Kinetics of the Reactions of Nitrous Acid with Olefins. Kinetic Identification of Probable Nitrosating Agents

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The overall reactivity of the following olefins towards nitrous acid in water has been found to decrease along the series 2,3-dimethylbut-2-ene (I) > 2-methylbut-2-ene (II) ≫ 2-methylprop-2-enol (III) > 2-methylprop-2-enyl chloride (IV), indicating the electrophilic nature of the reagent. At low acidity for (I) and (II) the reaction was of the second order in nitrous acid suggesting reaction *via* N_2O_3, whereas at higher acidities for all four olefins the reaction was of the first order in nitrous acid and also of first order in mineral acid, which is interpreted in terms of reaction *via* $H_2N^+O_2$. Both chloride- and bromide-ion catalysis was observed, the kinetics of these catalysed reactions being consistent with the formation of and reaction by the nitrosyl halides, with nitrosyl chloride being *ca.* 6 times more reactive than nitrosyl bromide towards (III). The nitrosyl halide reactions showed only a small dependence upon the substituents in the olefin whereas the nitrous acidium ion ($H_2N^+O_2$) had selectivity comparable with that shown in bromination. The results are compared with those obtained for the nitrosation of aromatic amines.

AQUEOUS acid solutions of an inorganic nitrite contain reagents capable of effecting electrophilic nitrosation particularly at nitrogen sites. Diazotisation of primary aromatic amines involves *N*-nitrosation,[1] followed by a series of fast reactions which yield finally the diazonium ion, whereas for secondary aromatic amines the *N*-nitroso-compound is generally the product of reaction. In both cases the effective nitrosating agents have been identified kinetically as the nitrous acidium ion $H_2N^+O_2$, the

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

nitrosonium ion NO^+, dinitrogen trioxide N_2O_3, and the nitrosyl halides NOX. Generally reaction by any one reagent predominates depending upon the concentration, acidity, and presence of halide ions. In some cases either the rate of formation of, or of reaction by, the nitrosating agent may be the rate-determining step, depending upon the reactivity of the substrate. Most of the kinetic work involving nitrosation has been confined to the reactions of aromatic amines although it is known that aqueous acidic solutions of nitrites will nitrosate other materials such as olefins[2] and some activated aromatic compounds (*e.g.*, ref. 3). Relatively few mechanistic studies have been concerned with nitrosation with other nitrosating agents, although it has been shown[4] that the kinetics of the reaction between nitrosyl chloride and olefins in chloroform are consistent with an electrophilic process.

It was the purpose of this work to examine kinetically the reaction of nitrous acid with olefins in an attempt to identify the effective nitrosating agents and so to compare the behaviour of *C*- and *N*-nitrosations.

RESULTS AND DISCUSSION

Rates of reaction of nitrous acid with the four olefins (I)—(IV) were determined over a wide range of acidity.

$Me_2C=CMe_2$
(I)

$MeCH=CMe_2$
(II)

$CH_2=CMe\cdot CH_2OH$
(III)

$CH_2=CMe\cdot CH_2Cl$
(IV)

In all cases the reactions were of the first order with respect to the olefin concentration since at several acidities the plot of log (initial rate) against log [olefin] was linear with unit slope for a wide range of olefin concentrations.

Dependence upon Nitrous Acid Concentration.—For 2,3-dimethylbut-2-ene (I) at 1×10^{-4}M-perchloric acid the reaction was of the second order in ' total nitrite ' as the second-order rate coefficients $\bar{k}_2$* (for a given excess of olefin concentration) are constant throughout any one run whereas the corresponding first-order values $\bar{k}_1$ decrease markedly during the same period as shown in Table 1. At this low acidity the rate equation is given by equation (1), which can readily be interpreted as a rate-determining attack on the olefin by the dinitrogen

$$\text{Rate} = {}^2k_3[\text{Olefin}][HNO_2]^2 \qquad (1)$$

trioxide molecule N_2O_3 which is formed from two molecules of nitrous acid as is shown in Scheme 1. The

$$\begin{array}{lll} 2HNO_2 \rightleftharpoons N_2O_3 + H_2O & & \text{fast} \\ N_2O_3 + {>}C{=}C{<} \longrightarrow \text{products} & & \text{slow} \end{array}$$

SCHEME 1

average value of the rate coefficient ${}^2k_3$ from several runs is $7\cdot0 \times 10^4$ mol^{-2} l^2 min^{-1}. At higher acidities the second-order dependence upon nitrite disappeared to be replaced at acidities greater than 1×10^{-3}M-perchloric acid by a first-order dependence as shown in Table 2 where the $\bar{k}_2$ values now increase whilst the $\bar{k}_1$ values are effectively constant. At intermediate acidities mixed-order kinetics were observed, each run being analysed in terms of concurrent first- and second-order processes. The reaction is also of the first order in

$$\text{Rate} = {}^1k_3[\text{Olefin}][HNO_2][H^+] \qquad (2)$$

$[H^+]$ above 8×10^{-4}M as shown in the constancy of the rate-coefficient ${}^1k_3$ from equation (2) which is shown in Table 3 for a range of acid concentrations. These results are consistent with Scheme 2, whereby the protonated

TABLE 1

A typical run for the reaction of olefin (I) ($1\cdot20 \times 10^{-3}$M) with HNO_2 (1×10^{-4}M) and $HClO_4$ ($1\cdot07 \times 10^{-4}$M)

t/h	Optical density	$10^3\ \bar{k}_1$/h^{-1}	$10^{-2}\ \bar{k}_2$/ mol^{-1} l h^{-1}
0·00	0·389		
23·43	0·298	11·3	1·30
37·52	0·260	10·7	1·32
51·57	0·230	10·1	1·34
78·30	0·203	8·3	1·17
102·47	0·184	7·3	1·09
132·90	0·156	6·8	1·12
167·62	0·127	6·6	1·23
222·23	0·109	5·7	1·16

TABLE 2

A typical run for the reaction of olefin (I) ($1\cdot17 \times 10^{-3}$M) with HNO_2 ($0\cdot6 \times 10^{-4}$M) and $HClO_4$ ($7\cdot56 \times 10^{-4}$M)

t/h	Optical density	$10\ \bar{k}_1$/h^{-1}	$10^{-3}\ \bar{k}_2$/ mol^{-1} l h^{-1}
0	0·392		
1·0	0·319	2·06	2·29
1·5	0·301	1·76	2·01
2·0	0·263	1·99	2·45
3·5	0·207	1·82	2·55
4·5	0·175	1·79	2·75
6·0	0·133	1·80	3·24
8·0	0·095	1·77	3·91
10·0	0·068	1·75	4·76

TABLE 3

Values of ${}^1k_3$ over a range of acid concentrations

$10^4[HClO_4]$/M	$10^{-3}\ {}^1k_3$/mol^{-2} l^2 min^{-1}
8·56	4·58
12·85	5·00
17·13	4·45
42·6	4·74
85·2	4·80
211·1	4·82

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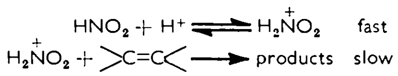
* $\bar{k}_2$ Is the stoicheiometric rate coefficient. Molecular rate coefficients k_2 (without the bar) are calculated with reference to the molecular concentrations of the reactants. $\bar{k}_2$ and k_2 Differ at low acidities since a significant fraction of the nitrous acid exists as the nitrite anion.

[2] E. C. Kooyman, E. Farenhorst, and E. G. G. Werner, *Rec. Trav. chim.*, 1951, **70**, 689.

[3] R. O. C. Norman and R. Taylor, ' Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, p. 315.

[4] T. Beier, H. G. Hauthal, and W. Pritzkow, *J. prakt. Chem.*, 1964, **4**, 304.

form of nitrous acid (the nitrous acidium ion $H_2N^+O_2$) acts as the nitrosating agent. So far as the kinetic results are concerned nitrosation by the free nitrosonium ion NO^+ (formed from $H_2N^+O_2$) would be equally consistent with our results but this is considered unlikely at the relatively low acid concentrations studied.



$$HNO_2 + H^+ \rightleftharpoons H_2\overset{+}{N}O_2 \quad \text{fast}$$
$$H_2\overset{+}{N}O_2 + >C{=}C< \longrightarrow \text{products} \quad \text{slow}$$

SCHEME 2

Thus both N_2O_3 and $H_2N^+O_2$ are considered to be effective nitrosating agents here as in the diazotisation of amines where both mechanisms have been well established kinetically for a number of substrates.[1]

Similar behaviour was observed in the reaction of 2-methylbut-2-ene (II). At acidities less than 7×10^{-4}M the reaction was of the second order in nitrous acid, the molecular rate coefficient $^2k_3$ [equation (1)] having the value $1{\cdot}0 \times 10^4$ mol^{-2} l^2 min^{-1}. Thus, as expected for an electrophilic process, we have the reactivity sequence (I) > (II), the ratio of the rate coefficients $^2k_3$ being *ca.* 7. At higher acidities the reaction became of mixed order in nitrous acid, but did not, even at 0·1M-perchloric acid, become of pure first order in nitrous acid. From a detailed analysis of the rate equation for concurrent first- and second-order processes [equation (3)] it was possible to determine the values of both $^1k_3$ and $^2k_3$ as $4{\cdot}2 \times 10^2$ and $0{\cdot}9 \times 10^4$ mol^{-2} l^2 min^{-1} respectively. The value of $0{\cdot}9 \times 10^4$ agrees well with the value

$$\text{Rate} = {}^1k_3[\text{Olefin}][HNO_2][H^+] + {}^2k_3[\text{Olefin}][HNO_2]^2 \quad (3)$$

($1{\cdot}0 \times 10^4$) obtained at very low acidities where the reaction is of pure second order in nitrous acid. The value of $^1k_3$ ($4{\cdot}2 \times 10^2$) indicated that (I) is about ten times more reactive than (II) towards $H_2N^+O_2$ again as expected for an electrophilic process. Similar rate ratios have been observed [5] in bromination.

The olefin reactivity range was extended to include 2-methylprop-2-enol (III) and 2-methylprop-2-enyl chloride (IV). Both were too unreactive to enable the reaction *via* N_2O_3 in the very low acid region to be detected, since convenient rate measurements were only obtained in perchloric acid greater than 0·4M.

In this acid region the reaction of (IV) with nitrous acid was of the first order in nitrous acid and apparently acid-catalysed since a linear plot of log k_{obs} against $-H_0$ was obtained with a slope of 0·8. However experiments at constant ionic strength with sodium perchlorate showed that the observed catalysis was due at least in part to some medium effect produced by the perchlorate anion which appears to supersede the acid catalysis by the proton under these conditions. The medium effect has also been observed in the diazotisation of aniline [6] and can be expressed by equation (4). In our case m is *ca.* 0·22 compared with 0·27 for the diazotisation of aniline [6] and 0·22 for the diazotisation of 4-aminopyridine.[7] In order to avoid confusion due to

$$\log k = \log k^0 + m[ClO_4^-] \quad (4)$$

this medium effect at these relatively high concentrations of the perchlorate anion further kinetic measurements with (III) and (IV) were carried out in sulphuric acid where no such medium effect has been observed. Both olefins showed a first-order dependence upon nitrous acid and olefin concentration and again acid catalysis was evident as shown in Table 4, by the variation of $^1k_2$ from equation (5) with h_0. A plot of log $^1k_2$ against

$$\text{Rate} = {}^1k_2[HNO_2][\text{Olefin}] \quad (5)$$

$-H_0$ is quite a good straight line of slope 1·3. These results suggest a mechanism whereby the rate-determining stage is the attack of the nitrous acidium ion $H_2N^+O_2$ upon the olefin. The solvent isotope effect $k_{D_2O} : k_{H_2O}$ was measured at 4 °C in a solution of 1·5M-sulphuric acid and was found to be 2·2 which would correspond to a twofold increase in the concentration of the nitrous acidium ion on changing the solvent from H_2O to D_2O. Solvent isotope effects of this magnitude are common for acid-catalysed reactions proceeding by way of a protonated base and in particular for diazotisation of *p*-nitroaniline [8] under conditions where the effective nitrosating agent is thought to be the nitrous acidium ion.

TABLE 4

Variation of $^1k_2$ with acidity in the nitrosation of olefin (III)

$[H_2SO_4]$/M	h_0 *	$10^2\ {}^1k_2$/ mol^{-1} l min^{-1}
0·225	0·30	3·7
0·45	0·66	7·9
0·90	1·58	28·3
1·35	3·10	83·3
1·80	5·89	111
2·25	10·6	285
2·70	17·5	847

* E. B. Robertson and H. B. Dunford, *J. Amer. Chem. Soc.*, 1964, **86**, 5080.

The same rate equation (6) is obeyed for the reaction of (IV) with nitrous acid over the same acidity range.

$$\text{Rate} = {}^1k_3[HNO_2][\text{Olefin}]h_0 \quad (6)$$

As expected, compound (III) is more reactive than (IV), the ratio of the rate coefficients $^1k_3$ being *ca.* 30. It was found that $^1k_3$ was greater by a factor of two in perchloric acid than in sulphuric acid for the reaction of (IV), supporting the idea, already discussed, of a catalytic medium effect by the perchlorate anion. For olefins (I) and (IV) the ratio of $^1k_3$ is of the order of 10^5 which is comparable with that observed in bromination of these olefins in methanol [5] suggesting that the reagents bromine and the nitrous acidium ion have similar

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[5] J. E. Dubois and E. Goetz, *J. Chim. phys.*, 1966, 780; D. L. H. Williams, unpublished work.

[6] B. C. Challis and J. H. Ridd, *J. Chem. Soc.*, 1962, 5197.

[7] E. Kalatzis, *J. Chem. Soc.* (*B*), 1967, 277.

[8] B. C. Challis, L. F. Larkworthy, and J. H. Ridd, *J. Chem. Soc.*, 1962, 5203.

selectivities. This contrasts with the apparent lack of discrimination shown by the nitrous acidium ion in diazotisation for variously substituted aniline derivatives where, however, it has been suggested [1] that the reactions are encounter-controlled. In the present work the olefins studied are much less reactive towards nitrous acid than are the aniline derivatives and the rate coefficients are far from the encounter-controlled values so that the reactions of nitrous acid with olefins give a clearer picture of the relative reactivity of the nitrous acidium ion.

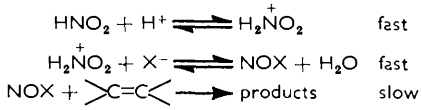
Catalysis by Halide Ion.—It is well known that in diazotisation [9] catalysis is brought about by added halide ion by, it is thought, formation of the corresponding nitrosyl halide which then becomes the effective nitrosating agent. We have examined the effect of added sodium bromide and sodium chloride in the reaction of nitrous acid with (III) and (IV). The results for (III) are set out in Table 5 as the variation of ${}^1k_3{}^{\text{obs}}$ [from equation (7)] with added halide ion. The catalysed reaction showed the same kinetic dependence upon the olefin concentration and h_0 as did the uncatalysed reaction so we can write the rate equation for the catalysed reaction as equation (7). If the reaction now involves concurrent reactions of $H_2N^+O_2$ and NOX with the olefin (Scheme 3) then it can be shown that ${}^1k_3{}^{\text{obs}} = {}^1k_3 + {}^1k_3{}^xK^x[X^-]$ where K^x is the equilibrium constant for the formation of the nitrosyl halide from nitrous acid and the halide ion X^- and ${}^1k_3$ and ${}^1k_3{}^x$ refer to equations (8) and (9). With the somewhat limited data from Table 5 the plot of ${}^1k_3{}^{\text{obs}}$ against $[Br^-]$ is reasonably linear (although the point for $0{\cdot}2$M-$[Br^-]$ is a little low). From the slope of this line and the value [10] of K^x for nitrosyl bromide ($2{\cdot}2 \times 10^{-2}$) we get ${}^1k_3$ for the bromide-catalysed reaction to be 28 ± 4 mol^{-2} l^2 min^{-1}. Catalysis by chloride ion is less pronounced than that by bromide ion as is evident from Table 5 but this is due to the much smaller value [11] for K^x for nitrosyl chloride formation ($5{\cdot}4 \times 10^{-4}$), yielding a value of $1{\cdot}6 \pm 0{\cdot}3 \times 10^2$ mol^{-2} l^2 min^{-1} for ${}^1k_3$ for the nitrosyl chloride reaction, so that nitrosyl chloride is about six times more reactive towards olefin (III) than is nitrosyl bromide. There appears to be little relevant direct comparison in the literature of the relative reactivities of the nitrosyl halides. In diazotisation of aniline derivatives [11] the rate coefficients for the reaction of nitrosyl chloride and nitrosyl bromide are both of the order of magnitude of the diffusion-controlled rates, so that comparison of their reactivities is not meaningful. For the halide-catalysed nitrosation of hydroxylamines [12] where the rate coefficients for reaction of the nitrosyl halides are less than would be expected for the diffusion-controlled process, nitrosyl chloride and nitrosyl bromide appear to have the same reactivity. It would be expected merely from consideration of the relative inductive effects of the halogens that nitrosyl chloride might be the more effective electrophile as our results indicate for the halide-ion catalysed nitrosations of olefins in water.

TABLE 5

Variation of ${}^1k_3{}^{\text{obs}}$ with added Br^- and Cl^- in the nitrosation of olefin (III) at $[H_2SO_4] = 0{\cdot}45$M

$[Br^-]$/M	$10^2\ {}^1k_3{}^{\text{obs}}$ / mol^{-2} l^2 min^{-1}	$[Cl^-]$/M	$10^2\ {}^1k_3{}^{\text{obs}}$ / mol^{-2} l^2 min^{-1}
0	12·0	0	12·0
0·1	16·9	0·3	13·8
0·2	19·3	0·5	17·8
0·5	44·5		

$$\text{Rate} = {}^1k_3{}^{\text{obs}}[HNO_2][\text{Olefin}]h_0 \qquad (7)$$



$$HNO_2 + H^+ \rightleftharpoons H_2\overset{+}{N}O_2 \quad \text{fast}$$
$$H_2\overset{+}{N}O_2 + X^- \rightleftharpoons NOX + H_2O \quad \text{fast}$$
$$NOX + {>}C{=}C{<} \longrightarrow \text{products} \quad \text{slow}$$

SCHEME 3

$$\text{Rate} = {}^1k_3[HNO_2][\text{Olefin}]h_0 \qquad (8)$$
$$\text{Rate} = {}^1k_3{}^x[NOX][\text{Olefin}]h_0 \qquad (9)$$

Bromide-ion catalysis was also observed for the nitrosation of olefin (IV) as is shown in Table 6, from which a value for ${}^1k_3{}^x$ [equation (9)] of 16 mol^{-2} l^2 min^{-1} was obtained from a plot of the observed rate coefficient against the bromide ion concentration. This gives a reactivity ratio (III) : (IV) for reaction with nitrosyl bromide of *ca.* 1·5. The comparison with the results of diazotisation by nitrosyl halides [1] with regard to substituent effects is not appropriate since again the rate coefficients for diazotisation are very large and are probably diffusion-controlled. It is clear however from our results that the nitrous acidium ion $H_2N^+O_2$ is a much more selective reagent than is nitrosyl bromide since the ratio of ${}^1k_3{}^{\text{obs}}$ values from Tables 5 and 6 at $[Br^-] = 0$ gives the reactivity ratio (III) : (IV) as *ca.* 65. Earlier we showed that for the more reactive olefins (I) and (II) the ratio of their reactivities towards $H_2N^+O_2$ was comparable with that towards bromination by the bromine molecule. This and the observed ratio of

TABLE 6

Variation of ${}^1k_3{}^{\text{obs}}$ with added Br^- in the nitrosation of olefin (IV) at $[H_2SO_4] = 1{\cdot}35$M

$[Br^-]$/M	$10^3\ {}^1k_3{}^{\text{obs}}$/ mol^{-2} l^2 min^{-2}
0	8·7
0·1	51·9
0·3	107·2
0·5	151·2

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[9] L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1940, p. 294; E. D. Hughes, C. K. Ingold, and J. H. Ridd, *J. Chem. Soc.*, 1958, 88.

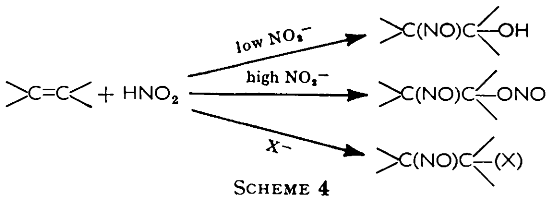
[10] H. Schmid, *Monatsh.*, 1957, **88**, 631.

[11] H. Schmid and E. Hallaba, *Monatsh.*, 1956, **87**, 568; H. Schmid and M. G. Fouad, *ibid.*, 1957, **88**, 631; H. Schmid and C. Essler, *ibid.*, p. 1110.

[12] T. D. B. Morgan, G. Stedman, and M. N. Hughes, *J. Chem. Soc.* (*B*), 1968, 344.

65 for (III) : (IV) would suggest a high degree of selectivity by the nitrous acidium ion. In contrast we find that nitrosyl bromide is much less selective. The kinetics of the reaction of nitrosyl chloride and substituted ethylenes in non-aqueous solvents [4] also show a relatively small spread of rate coefficients with substituents and although the rate coefficients do increase generally with the polarity of the solvent the effect is quite small when compared with other electrophilic additions. It may well be that the large difference between the selectivities of the nitrous acidium ion and nitrosyl bromide results from there being two different mechanisms for these reactions, *viz.*, the formation of a nitroso-carbonium ion from $H_2N^+O_2$ whereas the reaction of the nitrosyl bromide may proceed *via* a concerted addition mechanism. There is evidence [13] from the stereochemistry of the addition of nitrosyl chloride to cyclic olefins, and also from the lack of rearrangement products, that this reaction does involve *cis*-addition through a four-centre transition state. If indeed there are these two different mechanisms occurring then this would account for the significantly different rate ratios obtained from the reaction of the nitrous acidium ion and of nitrosyl bromide in these systems.

Products of the Reactions.—Products were isolated from the reactions carried out under the conditions of the kinetics experiment by adding small quantities of sodium nitrite periodically. Under these conditions, at least for the less reactive olefins where the time involved was sometimes weeks, the expected products appeared to have undergone partial hydrolysis as both nitroso- and carbonyl groups were identified in the product. For the more reactive olefin (I), however, 2,3-dimethyl-3-nitrosobutan-2-ol was recovered as the sole product and was characterised by elemental analysis and by its i.r. spectrum. At higher concentrations of nitrite (or by use of dinitrogen trioxide in ether) the nitroso-nitrite is formed.[14] In the presence of added sodium bromide the corresponding nitrosyl bromide adducts are formed as exemplified by the formation of 2-bromo-2-methyl-3-nitrosopropanol from methylprop-2-enol. The i.r. spectrum of this product showed a weak absorption at 1720 cm^{-1} and a medium-intensity band at 1640 cm^{-1}. The latter is almost certainly due to the free N=O group which has a stretching frequency in this region.[15] We attribute the 1720 cm^{-1} band to the C=N group although in general oximes absorb in the 1640—1670 cm^{-1} range. However Scheinbaum [16] has found C=N frequencies in a number of nitro-oximes at *ca.* 1790 cm^{-1} whilst the band at 1720 cm^{-1} in the chloro-oxime from nitrosyl chloride and 3,3-dimethylbut-1-ene [17] has been attributed to the C=N group. We have also observed [18] frequencies in the range 1720—1760 cm^{-1} in the products derived from dinitrogen trioxide and olefins, which we attribute to oxime formation. Further in the case of our nitrosyl bromide adduct the intensity of the 1720 cm^{-1} band increased slowly during several months, whilst that of the band at 1640 cm^{-1} decreased, indicating clearly a slow transformation from the free nitroso-form to the oxime form. This conversion was essentially complete in material that had been left standing at 0 °C for two years; there was no other significant change in the spectrum. This slow nitroso→oxime change has previously been observed spectroscopically in nitrosomethane and nitrosocyclohexane in the vapour phase.[19] In our case this also establishes beyond doubt the orientation of the addition, since only one oxime can be formed. Thus the product formed depends significantly upon the conditions of the experiment as set out in Scheme 4. No attempt has been made to differentiate between mechanisms involving carbonium ions and those proceeding by way of concerted addition, both of which are consistent with our kinetic results, since we have been more concerned with the identification of the probable nitrosating agents. There is nevertheless the suggestion from the kinetic substituent effects that the reactions *via* the nitrous acidium ion $H_2N^+O_2$ and those *via* the nitrosyl halides may proceed by different mechanisms.



SCHEME 4

EXPERIMENTAL

Commercial samples of the olefins were purified by preparative g.l.c. before use in the kinetic work. 2,3-Dimethylbut-2-ene (I) was prepared [20] from 3,3-dimethylbutan-2-ol and 85% phosphoric acid at 135 °C. The distillate was purified by preparative g.l.c. AnalaR sodium nitrite was recrystallised from distilled water and dried over phosphoric oxide.

Kinetics.—All reactions were carried out at $0 \pm 0{\cdot}1$ °C except those involving deuterium oxide when the temperature was 4 °C. Aqueous solutions of the olefin in the appropriate acid concentration were prepared and the olefin concentrations determined by a sodium thiosulphate titration with standard bromate–bromide solution. Reaction was started by adding an aliquot portion of a standard sodium nitrite solution. Samples were withdrawn at intervals and analysed for total nitrite by the Ridd–Halevi variation of the Griess–Ilosvay colorimetric method,[21] where nitrous acid is allowed to react with sulphanilic acid, the resulting diazonium ion coupled with 2-hydroxynaphthalene-3,6-disulphonic acid in borax, and the optical

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[13] J. Meinwald, Y. C. Meinwald, and T. N. Baker, *J. Amer. Chem. Soc.*, 1963, **85**, 2513.

[14] J. R. Park and D. L. H. Williams, *Chem. Comm.*, 1969, 332.

[15] J. F. Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.

[16] M. L. Scheinbaum, *J. Org. Chem.*, 1970, **35**, 2790.

[17] K. A. Ogloblin, V. N. Kalikhevich, A. A. Potekhim, and V. P. Semenov, *Zhur. obshchei Khim.*, 1964, **34**, 1227.

[18] J. R. Park and D. L. H. Williams, unpublished work.

[19] W. Lüttke, *Z. Elektrochem.*, 1957, **61**, 302, 976.

[20] M. L. Poutsma, *J. Amer. Chem. Soc.*, 1965, **87**, 4285.

[21] C. A. Bunton, E. A. Halevi, and D. R. Llewellyn, *J. Chem. Soc.*, 1952, 4913.

density of the resulting solution measured at 492 nm on a Unicam SP 500 spectrophotometer. All runs were carried out in duplicate and generally agreed to better than ±3%. Typical runs are shown in Tables 1 and 2 where respectively second- and first-order dependence upon nitrous acid is shown. A typical run of mixed-order in nitrous acid is shown in Table 7 where neither the first- nor the second-order rate coefficients are constant throughout the run.

TABLE 7

A typical mixed-order run for the reaction of olefin (II) ($3\cdot6 \times 10^{-2}$M) with HNO_2 (1×10^{-4}M) and $HClO_4$ ($3\cdot1 \times 10^{-2}$M)

t/min	Optical density	$10^2\,k_1$/min^{-1}	$10^{-2}\,k_2$/l mol^{-1} min^{-1}
0	0·326		
1·00	0·293	10·61	1·24
2·00	0·255	12·27	1·53
4·00	0·197	12·58	1·79
6·00	0·169	10·94	1·70
9·00	0·128	10·38	1·89
13·00	0·105	8·71	1·78
21·00	0·066	7·61	2·06
34·00	0·037	6·40	2·51
50·00	0·024	5·22	2·77

Corrections were applied where necessary in the longer runs at high acidity for the decomposition of the nitrous acid which was followed separately. In all runs the nitrous acid concentration was *ca.* 1×10^{-4}M.

Product Analyses.—As mentioned in the Discussion section it was not possible to obtain the primary product from the reaction of the less reactive olefins owing to partial hydrolysis; thus from the reaction of 2-methylprop-2-enyl chloride the product obtained by ether extraction of the mixture contained a nitroso-group and also a carbonyl group and a hydroxy-group as shown by the i.r. spectrum. This difficulty was not encountered with the more reactive olefins since less time was required to produce a significant quantity of the product. The *product* extracted with ether from the reaction of 2,3-dimethylbut-2-ene with nitrous acid was purified by distillation at low pressure. It was a blue liquid indicating the presence of a free N=O group. This was confirmed by the i.r. spectrum which contained a medium-intensity band at 1640 cm^{-1}. There was also a large broad band at *ca.* 3450 cm^{-1} showing the presence of an OH group (Found: C, 54·6; H, 9·8; N, 10·1. $C_6H_{13}NO_2$ requires C, 55·0; H, 9·9; N, 10·7%).

The reaction of nitrous acid with 2-methylprop-2-enol in the presence of a large excess of sodium bromide was also carried out under the conditions of the kinetic experiments. The product was extracted with ether, the solvent removed, and the resulting brown oil distilled at low pressure. The i.r. spectrum of the product showed the usual nitroso-group frequency and the mass spectrum was consistent with the structure 2-bromo-2-methyl-3-nitrosopropanol, $C_4H_8BrNO_2$, having peaks at *m/e* 152—153 ($C_4H_8BrNO_2$ — NO), 137—139 ($C_4H_8BrNO_2$ — CH_2NO), 72 ($C_4H_8BrNO_2$ — NOBr) and 30 (NO^+) (Found: C, 26·9; H, 4·3; N, 7·4; Br, 43·0. $C_4H_8BrNO_2$ requires C, 26·4; H, 4·4; N, 7·7; Br, 43·9%). A nitroso-bromide was similarly obtained from 2,3-dimethylbut-2-ene and nitrous acid in the presence of excess of sodium bromide.

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