Kinetics and Mechanism of the Nitrosation of 2-Nitropropane, 1-Nitropropane, and Nitroethane

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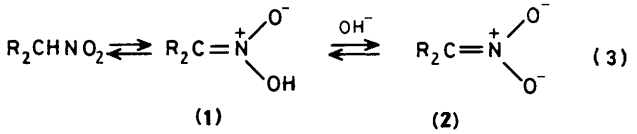
The kinetics of the nitrosation of the nitronic acids derived from 2-nitropropane, 1-nitropropane, and nitroethane, in aqueous perchloric acid using nitrous acid, show a first-order dependence upon the [nitronic acid] and a curved acidity dependence. The results are readily explained by a mechanism in which nitrosation (by $H_2NO_2^+$ or NO^+) occurs initially at an *oxygen* atom, and releasing a proton. The *O*-nitroso intermediate, which is formed reversibly, then undergoes an internal *O*- to *C*-nitroso group rearrangement to give the nitroso nitro product (pseudonitrole) from the secondary nitro compound, and (after tautomerisation) the nitro oxime product (nitrolic acid) from the primary nitro compounds. Neither the first nor the second step is fully rate-limiting, under the conditions used, but the first step is probably close to the diffusion-controlled limit. The reactions are strongly catalysed by Cl^-, Br^-, and SCN^-, but the measured rate constants show a curved dependence on $[Cl^-]$ and $[Br^-]$, suggesting that the intermediates are formed reversibly. However, the reactions are first-order in $[H^+]$, so that reaction now occurs *via* ClNO, BrNO, and ONSCN at the *carbon* atom of the nitronic acid. The results are discussed, together with those in the literature which describe nitrosation reaction where different nitrosating agents attack the same molecule at different sites. In all three cases studied a further, much slower reaction occurs, which results in the formation of more of the same products (when $[\text{nitronic acid}]_0 \gg [HNO_2]_0$). This reaction which is first-order in $[H^+]$ and [nitronic acid], but is not chloride or bromide ion-catalysed, also occurs when no nitrous acid is added. The product is formed by the slow hydrolysis of the protonated form of the nitronic acid, releasing nitrous acid, which reacts further with the unchanged nitronic acid.

It has long been known, since the pioneering work of Victor Meyer,[1] that aliphatic nitro compounds react in their nitronic acid (or nitronate ion) forms with a variety of nitrosating agents to give nitro oximes (nitrolic acids) if the nitro compounds are primary [equation (1)], or nitrosonitroalkanes (pseudonitroles) if the nitro compounds are secondary [equation (2)]; tertiary

$$RCH_2NO_2 \xrightarrow{HNO_2} RC(NOH)NO_2 \quad (1)$$

$$R_2CHNO_2 \xrightarrow{HNO_2} R_2C(NO)NO_2 \quad (2)$$

nitro compounds do not react. The usual procedure is to convert the nitro compound into the nitronate anion by dissolution in aqueous alkaline solution, then to acidify the solution and add nitrous acid. Reaction has also been effected by reaction of dinitrogen tetraoxide[2] with nitronic acids or nitronate anions. The reaction is quite general and a review exists[3] which lists the reactions known up to 1953. Although no mechanistic studies have been reported, the reaction appears to be one of electrophilic addition to the nitronic acid (**1**) or



(1) (2) (3)

nitronate anion (**2**) forms [equation (3)]. The various equilibria involved have been much studied,[4–6] and an unusual feature is the slow transformation of the nitro compound to the tautomeric nitronic acid. Acidification of (**2**) gives (**1**) which is stable enough relative to the nitro compound to allow other reactions to occur. In principle electrophilic reaction with (**1**) or (**2**) can take place either at oxygen or at carbon. Examples of both are known, *e.g.* alkylation and acylation[7] occur at oxygen whilst halogenation yields the halogenonitroalkane[8] which must involve *C*-halogenation. Electrophilic reactions of nitronates thus formally resemble such reactions of enols. Recently[9] a mechanistic investigation of the nitrosation of ketones has shown conclusively that the enols are the reactive species, at least in acid solution. Under certain experimental conditions, the rate of enolisation is rate-limiting, as is the case for halogenation and other electrophilic additions.

In this paper we report the results of a kinetic investigation of the nitronic acids derived from 2-nitropropane (2NP), 1-nitropropane (1NP), and nitroethane (NE), as typical aliphatic nitroalkanes, whose nitrosation products have already been described.[3] The objective is to establish for the first time the mechanistic pathway for these well known reactions.

Experimental

The three nitro compounds were fractionally distilled before use, using a middle fraction for the kinetic studies. All the other materials used were of the highest purity grade available. Stock solutions of the nitro compounds in aqueous sodium hydroxide were found to be stable over a period of days, but fresh solutions were prepared for each set of experiments.

Kinetic measurements were all carried out at 25 °C in aqueous solution. Two reactions were observed (a) a fast reaction corresponding to the complete disappearance of nitrous acid and this was followed by stopped-flow spectrophotometry at 370 nm (2NP) or 340 nm (1NP and NE) and (b) a slower reaction which was followed in a conventional spectrophotometer noting (for 2NP) the increasing blue absorbance at 637 nm due to the product nitrosonitroalkane. In all cases reaction was effected by addition of the stock solution of

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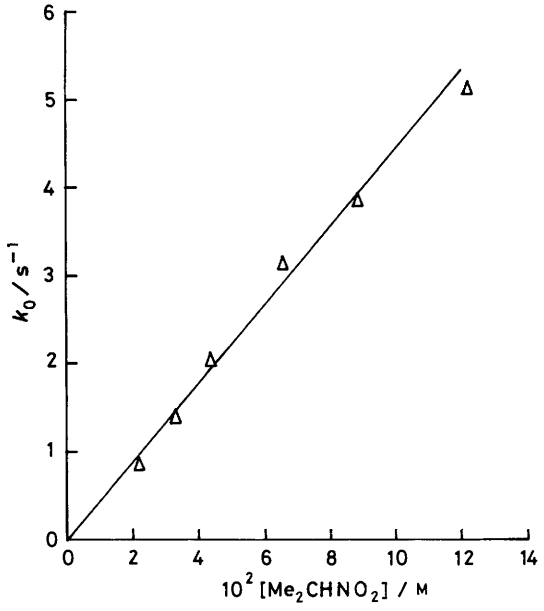


Figure 1. First-order dependence on the substrate in the nitrosation of the nitronic acid from 2NP

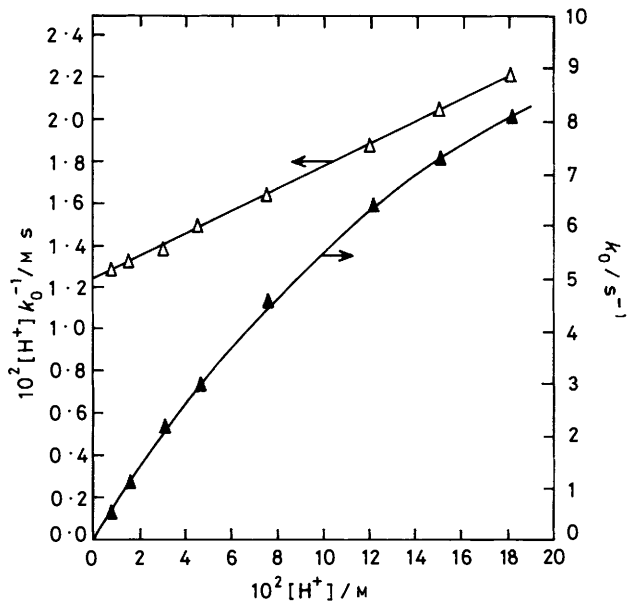


Figure 2. Acidity dependence and plot of $[H^+]/k_0$ *vs.* $[H^+]$ for the nitrosation of the nitronic acid from 2NP

the nitronate ion in aqueous alkali to one containing perchloric acid, sodium nitrite and sodium perchlorate (to maintain a constant ionic strength). For the nucleophile-catalysed reactions the latter solution also contained appropriate amounts of NaCl, NaBr, or NaSCN. The kinetic experiments were carried out under first-order conditions, with $[Nitronate]_0 \gg [HNO_2]_0$. Excellent first-order behaviour was found over at least three half-lives of the reactions, both for the first (faster) reaction and the second (slower) reaction. The quoted first-order rate constant k_0 (defined by $-d[HNO_2]/dt = k_0[HNO_2]$ for the faster reaction and by $-d[Nitronic\ acid]/dt = k_0[Nitronic\ acid]$ for the slower reaction) is the mean of at least five determinations for the stopped-flow measurements. Acid concentrations are corrected for the ionisation of nitrous acid where appropriate.

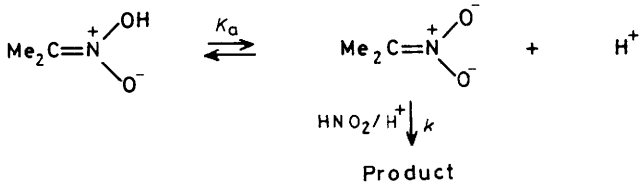
Blue colour developed slowly from the acidified solutions of the nitronate from 2NP even when no nitrous acid was added. This reaction yielded later a white precipitate which analysed as follows: C, 30.4; H, 5.1; N, 23.8; $C_3H_6N_2O_3$ requires C, 30.5; H, 5.1; N, 23.7%. This white solid, which dissolved in organic solvents to give blue solutions, gave an i.r. spectrum identical with that of the nitroso nitroalkane dimer obtained from 2-nitropropane (in its nitronic acid form) and nitrous acid.

Results and Discussion

(a) *Experiments with 2-Nitropropane (2NP).*—Acidic solutions of 2NP gave no perceptible nitrosation reaction (*i.e.* no blue colour) with nitrous acid. Indeed the only observable change over a significant time (even at quite high acidities) is the decomposition of nitrous acid. It appears that the tautomerisation of Me_2CHNO_2 in acid solution is too slow to be measured in this way. This contrasts with the behaviour of ketones in a whole range of reactions involving electrophilic addition (including nitrosation[9]) to the enol form. However if the nitro compound is first converted into its nitronate anion by dissolution in aqueous sodium hydroxide, then when the solution is acidified with a solution containing nitrous acid then the blue colour of the nitroso product is obtained very rapidly. Kinetic measurements of this reaction were carried out using stopped-flow spectrophotometry. At a constant final acidity, the reaction is strictly first-order in $[2NP]_0$ as shown by the excellent linear plot in Figure 1 of k_0 *vs.* $[2NP]_0$. The dependence of the rate constant upon acidity however is not linear, but has a downward curvature, as shown typically in Figure 2. There is a tendency for the reaction to lose its first-order acid dependence at high $[H^+]$, but we have not achieved the limiting zero-order situation in the acid range used in our experiments. This type of behaviour results if the acid dependence of k_0 is of the type given in equation (4). This

$$k_0 = a[H^+]/(1 + b[H^+]) \quad (4)$$

relationship is confirmed quantitatively by the observation of a good straight line plot between $[H^+]/k_0$ *vs.* $[H^+]$, with a positive intercept and positive slope, again as shown typically in Figure 2. One explanation of this would be if reaction occurs *via* the nitronate anion and not the nitronic acid species as outlined in Scheme 1. The rate equation expected from Scheme 1 is that



Scheme 1.

given in equation (5), which is the same form as equation (4).

$$k_0 = k[2NP]_0K_a[H^+]/(K_a + [H^+]) \quad (5)$$

Here k is the third-order rate constant for the reaction of $H_2NO_2^+$ (or NO^+),* $[2NP]_0$ is the total stoicheiometric

* There is some uncertainty over the exact nature of the nitrosating agent in dilute aqueous acid solution. We shall refer to $H_2NO_2^+$ for the remainder of this paper, but the choice is not relevant to the main mechanistic arguments presented.

Table 1. Values of d (l mol^{-1} s^{-1}) from equation (7) for the nitrosation of 2NP *via* ClNO and BrNO[a]

ClNO		BrNO	
[H$^+$]/M	d	[H$^+$]/M	d
1.00 × 10^{-2}	33	9.22 × 10^{-3}	79
1.92 × 10^{-2}	64	1.23 × 10^{-2}	100
3.90 × 10^{-2}	132	1.39 × 10^{-2}	101
		1.98 × 10^{-2}	195
		4.00 × 10^{-2}	315
		7.00 × 10^{-2}	510

[a] *Experimental conditions.* [2NP]$_0$ 3.22 × 10^{-2}M, Cl$^-$ 0—0.4M (constant ionic strength 0.45M), Br$^-$ 0—0.2M (constant ionic strength 0.35M).

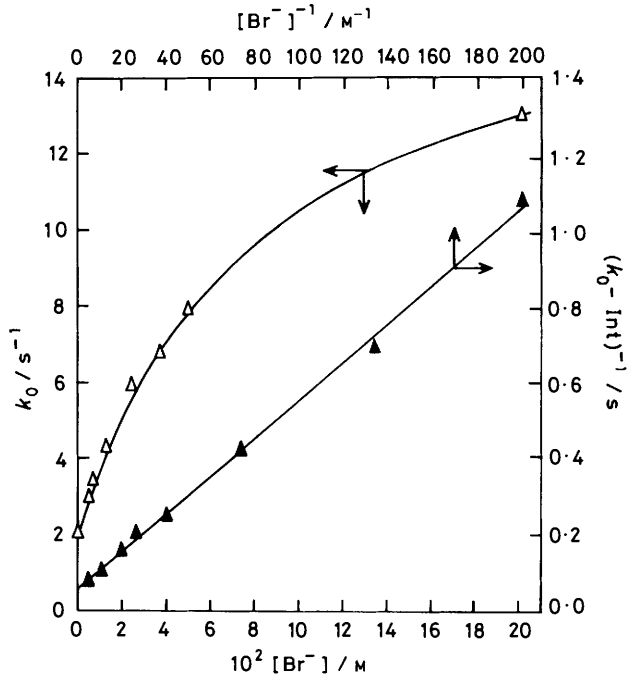


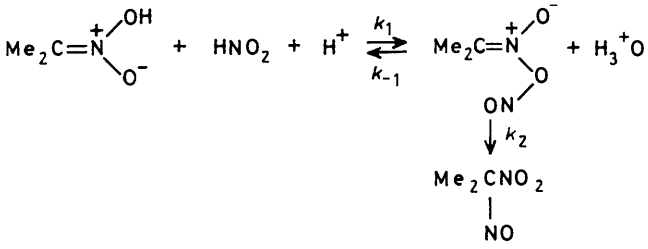
Figure 3. Bromide ion catalysis and double reciprocal plot for the nitrosation of the nitronic acid from 2NP

concentration of the reactant and K_a for this nitronic acid is known[6] to be 7.9 × 10^{-6}, so that under our experimental conditions [H$^+$] is always $\gg K_a$, so that equation (6) is reduced to a form which predicts that k_0 should be independent of acidity. This is clearly not so, and so we can rule out reaction *via* the nitronate anion species.

An alternative explanation, which does fit with the experimental results, emerges if we consider that nitrosation occurs initially and reversibly at the oxygen atom of the nitronic acid (concurrently with a proton-loss) and that the *O*-nitroso intermediate then undergoes an internal nitroso group rearrangement from oxygen to carbon to give the final product, as is shown in Scheme 2. Again k_1 is the third-order rate constant (from rate = k_1[HNO$_2$][H$^+$][Substrate]), and k_2 is the rate constant for the rearrangement process. This mechanism leads to the general expression for k_0 given in equation (6) which is

$$k_0 = k_1[2NP]_0[H^+]/(1 + k_{-1}[H^+]/k_2) \qquad (6)$$

also the same form as that found experimentally [equation (4)]. Analysis of the data in Figure 2 yields a value of 3 700 l^2 mol^{-2} s^{-1} for k_1 and 4.4 l mol^{-1} for k_{-1}/k_2. A duplicate set of results



Scheme 2.

similarly gave k_1 as 3 200 l^2 mol^{-2} s^{-1} and k_{-1}/k_2 as 3.9 l mol^{-1}. Using the average values, the calculated slope for Figure 1 is 46.3 l mol^{-1} s^{-1}, compared with the measured value of 44.7 l mol^{-1} s^{-1}. The magnitude of k_1 suggests that the reaction of $H_2NO_2^+$ at the oxygen atom occurs at or close to the diffusion-controlled limit,[10] since for a wide variety of substrates there appears to be a limiting value for the third-order rate constant which is around 7 000 l^2 mol^{-2} s^{-1} at 25 °C.

Nitrosation at one reactive point in a molecule followed by rearrangement to yield the final product where the nitroso group is attached elsewhere is not a new idea. It has been established in recent years in a number of cases, for example in the diazotisation of amino acids containing the –SR group[11] (*S* to *N* rearrangement), the nitrosation of tryptophan[12] (*C* to *N* rearrangement), and also in the nitrosation of amides[13] (*O* to *N* rearrangement). In the present case the rearrangement implies that a four-membered cyclic transition state is involved, which is less favourable sterically than the five- or six-membered ring situations. The same point applies to the rearrangement proposed in the nitrosation of tryptophan[12] and of amides.[13] In all of these cases it is not possible to be certain that the rearrangement is concerted, and may occur in a step-wise fashion, as is thought to be the case in 1,3 rearrangements of the nitro group in some electrophilic aromatic nitration reactions involving *ipso* attack.[14]

Nitrosation of amines and other substrates are generally catalysed strongly by the presence of non-basic nucleophiles such as halide ions. When strongly electron-withdrawing groups are present (as in amides for example) this catalysis disappears. This has been rationalised[15] in terms of whether the attack of the nitrosating agent, or the subsequent reaction of the intermediate, is the rate-limiting step. Nucleophilic catalysis (or its absence) has not previously been reported in the nitrosation of nitronic acids.

We find that Cl$^-$, Br$^-$, and SCN$^-$ strongly catalyse the nitrosation of the nitronic acid derived from 2NP. For both Cl$^-$ and Br$^-$ the rate constant is not linearly dependent upon [Cl$^-$] or [Br$^-$], as shown typically in Figure 3. The intercept represents the non-catalysed part of the reaction (*i.e.* reaction *via* $H_2NO_2^+$). At low [Br$^-$], k_0 is approximately proportional to [Br$^-$] but as [Br$^-$] is increased there is a tendency for k_0 to become independent of [Br$^-$], although we do not achieve the limiting condition here. This type of behaviour is also known for other reactions *e.g.* in the nitrosation (diazotisation) of some anilines and naphthylamines in water,[16,17] anilines in methanol,[18] the nitrosation of naphthols,[19] and also for some nitrosations in an alcohol solvent using an alkyl nitrite.[20] These situations are thought to represent intermediate conditions when neither the attack of the reagent nor the subsequent reaction of the intermediate is fully rate-limiting.

Such a mechanism requires the dependence of k_0 upon a general nucleophile X$^-$ to be of the form given in equation (7),

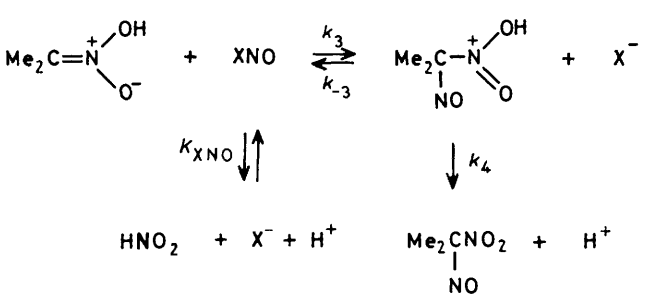
$$k_0 = \text{Int} + \{d[X^-]/(1 + e[X^-])\} \qquad (7)$$

where Int represents the non-catalysed component. Plots of

Table 2. Rate constants for the reaction of various nitrosating agents with nitronic acids derived from 2NP, 1NP, and NE[a]

	$H_2NO_2^+/NO^+$		ClNO		BrNO		ONSCN
Nitro compound	k_1[d]	k_{-1}/k_2[e]	k_3[f]	k_{-3}/k_4[g]	k_3[f]	k_{-3}/k_4[g]	k_3[f]
2-Nitropropane (2NP)	3 650[b]	4.3[b]	8.8×10^7	5.4	5.1×10^6	13	8.6×10^3
	3 150[c]	3.9[c]					
1-Nitropropane (1NP)	3 500	4.0	1.0×10^8	3.6	8.2×10^6	5.9	3.3×10^4
Nitroethane (NE)	3 550[b]	4.1[b]	8.4×10^7	2.8	7.8×10^6	5.7	2.2×10^4
	3 680[b]	3.8[c]					

[a] All values refer to reactions at ionic strength 0.35M except those for ClNO reactions (0.40M). [b,c] Duplicate experiments. [d] In l^2 mol^{-2} s^{-1}, see Scheme 2. [e] In l mol^{-1}, see Scheme 2. [f] In l mol^{-1} s^{-1}, see Scheme 3. [g] In l mol^{-1}, see Scheme 3.



Scheme 3.

$(k_0 - \text{Int})^{-1}$ *vs.* $[X^-]^{-1}$ should then be linear with positive slopes and intercepts. We found such behaviour for all the Cl^-- and Br^--catalysed reactions. A typical plot is also shown in Figure 3. These experiments have been extended over a range of acidity (for both Cl^- and Br^-), and all give good double reciprocal plots. Values of d are given in Table 1 for the two nucleophiles. In both cases d is found to be directly proportional to $[H^+]$, with no hint of curvature. The implication of this is that ClNO and BrNO react with the nitronic acid (and not the nitronate anion), directly at the carbon atom, to yield the product nitroso nitroalkane. Such a mechanism is set out in Scheme 3 and the expression for k_0 expected from this Scheme is given in equation (8). This equation is the same form as the

$$k_0 = k_3K_{XNO}[H^+][X^-][2NP]_0/(1 + k_{-3}[X^-]/k_4) \quad (8)$$

second part of equation (7) which represents the X^--catalysed pathway. When $k_4 \gg k_{-3}[X^-]$ (at low $[X^-]$) there is a first-order $[X^-]$ dependence, and when $k_4 \ll k_{-3}[X^-]$ then X^- catalysis should disappear. Similar curved plots of k_0 *vs.* $[X^-]$ occur when a reverse reaction can be examined, *e.g.* such as the denitrosation of nitrosamines,[21] when the same rate constant inequalities apply. In the present case values of k_3 determined from the double reciprocal plots are 8.8×10^7 l mol^{-1} s^{-1} (ClNO) and 4.6×10^6 l mol^{-1} s^{-1} (BrNO); this demonstrates further the usual reactivity sequence ClNO > BrNO. Similarly k_{-3}/k_4 values are 5.4 l mol^{-1} (Cl^-) and 13 l mol^{-1} (Br^-), which reflects the greater nucleophilicity of bromide ion in water.

Marked catalysis is also found by the addition of low concentrations of SCN^-. In this case however k_0 *vs.* $[SCN^-]$ is linear at all acidities over the range studied. Plots for three acid concentrations are shown in Figure 4. No curvature exists here since $k_{-3}[SCN^-]$ is not comparable with k_4. A value of k_{-3}/k_4 for SCN^- can be estimated from the data for Cl^- and Br^- and using the Pearson nucleophilicity parameter.[22] From the data in Figure 4 (and from the results for two other acidities not shown), we obtained a value of 8.6×10^3 l mol^{-1} s^{-1} for k_3 for the reaction of ONSCN with the nitronic acid. Again this fits in well with the well established reactivity trend, ClNO > BrNO > ONSCN. The nitronic acid derived from 2NP has a reactivity towards all nitrosating species which lies between those of the enols from acetyl acetone and acetone.[9]

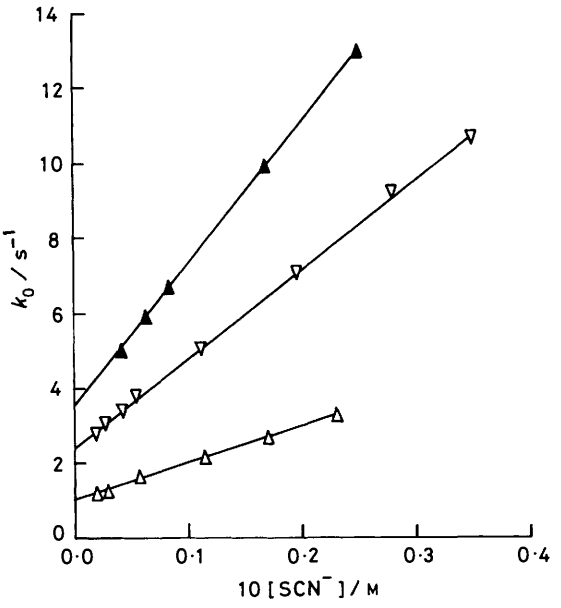


Figure 4. Thiocyanate catalysis at different acidities in the nitrosation of the nitronic acid from 2NP. △ $[H^+]$ 1.25×10^{-2}M; ▽ $[H^+]$ 2.53×10^{-2}M; ▲ $[H^+]$ 4.10×10^{-2}M

(b) *Reactions of* 1-*Nitropropane* (1*NP*) *and Nitroethane* (*NE*).—Both these primary nitroalkanes reacted in their nitronic acid forms rapidly with nitrous acid. In these cases no blue colour developed since the products are known[3] to be the nitro oximes. The first (fast) reaction was studied kinetically as in (a) and the pattern of behaviour was very similar to that found for 2NP. The derived rate constants are also very similar and are shown in Table 2. All three substrates show curved k_0 *vs.* $[H^+]$ plots and also curved k_0 *vs.* $[Br^-]$ and $[Cl^-]$ plots. The mechanistic conclusions are probably general for all nitronic acids, and are summarised in Schemes 2 and 3. Reaction *via* $H_2NO_2^+$ probably occurs reversibly at the oxygen atom of the nitronic acid and this is followed by a rearrangement reaction of the nitroso group. Over the acid range studied (0—0.2M) neither step is fully rate-limiting, but in principle either could be made so. The first step probably occurs close to the encounter limit. Similarly reactions *via* XNO occur by reversible formation of an intermediate and again over our range of concentrations neither its formation nor subsequent reaction is fully rate-limiting.

The unusual feature of the mechanistic conclusions is that $H_2NO_2^+$ attacks the oxygen atom of the nitronic acid (at least

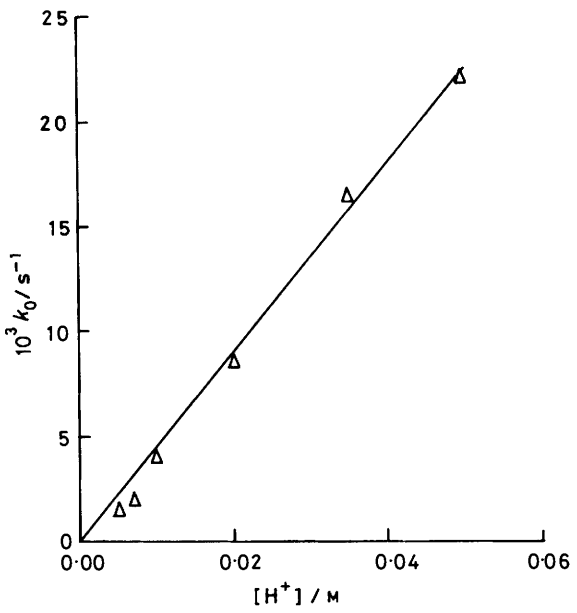
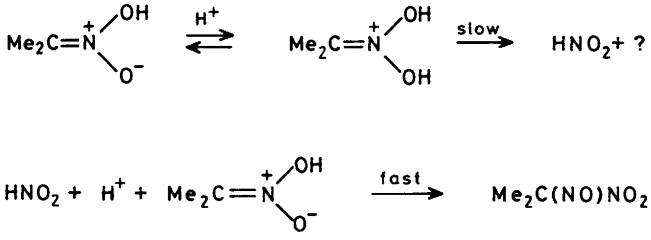


Figure 5. First-order acidity dependence in the reaction of the nitronic acid from 2NP (without added nitrous acid)

initially), whereas ClNO, BrNO, and ONSCN appear to react directly at the carbon atom. There are however other examples in the literature which describe the same situation. The kinetic results for the nitrosation of both thioproline[23] and thiourea[24] fit mechanistic schemes in which $H_2NO_2^+$ reacts initially at the sulphur atom, and this is followed by a *S* to *N* rearrangement, whereas XNO species generally react directly at the nitrogen atom. Similarly, in the nitrosation of proline,[13] there is a significant pathway involving *O*-nitrosation (followed by *O* to *N* rearrangement) in addition to a direct *N*-nitrosation. In the corresponding reactions of XNO with proline the pathway *via* *O*-nitrosation is very much smaller.[25] These differences may be rationalised in terms of HASB theory, from which it is to be expected that the relatively soft $H_2NO_2^+$ (hydrated NO^+) would react preferentially at the soft sulphur (or oxygen) atom, rather than at the harder nitrogen atom. In our reactions with the nitronic acids the explanation may simply be that the positively charged $H_2NO_2^+$ is drawn electrostatically to the (partially) negatively charged oxygen atom in the nitronic acid.

(c) *The Slower Nitrosation Reaction.*—For all three substrate a further slower reaction was observed when all the nitrous acid initially added had disappeared. This reaction is sufficiently slow not to interfere with the initial faster reaction, and both can be studied separately. This reaction was studied kinetically only for the nitronic acid derived from 2NP. A further increase of absorbance at 637 nm was noted. The blue solution in some cases precipitated a white solid which was shown to be the dimer of the nitrosonitroalkane *i.e.* $[Me_2C(NO)NO_2]_2$, by elemental analysis and by comparison of its i.r. spectrum with that of a sample prepared directly from 2NP (in its nitronic acid form) and nitrous acid. The reaction is indeed known in the literature[5,26] and occurs alongside the Nef reaction[27] (which yields carbonyl compounds), when alkaline solution of nitronic acids are acidified. Both these reactions also compete with the slow tautomerisation of the nitronic acid to the nitro compound. Some patent references[28] refer to the choice of the best experimental conditions for the direct production of nitrosonitroalkanes by this procedure. A transient blue colour only is seen in the corresponding reactions of 1NP and NE, no doubt because the nitroso compound undergoes a tautomeric shift to give the nitro oxime (a nitrolic acid), again a known literature reaction.

The kinetics of the formation of the blue product were carried out (a) as the slow reaction after all the added nitrous acid has been used up and also (b) as the reaction occurring when the nitronate anion is acidified without the addition of nitrous acid. The results of (a) and (b) are the same. The reaction is a first-order process in [nitronic acid] and is also first-order in $[H^+]$ (see Figure 5) over the range 0—0.5M (at ionic strength 0.35M). The value of the second-order rate constant is 0.474 l mol^{-1} s^{-1} at 25 °C, which compares reasonably with the value reported by Armand[26] (over a different acid range) of 0.283 l mol^{-1} s^{-1} at 21 °C. The rate constant is unaffected by the addition of Cl^- and Br^- up to 0.2M. Using the quoted extinction coefficient[26] for the blue product, we find that the yield in these reactions is ~40%, based on the 2NP used up. The results confirm those of Armand[26] and show that nitrous acid is formed in the rate-limiting step from the nitronic acid, in an acid-catalysed reaction, probably involving the protonated form. The nitrous acid released reacts rapidly (*via* $H_2NO_2^+$ or ClNO if Cl^- is present) with the unchanged nitronic acid to give the blue product (see Scheme 4). The mechanism for the release of



Scheme 4.

nitrous acid (and the nature of the organic product formed) is a matter for conjecture at this stage.

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