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Kinetic Studies on the Formation of *N*-Nitroso Compounds VII. Nitrosation of Morpholine in Acetate Buffer

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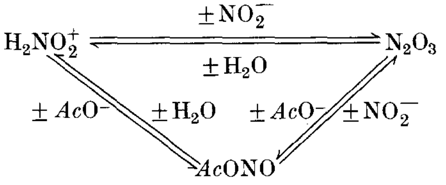
The kinetics of the nitrosation of morpholine in acetate buffer have been studied. It was found that in the experimental conditions used the effective nitrosating agent is dinitrogen trioxide, whose formation is promoted by the acetate ion in accordance with the scheme:



No reaction between nitrosyl acetate and the amine was observed, probably owing to the low concentration of the former. The proposed mechanism explains the experimental facts that no catalysis by the buffer is observed in conditions in which the rate controlling step is the reaction of N_2O_3 with the amine, and that the catalytic effect has only been observed when the formation of the nitrosating agent is also rate controlling. Values have been calculated for several equilibrium and kinetic constants involved in the mechanism proposed.

(Keywords: Acetate buffer; Kinetics of nitrosation; Morpholine; N-Nitrosomorpholine)

Kinetische Untersuchungen zur Bildung von N-Nitroso-Verbindungen, 7. Mitt.: Nitrosierung von Morpholin in Acetat-Puffer

Es wurde die Kinetik der Nitrosierung von Morpholin in Acetat-Puffer untersucht. Unter den gewählten Reaktionsbedingungen ist das effektive

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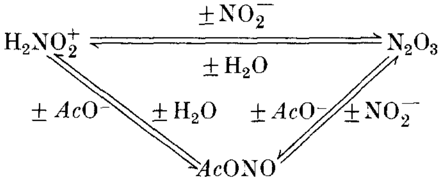
Agens N_2O_3, dessen Bildung von Acetat-Ionen im Einklang mit dem gezeigten Schema gefördert wird:



Zwischen Nitrosylacetat und Amin wurde keine Reaktion beobachtet, vermutlich wegen der niederen Konzentration des ersteren. Der vorgeschlagene Mechanismus erklärt, daß keine Katalyse mittels Puffer unter Bedingungen zu beobachten ist, wo der geschwindigkeitsbestimmende Schritt die Reaktion von N_2O_3 mit dem Amin ist und daß der katalytische Effekt nur dann beobachtet wird, wenn die Bildung des Nitrosierungsagens geschwindigkeitsbestimmend ist. Gleichgewichts- und kinetische Konstanten, die für den Mechanismus von Bedeutung sind, wurden ermittelt.

Introduction

As part of our systematic general study of the mechanisms of formation of *N*-nitroso compounds in aqueous perchloric media, both in the presence[1,2] and in the absence[3–6] of catalysts, this article presents the results of a study of the influence of acetate buffer on the nitrosation of morpholine (*MOR*).

The influence of acetate buffer on the nitrosation of dimethylamine has been studied by *Masui* et al.[7], but without any interpretation of the results as regards the reaction mechanism involved. Its influence on the reaction of nitrous acid with the azide ion[8,9] and with hydroxylamine[10] and on the diazotisation of aniline[11–13] has also been studied, a great variety of mechanisms having been put forward to explain its catalytic effect. Several authors agree in indicating the desirability of a fuller study of the subject, given the complexity of the mechanisms involved.

Experimental

Merck p. a. reagents were used except in the case of *N*-nitrosomorpholine (*NMOR*), which was supplied by Serva. The experimental techniques employed have been described in previous articles[3,5]. A Pye-Unicam SP 8-200 Vis-UV spectrophotometer was used for kinetic measurements and a Radiometer model 26 *pH*-meter to measure acidity. It was chosen to work at a wavelength of 260 nm, at which the only substance involved which exhibits appreciable absorption is *NMOR* (molar absorptivity $\varepsilon = 3035 \pm 6\,M^{-1}\,\mathrm{cm}^{-1}$), the absorption by nitrite ($\varepsilon \simeq 6\,M^{-1}\,\mathrm{cm}^{-1}$) being negligible. All experiments were carried out at 25 °C and at an ionic strength of $0.5\,M$ ($NaClO_4$).

Results

With *pH* and the concentration of morpholine constant, the concentration of buffer was varied for various initial concentrations of nitrite. In all cases v_0, the initial rate of formation of *NMOR*, was found to depend on the total concentration of buffer (acetic acid + acetate ion) in accordance with the equation

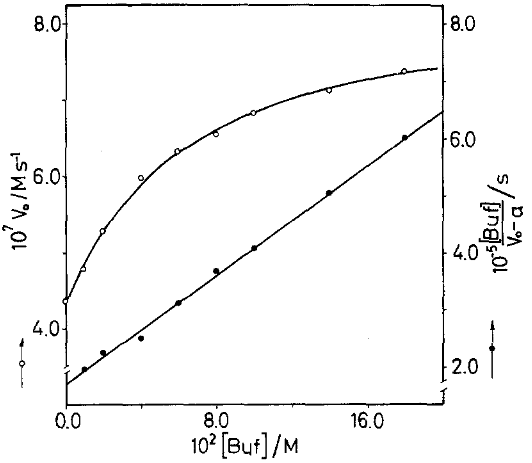


Fig. 1. Dependence of initial rate of *MOR* nitrosation on buffer concentration at 25 °C, $\mu = 0.5\,M$, $[MOR]_0 = 0.180\,M$, $[\text{nit}]_0 = 1.67 \cdot 10^{-2}\,M$ and $pH = 4.83$. a is the value of v_0 in the absence of buffer

$$v_0 = a + \frac{[\text{Buf}]}{b + c\,[\text{Buf}]} \qquad (1)$$

which in the form

$$\frac{[\text{Buf}]}{v_0 - a} = b + c\,[\text{Buf}] \qquad (2)$$

is illustrated in Fig. 1 by the data for one of the series of experiments run. As Eq. (1) shows, the value of a is given experimentally by the value of v_0 in the absence of buffer. Table 1 lists the values of a, b and c obtained experimentally for various initial concentrations of nitrite. Between these parameters and the initial stoichiometric concentration

Table 1. *Influence of the concentration of nitrite on the values of the parameters a, b and c* (Eq. 1) *at 25 °C, $\mu = 0.5\,M$, $[MOR]_0 = 0.180\,M$ and $pH = 4.83$*

$10^2\,[\text{nit}]_0/M$	$10^7\,a/M\,\text{s}^{-1}$	$10^{-5}\,b/\text{s}$	$10^{-6}\,c/M^{-1}\,\text{s}$
3.00	14.5	0.87 ± 0.05	0.82 ± 0.05
2.67	11.0	0.97 ± 0.03	1.00 ± 0.04
2.33	8.48	1.22 ± 0.04	1.16 ± 0.03
2.00	6.59	1.40 ± 0.07	1.87 ± 0.08
1.67	4.39	1.67 ± 0.04	2.41 ± 0.05
1.33	2.77	2.48 ± 0.07	3.66 ± 0.07
1.00	1.68	3.95 ± 0.12	7.52 ± 0.13
0.500	0.432	9.4 ± 0.4	31.7 ± 0.4

of nitrite the following relations can be deduced (Fig. 2)

$$a = d\,[\text{nit}]_0^2 \tag{3}$$

$$b = \frac{e + f\,[\text{nit}]_0}{[\text{nit}]_0^2} \tag{4}$$

$$c = \frac{g}{[\text{nit}]_0^2} \tag{5}$$

In the experimental conditions under which the data shown in Fig. 2 were obtained, $d = (1.61 \pm 0.02) \cdot 10^{-3}\,M^{-1}\,\text{s}^{-1}$, $e = (13.8 \pm 1.7)\,M^2\,\text{s}$, $f = (2.15 \pm 0.12) \cdot 10^3\,M\,\text{s}$ and $g = (7.1 \pm 0.2) \cdot 10^2\,M\,\text{s}$.

Combination of (1), (3), (4) and (5) gives

$$v_0 = \frac{de + df\,[\text{nit}]_0 + (dg + 1)\,[\text{Buf}]}{e + f\,[\text{nit}]_0 + g\,[\text{Buf}]}\,[\text{nit}]_0^2 \tag{6}$$

The influence of the concentration of morpholine upon the rate of reaction was studied for various concentrations of buffer, *pH* and the concentration of nitrite being kept constant. In all cases v_0 was found to obey the equation

$$v_0 = \frac{[MOR]_0}{h + i\,[MOR]_0} \tag{7}$$

illustrated in Fig. 3 by the data for one of the series run. Table 2 lists the values of h and i obtained for the various concentrations of buffer from plots of $[MOR]_0/v_0$ against $[MOR]_0$. Whereas h can be seen to be independent of the concentration of buffer, Fig. 4 shows the latter to be related linearly to $1/i$:

$$1/i = j + k\,[\text{Buf}] \tag{8}$$

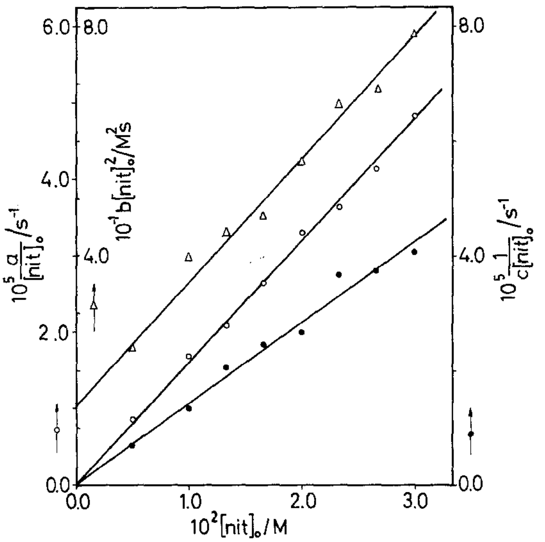


Fig. 2. Dependence of parameters a (○), b (Δ) and c (●) (Eq. 1) on nitrite concentration at 25 °C, $\mu = 0.5\,M$, $[MOR]_0 = 0.180\,M$ and $pH = 4.83$

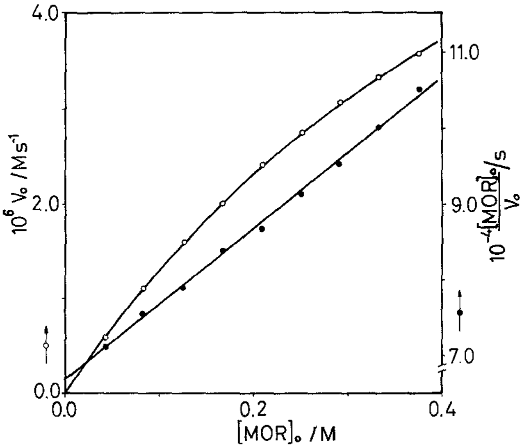


Fig. 3. Dependence of initial rate of *NMOR* formation on *MOR* concentration at 25 °C, $\mu = 0.5\,M$, [Buf] $= 0.120\,M$, $[\mathrm{nit}]_0 = 2.69 \cdot 10^{-2}\,M$ and $pH = 4.73$

Table 2. *Influence of the concentration of buffer on the values of the parameters h and i* (Eq. 7) *at 25 °C,* $\mu = 0.5\,M$, $[\mathrm{nit}]_0 = 2.69 \cdot 10^{-2}\ M$ *and* $pH = 4.73$

$[\mathrm{Buf}]/M$	$10^{-4}h/\mathrm{s}$	$10^{-4}i/M^{-1}\,\mathrm{s}$
0.180	6.57 ± 0.05	7.9 ± 0.2
0.140	6.65 ± 0.03	9.16 ± 0.12
0.120	6.68 ± 0.05	9.9 ± 0.2
0.100	6.67 ± 0.07	11.1 ± 0.3
0.0800	6.58 ± 0.11	12.7 ± 0.5
0.0600	6.62 ± 0.07	14.7 ± 0.3
0.0400	6.55 ± 0.14	17.4 ± 0.6
0.0200	6.62 ± 0.11	23.1 ± 0.5
0.00	6.66 ± 0.16	27.7 ± 0.7

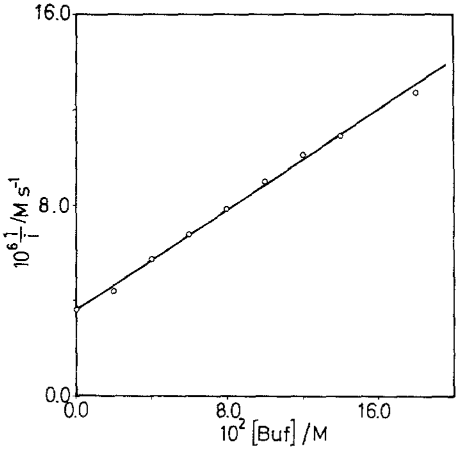


Fig. 4. Effect of buffer concentration on the parameter i (Eq. 7) at 25 °C, $\mu = 0.5\,M$, $[\mathrm{nit}]_0 = 2.69 \cdot 10^{-2}\,M$ and $pH = 4.73$

In the experimental conditions used to obtain Table 2, $h = (6.62 \pm 0.05) \cdot 10^4\,\mathrm{s}$, $j = (3.53 \pm 0.08) \cdot 10^{-6}\,M\,\mathrm{s}^{-1}$ and $k = (5.31 \pm 0.14) \cdot 10^{-5}\,\mathrm{s}^{-1}$.

Combining (7) and (8) yields

$$v_0 = \frac{j + k\,[\mathrm{Buf}]}{hj + hk\,[\mathrm{Buf}] + [MOR]_0}\,[MOR]_0 \tag{9}$$

The effect of the concentration of morpholine upon the rate of reaction was also investigated for various initial concentrations of nitrite while keeping pH and the concentrations of buffer constant. The same relationship as is represented by Eq. (7) was obtained in all cases.

Table 3 lists the values of h and i obtained for the various concentrations of nitrite. Fig. 5 shows how these data, together with that summarized by Eq. (6), imply the relations

$$h = l/[\mathrm{nit}]_0^2 \tag{10}$$

$$i = \frac{m + n\,[\mathrm{nit}]_0}{(1 + p\,[\mathrm{nit}]_0)\,[\mathrm{nit}]_0^2} \tag{11}$$

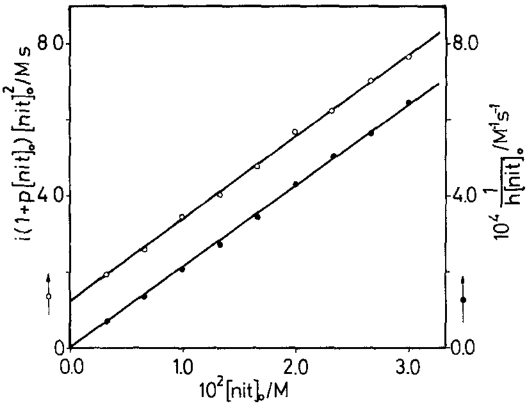


Fig. 5. Effect of nitrite concentration on the parameters h and i

Table 3. *Influence of the initial concentration of nitrite upon the parameters h and i* (Eq. 7) *at 25 °C,* $\mu = 0.5\,M$, [Buf] $= 0.160\,M$ *and* $pH = 4.73$

$10^2\,[\mathrm{nit}]_0/M$	$10^{-4}\,h/\mathrm{s}$	$10^{-4}\,i/M^{-1}\,\mathrm{s}$
3.03	5.11 ± 0.12	7.1 ± 0.2
2.69	6.61 ± 0.05	8.4 ± 0.2
2.35	8.43 ± 0.07	9.9 ± 0.3
2.02	11.6 ± 0.13	12.4 ± 0.6
1.68	17.4 ± 0.15	15.4 ± 0.6
1.35	27.4 ± 0.2	20.5 ± 0.9
1.01	47.9 ± 0.9	32.1 ± 0.4
0.673	109 ± 0.8	54 ± 2
0.336	417 ± 2	167 ± 6

where p is obtained by optimization using the one-dimensional search algorithm of *Davies*, *Swann* and *Campey*[14]. In the experimental conditions under which Fig. 5 was obtained, $l = (48.1 \pm 1.3)\,M^2\,\mathrm{s}$, $m = (11.8 \pm 0.4)\,M\,\mathrm{s}$, $n = (2.15 \pm 0.04)\cdot 10^3\,\mathrm{s}$ and $p = 5.7\,M^{-1}$.

Eqs. (7), (10) and (11) yield

$$v_0 = \frac{(1 + p\,[\mathrm{nit}]_0)\,[MOR]_0\,[\mathrm{nit}]_0^2}{l + pl\,[\mathrm{nit}]_0 + m\,[MOR]_0 + n\,[MOR]_0\,[\mathrm{nit}]_0} \tag{12}$$

From Eqs. (6), (9) and (12) and the numerical value of their parameters, the following experimental rate equation at constant *pH* can be deduced*:

$$v_0 = \frac{(1 + A\,[\mathrm{nit}]_0 + B\,[\mathrm{Buf}])\,[MOR]_0\,[\mathrm{nit}]_0^2}{C + D\,[\mathrm{nit}]_0 + E\,[\mathrm{Buf}] + F\,[MOR]_0 + G\,[MOR]_0\,[\mathrm{nit}]_0} \tag{13}$$

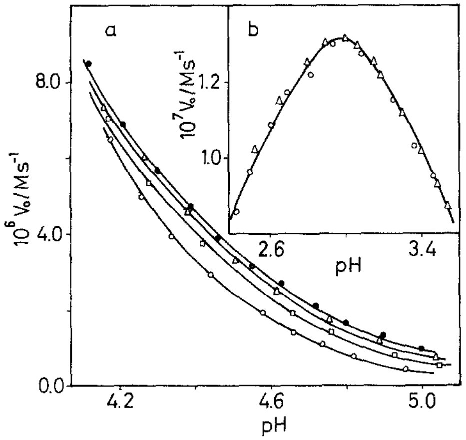


Fig. 6. Effect of *pH* on the initial rate of *MOR* nitrosation at 25 °C, $\mu = 0.5\,M$ and various buffer concentrations; (a) $[MOR]_0 = 0.291\,M$, $[\mathrm{nit}]_0 = 2.02 \cdot 10^{-2}\,M$ and $[\mathrm{Buf}]/M$ = (○) 0.00, (□) 0.060, (Δ) 0.120, (●) 0.180; (b) $[MOR]_0 = 1.56 \cdot 10^{-2}\,M$, $[\mathrm{nit}]_0 = 5.17 \cdot 10^{-3}\,M$ and $[\mathrm{Buf}]/M$ = (○) 0.00, (Δ) 0.100

The influence upon the rate of reaction of the acidity of the medium was studied in the range *pH* 2.2–5.2. The results obtained, shown in Fig. 6, will be used below to discuss the reaction mechanism proposed.

Finally studies were carried out in which drastic reduction of the concentration of morpholine permitted reduction of Eq. (7) to

$$v_0 = \frac{1}{h}\,[MOR]_0 \tag{14}$$

where $1/h = (1.159 \pm 0.004) \cdot 10^{-5}\,\mathrm{s}^{-1}$ (Fig. 7). In such conditions

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[*] The parameter C arranges for quantitative consistency on combining (6), (9) and (12) into (13).

($pH = 4.83$, $[\text{nit}]_0 = 2.67 \cdot 10^{-2}\,M$, $[MOR]_0 = 1.66 \cdot 10^{-2}\,M$) the concentration of buffer was varied between 0.0 and 0.2 M without any variation in the rate of reaction being observed (see also Fig. 6 b). The influence of the initial concentration of nitrite was likewise investigated with the results shown in Fig. 7, according to which under these conditions

$$v_0 = q[\text{nit}]_0^2 \tag{15}$$

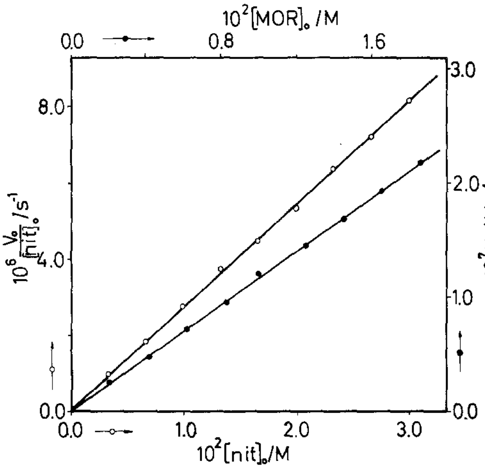


Fig. 7. (●) Dependence of initial rate of $NMOR$ formation on MOR concentration at 25 °C, $\mu = 0.5\,M$, $[\text{nit}]_0 = 2.67 \cdot 10^{-2}\,M$, $[\text{Buf}] = 0.180\,M$ and $pH = 4.83$. (○) Dependence of initial rate of MOR nitrosation on nitrite concentration at 25 °C, $\mu = 0.5\,M$, $[MOR]_0 = 1.66 \cdot 10^{-2}\,M$, $[\text{Buf}] = 0.180\,M$ and $pH = 4.83$

where $q = (2.719 \pm 0.011) \cdot 10^{-4}\,M^{-1}\,\text{s}^{-1}$. These results seem to indicate that in the equation

$$v_0 = \frac{1 + A\,[\text{nit}]_0 + B\,[\text{Buf}]}{C + D\,[\text{nit}]_0 + E\,[\text{Buf}]}\,[MOR]_0\,[\text{nit}]_0^2 \tag{16}$$

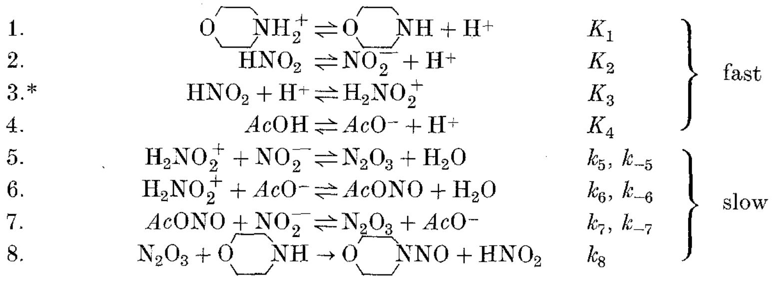
to which (13) reduces for low concentrations of the amine,

$$C + D\,[\text{nit}]_0 + E\,[\text{Buf}] = \text{constant} \cdot (1 + A\,[\text{nit}]_0 + B\,[\text{Buf}]) \tag{17}$$

should hold. This confirms the need to include the parameter C in Eq. (13).

Discussion

It is generally accepted that in acidic nitrite solutions the acetate ion forms nitrosyl acetate, *Ac*ONO[8–13], in the same way as nitrosyl halides are formed from the corresponding anions. The experimental findings of the present investigation show that the direct reaction between nitrosyl acetate and the amine plays no appreciable part in determining the rate of reaction. When the reaction is of order one with respect to the amine there is no evidence of its also being order one with respect to nitrite and acetate which would be the case for direct attack by nitrosyl acetate as it has been found for nitrosyl halides (see Ref.[1]). That the buffer has only been observed to have catalytic effect in conditions in which the order of the reaction with respect to the amine is below one implies that instead of giving rise to a new effective nitrosating agent it catalyses the formation of an agent which exists even in its absence, its catalytic effect only being operative when one of the rate controlling steps is the formation of this agent. On the basis of these considerations together with other experimental observations made during the present study or previously[5], the following reaction mechanism in which the effective nitrosating agent is N_2O_3 is proposed:



1. $\mathrm{O\;\;NH_2^+ \rightleftharpoons O\;\;NH + H^+}$ K_1
2. $\mathrm{HNO_2 \rightleftharpoons NO_2^- + H^+}$ K_2
3.* $\mathrm{HNO_2 + H^+ \rightleftharpoons H_2NO_2^+}$ K_3
4. $\mathrm{\mathit{Ac}OH \rightleftharpoons \mathit{Ac}O^- + H^+}$ K_4

fast

5. $\mathrm{H_2NO_2^+ + NO_2^- \rightleftharpoons N_2O_3 + H_2O}$ k_5, k_{-5}
6. $\mathrm{H_2NO_2^+ + \mathit{Ac}O^- \rightleftharpoons \mathit{Ac}ONO + H_2O}$ k_6, k_{-6}
7. $\mathrm{\mathit{Ac}ONO + NO_2^- \rightleftharpoons N_2O_3 + \mathit{Ac}O^-}$ k_7, k_{-7}
8. $\mathrm{N_2O_3 + O\;\;NH \rightarrow O\;\;NNO + HNO_2}$ k_8

slow

According to the above scheme, the rate of reaction is given by

$$v_0 = k_8\,[N_2O_3]_0\,[OC_4H_8NH]_0 \tag{18}$$

If the steady-state approximation is assumed to hold for *Ac*ONO and N_2O_3, and bearing in mind that in the conditions used $[\text{nit}]_0 = [HNO_2]_0 + [NO_2^-]_0$, $[\text{Buf}] = [AcOH] + [AcO^-]$ and $[MOR]_0 = [OC_4H_8NH^+]_0$, then the following rate equation may be deduced:

$$v_0 = \frac{\left(1 + \gamma\dfrac{K_2\,[\text{nit}]_0}{K_2 + [H^+]} + \gamma\delta\dfrac{K_4\,[\text{Buf}]}{K_4 + [H^+]}\right)\alpha\beta\dfrac{K_2\,[\text{nit}]_0^2\,[MOR]_0\,[H^+]}{(K_2 + [H^+])^2}}{1 + \gamma\dfrac{K_2\,[\text{nit}]_0}{K_2 + [H^+]} + \gamma\delta\dfrac{K_4\,[\text{Buf}]}{K_4 + [H^+]} + \beta\dfrac{[MOR]_0}{[H^+]}\left(l + \gamma\dfrac{K_2\,[\text{nit}]_0}{K_2 + [H^+]}\right)} \tag{19}$$

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* Or $HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O$. The two are kinetically indistinguishable[2,4].

where $\alpha = K_3k_5$, $\beta = K_1k_8/k_{-5}$, $\gamma = k_7/k_{-6}$ and $\delta = k_6/k_5$. This equation agrees with that found experimentally at constant *pH* (Eq. 13), and Eq. (17) is likewise obeyed. By means of a non-linear optimization procedure described in a previous article[5] the rate constants which appear in Eq. (19) have been calculated on the basis of the 317 experiments carried out, with the following results*:

$\alpha = (1.63 \pm 0.02)\cdot 10^4\,M^{-2}\,s^{-1}$ $\quad$ $\delta = (0.54 \pm 0.04)$
$\beta = (7.60 \pm 0.09)\cdot 10^{-5}$ $\quad$ $K_2 = (1.070 \pm 0.007)\cdot 10^{-3}\,M$
$\gamma = (4.9 \pm 1.4)\cdot 10^2\,M^{-1}$ $\quad$ $K_4 = (6.6 \pm 1.8)\cdot 10^{-5}\,M$

The standard deviation of this fit, as defined by

$$\sigma = \left[\frac{1}{No-6}\sum_{i=1}^{No}\left(\frac{y_i-\hat{y}_i}{y_i}\right)^2\right]^{1/2}$$

is 0.028.

The values obtained above for the acidity constants of nitrous and acetic acids, K_2 and K_4, agree acceptably with published values obtained by other methods ($K_2 = 1.13\cdot 10^{-3}\,M$[15] and $K_4 = 4.39\cdot 10^{-5}\,M$[16] at $\mu = 0.5\,M$), which provides support for Eq. (19) when interpreting the influence of *pH* on the reaction. Eq. (19) also implies that the catalytic effect of the buffer should disappear not only when the concentration of amine is reduced which was indeed found experimentally, but also when the concentration of protons is increased which may be seen clearly in the curves of Fig. 6.

Several interesting kinetic constants may be calculated from the kinetic data obtained. In the first place, the rate constant for the formation of dinitrogen trioxide from nitrous acid ($2\,HNO_2 \xrightarrow{k} N_2O_3 + H_2O$, $k = K_2K_3k_5 = K_2\alpha$) is comparable with the value obtained by other authors at this temperature (Table 4) or at others[5]. The rate constant for the formation of nitrosyl acetate ($HNO_2 + H^+ + AcO^- \xrightarrow{k'} AcONO + H_2O$, $k' = K_3k_6 = \alpha\delta$) is also comparable with that obtained by *Döring* et al.[10] (Table 4).

The value of the constant k_8 can be calculated from various kinetic constants from published data for the acidity constant of morpholine ($pK_a = 8.70$ at $\mu = 0.5\,M$[19]) and the value of the equilibrium constant for the formation of N_2O_3 from nitrous acid recently determined by *Markovits* et al.[20]. ($K_{N_2O_3} = K_2K_3K_5 = (3.03 \pm 0.23)\cdot 10^{-3}\,M^{-1}$). The

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* A weighting factor of $1/y_i^2$ was used.

value obtained for $k_8 = \alpha\beta K_2/K_1 K_{N_2O_3}$ (Table 4)* is comparable with the value deduced from *Fan* and *Tannenbaum*'s data[21] for the nitrosation of morpholine in an aqueous perchloric medium.

The value of the rate constants k_{-7} and k_{-5} can also been calculated, for $k_{-7} = \alpha\gamma\delta K_2/K_{N_2O_3}$ and $k_{-5} = \alpha K_2/K_{N_2O_3}$ (since $k_5/k_{-5} = k_6 k_7/k_{-6} k_{-7}$). The values obtained are shown and compared with those of other authors in Table 4.

Table 4. *Rate constants obtained at 25 °C in the present study together with other published values*[a]

Reference	This paper	17	18	10	5	22	21
$k/M^{-1}\,s^{-1}$	17.4 ± 0.2	10	9.48	6.25[b]	29 ± 6	—	—
$10^{-4}\,k'/M^{-2}\,s^{-1}$	0.88 ± 0.07	—	—	2.1	—	—	—
$10^{-3}\,k_{-5}/s^{-1}$	5.7 ± 0.4	—	—	—	9 ± 2[c]	2	—
$10^{-8}\,k_8/M^{-1}\,s^{-1}$	2.2	—	—	—	—	—	0.75
$10^{-6}\,k_{-7}/M^{-1}\,s^{-1}$	1.5 ± 0.4	—	—	—	—	—	—
μ/M	0.5	0.1	—	1.0	1.0	—	—

[a] k and k' are the rate constants for the formation from nitrous acid of N_2O_3 and *Ac*ONO respectively, $k = K_2 K_3 k_5$ and $k' = K_3 k_6$.

[b] At an ionic strength of 0.2 *M*.

[c] Calculated from the results of Ref.[5] since $k_{-5} = 1/g\,K_{N_2O_3}$.

A further parameter that can be extracted from the kinetic data is $k_6/k_5 = 0.54$. Given that k_5, the rate constant for the reaction between the nitrous acidium and nitrite ions, is generally accepted[23] as being controlled by diffusion, the value found for k_6/k_5 implies that k_6 must likewise be diffusion controlled. The rate constant for the reaction of acetate with the nitrous acidium ion is therefore of an order lying within the narrow range found in studies of reactions between the nitrous acidium ion and a variety of anions[10,24].

Certain conclusions concerning the reactivity of N_2O_3 and *Ac*ONO may be drawn from the data obtained in the present study. The values for the rate constants k_8, k_{-7} and k_{-5} imply that the following order holds for the reactivity with N_2O_3: morpholine > acetate ion > water.

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* This value of k_8 has been included in the discussion published in Ref.[6] where it is accepted that the process is diffusion controlled.

The value of the ratio $k_7/k_{-6} = 490\,M^{-1}$ also shows that the nitrite ion reacts faster than water with AcONO. These relative reactivities of the various nucleophiles with respect to N_2O_3 and AcONO agree qualitatively with the order of their nucleophilicity constants n_{CH_3X} (X = Br, I) as established by the equation of *Swain* and *Scott*[25,26]. Good quantitative correlation should also be expected, since both the C of the CH_3X compounds and the N of XNO are rather soft acids[27]. *Biggs* and *Williams*[28] have indeed found a linear relationship between n_{CH_3Br} and the rate constants for the reactions of various anions with protonated nitrosamines ($R_2H\overset{+}{N}NO$). Although the data obtained in the present study are insufficient for us to draw quantitative conclusions, it is nevertheless logical to assume that the rate constant for the reaction of nitrosyl acetate with morpholine should be greater than those for its reaction with nitrite ion or with water. The fact that the nitrosyl acetate—morpholine reaction is not observed should therefore be due not to the low reactivity of nitrosyl acetate but rather to its concentration being much lower than that of N_2O_3, making this pathway undetectable. Since the value of the equilibrium constant K_6 is unknown, we are for the moment unable to confirm this hypothesis.

Final Remarks

When studying the kinetics of the nitrosation of dimethylamine in acetate buffer *Masui* et al.[7] found a simple rate equation with terms of order one with respect to amine and orders one and two with respect to nitrite, both terms being catalysed by the acetate. However, in previous studies carried out by ourselves[1,3] on the nitrosation of dimethylamine in perchloric media we have found only a single term that is of order two with respect to nitrite in the experimental conditions employed by *Masui*. The present study further shows that no catalysis is effected by the acetate in conditions in which the reaction is of order one with respect to morpholine, a discrepancy which might be explained by the concentrations of buffer used by *Masui* et al. having been much higher than those employed in the present study (4.5 M against 0.2 M), so that the catalytic effect they observed might be due to causes very different from those operative in our own work.

A final consideration is that our conclusions support those of *Döring*[10] and *Stedman*[9] to the effect that nitrosyl acetate is formed from the nitrous acidium and acetate ions in a reaction paralleling the formation of nitrosyl halides, rather than by the reaction between acetic and nitrous acids suggested by *Seel*[8].

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