constant measurements were larger than we would have wished, although each kinetic run was repeated many times. The characteristic spectrum of alkyl nitrites[5] (in the region 320—390 nm) was observed as soon as the full spectrum of the mixed solutions could be measured. All the kinetic experiments showed strict first-order behaviour in nitrous acid when the reactions were carried out in the presence of a large excess of methanol. The reactant concentrations were:—$[\mathrm{HNO_2}]$ 4×10^{-2} M, [MeOH] 0·2—1·5 M, and $[\mathrm{H_2SO_4}]$ 0·05—0·13 M.

The first-order rate constant k_0 (defined by $-\mathrm{d}[\mathrm{HNO_2}]/\mathrm{d}t = k_0[\mathrm{HNO_2}]$) varied with the initial concentration of methanol in a linear fashion with a positive intercept. This is readily analysed in terms of a reversible reaction [equation (1)] with k_0 given by equation (2), where k_1 is the second-order rate constant for the forward reaction and k_{-1} is the first-order rate constant for the reverse reaction.

$$\mathrm{HNO_2 + MeOH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{MeONO + H_2O} \qquad (1)$$

$$k_0 = k_1[\mathrm{MeOH}] + k_{-1} \qquad (2)$$

Values of k_1 and k_{-1} are thus readily obtained from the slope and intercept. As expected, both reactions were found to be subject to acid catalysis (see Table), both showing a first-order dependence upon $[\mathrm{H^+}]$. Values of $700 \pm 100\ \mathrm{l^2\ mol^{-2}\ s^{-1}}$ and $576 \pm 57\ \mathrm{l\ mol^{-1}\ s^{-1}}$, respectively, were evaluated for k_2 and k_{-2} [defined in equations (3) and (4)].

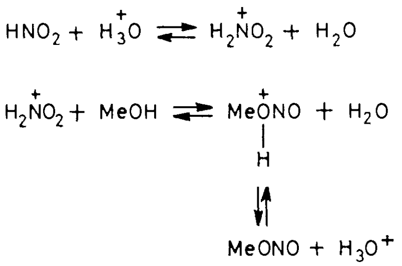
TABLE. Variation of k_1 and k_{-1} with acidity.

$10^2[\mathrm{H^+}]/\mathrm{M}$	$k_1/\mathrm{l\ mol^{-1}s^{-1}}$	$k_{-1}/\mathrm{s^{-1}}$
6·9	29·7 ± 3	34·9 ± 1·7
10·4	71·4 ± 0·7	44·4 ± 0·3
13·8	81·9 ± 1·4	75·7 ± 0·8
17·3	120 ± 6	101 ± 3

$$\text{Rate of forward reaction} = k_2[\mathrm{HNO_2}][\mathrm{MeOH}][\mathrm{H^+}] \qquad (3)$$

$$\text{Rate of reverse reaction} = k_{-2}[\mathrm{MeONO}][\mathrm{H^+}] \qquad (4)$$

For the nitrosation of methanol, the established rate law [equation (3)] is consistent with a mechanism involving rate-determining attack of methanol by either the nitrous acidium ion ($H_2\overset{+}{N}O_2$) or the free nitrosonium ion (NO^+), as in the Scheme. Earlier product studies by Allen[3] using optically active octan-2-ol (which gave the alkyl nitrite without racemisation) had established the reaction as one of *O*-nitrosation. The reaction is thus comparable with other nitrosation reactions, *e.g.* of amines. There is currently much interest in the chemistry of diffusion-controlled processes;[6] many acid-catalysed nitrosation reactions are believed to be in this category. The main evidence for this belief lies in the remarkable similarity between the k_2 values, for a wide range of substrates. These values average at *ca.* 640 $l^2\ mol^{-2}\ s^{-1}$ at 0 °C which is significantly greater than that expected at this temperature for the nitrosation of methanol (700 $l^2\ mol^{-2}\ s^{-1}$ at 25 °C). It would then appear that the present reaction, whilst having a large rate constant, does not quite come in to the realm of diffusion-controlled reactions. Without knowing the pK_a value of methyl nitrite it is not possible to determine the rate constant for the attack of water upon the protonated species in the reverse reaction.



SCHEME

Both the forward and reverse reactions were found to be chloride-ion and hydrogen-ion catalysed, as expected if nitrosation occurs *via* nitrosyl chloride and denitrosation by nucleophilic attack by chloride ion on the protonated form of methyl nitrite. The second-order rate constant for the reaction of nitrosyl chloride with methanol is determined to be $(4{\cdot}0 \pm 0{\cdot}5) \times 10^5\ l\ mol^{-1}\ s^{-1}$. This is well below the value expected for a diffusion-controlled reaction,[6] and observed, *e.g.*, in the case of diazotisation of some aniline derivatives.[7] For the reverse reaction, the denitrosation of methyl nitrite by H^+ and Cl^-, the third-order rate constant (which necessarily includes the equilibrium constant for protonation of methyl nitrite) is $865 \pm 100\ l^2\ mol^{-2}\ s^{-1}$. This is many orders of magnitude greater than the corresponding values for denitrosation of nitrosamines.[8] The difference includes the difference in basicities of these compounds (which are not known) but indications are that the actual rate constant for attack by chloride ion at the protonated methyl nitrite is significantly greater than for attack at a protonated nitrosamine.

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