Kinetics and Mechanism of the Hydrolysis of *N*-Methyl-*N*-nitroamides in Aqueous Sulphuric Acid

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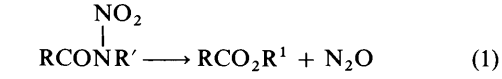
Pseudo first-order rate constants for the hydrolysis of *N*-methyl-*N*-nitroacetamide and various 4-substituted *N*-methyl-*N*-nitrobenzamides in sulphuric acid solutions are reported. *N*-Methyl-*N*-nitroacetamide undergoes an acid-catalysed process at all acidities studied for which the solvent deuterium isotope effect, $k_0^{H_2SO_4}/k_0^{D_2SO_4}$, is 0.87, and $\Delta S^{\ddagger}$ *ca.* −85 (±10) J K^{-1} mol^{-1}. These results suggest an $A_{Ac}2$ mechanism involving rapid pre-equilibrium protonation of the substrate followed by rate-limiting attack of water at the carbonyl C-atom to form a tetrahedral intermediate which collapses, in a fast step, to the products. The *N*-methyl-*N*-nitrobenzamides, however, exhibit both non-catalysed and acid-catalysed hydrolysis. The non-catalysed pathway operates at acidities up to *ca.* 5 mol dm^{-3} H_2SO_4, and is characterised by a solvent deuterium isotope effect, $k_0^{H_2SO_4}/k_0^{D_2SO_4}$, of 1.5, $\Delta S^{\ddagger}$ *ca.* −100 (±10) J K^{-1} mol^{-1} and a Hammett ρ value of 1.0 (±0.1). No catalysis by Br^- is observed and the results are most consistent with a thermal rearrangement and expulsion of N_2O. The acid-catalysed pathway operates at acidities >5 mol dm^{-3} H_2SO_4. The solvent deuterium isotope effect $k_0^{H_2SO_4}/k_0^{D_2SO_4}$ is 0.58, $\Delta S^{\ddagger} > 0$ JK^{-1} mol^{-1} and the Hammett ρ value is −3.4 (±0.1). Thus, a change in mechanism occurs at *ca.* 5 mol dm^{-3} H_2SO_4 to an Ac1 pathway involving protonation of the substrate, followed by rate-limiting cleavage of the amide C–N bond to form a benzoyl cation. The different acid-catalysed hydrolysis pathways for the *N*-nitroacetamide and *N*-nitrobenzamides is ascribed to the stabilisation afforded to the benzoyl cation as opposed to the acetyl carbonium ion. *N*-Nitroamides are hydrolysed exclusively *via* amide C–N bond cleavage whereas the corresponding *N*-nitrosoamides decompose *via* concurrent C–N and N–N (*i.e.* denitrosation) bond cleavage. This difference between *N*-nitro and *N*-nitroso-amides is discussed in terms of the greater stability of the NO^+ group.

Most amides are hydrolysed in aqueous sulphuric acid with rates that pass through a maximum value at 2–5 mol dm^{-3} H_2SO_4.[1] This maximum has been attributed to complete protonation of the amide, the decrease in the rate constant at higher acidities being due to the decrease in the activity of water. However, for acetanilides with electron-withdrawing substituents a continuing increase in the rate constants has been observed above 70% (w/w) H_2SO_4.[2] This has been interpreted as a change from an A2 to an A1 mechanism. The hydrolysis of esters in concentrated H_2SO_4 solutions has also been extensively studied.[3] Like amides, esters with poor leaving groups exhibit a rate maximum with increasing acidity, but esters with good leaving groups show only an increase in rate with acidity.

(1) **a**; R = CH_3
b; R = 4-MeO–C_6H_4
c; R = 4-Me–C_6H_4
d; R = C_6H_5
e; R = 4-Cl–C_6H_4
f; R = 4-CF_3–C_6H_4

N-Methyl-*N*-nitroamides (**1**) have been used to acylate nitrogen nucleophiles,[4] behaviour similar to that of esters with good leaving groups. Further, *N*-nitroamides are thermally labile and undergo pyrolysis with the expulsion of N_2O (equation 1) on heating, usually in organic solvents.[5] White and Field[6]



$$RCONR' \longrightarrow RCO_2R^1 + N_2O \qquad (1)$$

proposed a mechanism for these reactions involving ion-pair intermediates analogous to those proposed for the thermal decomposition of *N*-nitrosoamides. In this paper we report studies on the kinetics of hydrolysis of (**1**) in sulphuric acid solutions which show that, under these conditions too, *N*-nitroamides have very similar behaviour to esters with good leaving groups.

Experimental

Substrates and Reagents.—The *N*-methyl-*N*-nitroamides (**1**) were prepared by methods described elsewhere.[7,8] Carbonyl

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Table 1. Pseudo-first-order rate coefficients (k_0) for the hydrolysis of *N*-methyl-*N*-nitroamides (**1a–f**) in H_2SO_4 at 25 °C. Initial substrate concentration *ca.* 1×10^{-4} mol dm^{-3}.

	$[H_2SO_4]$/mol dm^{-3}	$k_0/10^{-4}$ s^{-1}
(**1a**)	1.00	2.2
	2.07	4.6
	4.07	9.4
	6.07	18.9
	7.65	37.3
	8.95	80.0
(**1b**)	0.99	0.59
	1.90	0.55
	3.40	0.86
	5.90	2.60
	7.70	37.0
	8.80	105.0
(**1c**)	0.99	0.84
	1.90	1.00
	3.40	1.05
	4.50	1.91
	5.50	1.87
	7.70	6.80
	8.80	36.0
(**1d**)	0.99	1.4
	2.05	1.4
	4.05	2.0
	6.10	3.3
	8.80	12.0
	9.16	13.5
	9.60	26.5
(**1e**)	1.50	2.30
	3.40	1.90
	4.50	1.80
	5.80	1.70
(**1f**)	0.99	3.10
	3.40	3.90
	5.80	3.10
	6.50	2.56
	8.00	0.20
	8.80	3.30
	10.00	10.60
	11.80	26.00

^{18}O-labelled *N*-methyl-*N*-nitrobenzamide was prepared by nitration of ^{18}O-labelled *N*-methylbenzamide with acetic anhydride–nitric acid. The ^{18}O-labelled parent amide was itself obtained by reaction of *N*-methylbenzimidoyl chloride with $H_2{}^{18}O$. Sulphuric acid was AnalaR grade and deuteriosulphuric acid (98%) was obtained from MSD.

Kinetics.—The hydrolysis of *N*-methyl-*N*-nitroamides was followed by monitoring of the decrease in the UV absorbance of the substrate, at an appropriate wavelength, using Pye-Unicam SP1800, SP8-500 or Perkin-Elmer Lambda 3 spectrophotometers. Reaction solutions were monitored continuously in cells thermostatted to ±0.1 °C. At the conclusion of each experiment the acidity of the solution was determined by titration against standard alkali. Values of the pseudo-first-order rate constants (k_0) were obtained from plots of $\ln(A_t - A_\infty)/(A_0 - A_\infty)$ *versus* time, and were reproducible to ±10%. *N*-Nitromethylamine, one of the products of the reaction, is unstable in acidic solutions. Problems associated with its subsequent decomposition were overcome by following the reaction at a wavelength where *N*-nitromethylamine did not absorb significantly.

Product Analysis.—Benzoic acid was isolated by extraction from large scale hydrolysis reactions of *N*-methyl-*N*-nitrobenzamide. The NMR spectrum of a reaction carried out in concentrated D_2SO_4 solution exhibited only resonances due to benzoic acid and methanol, the product of decomposition of *N*-nitromethylamine.[9]

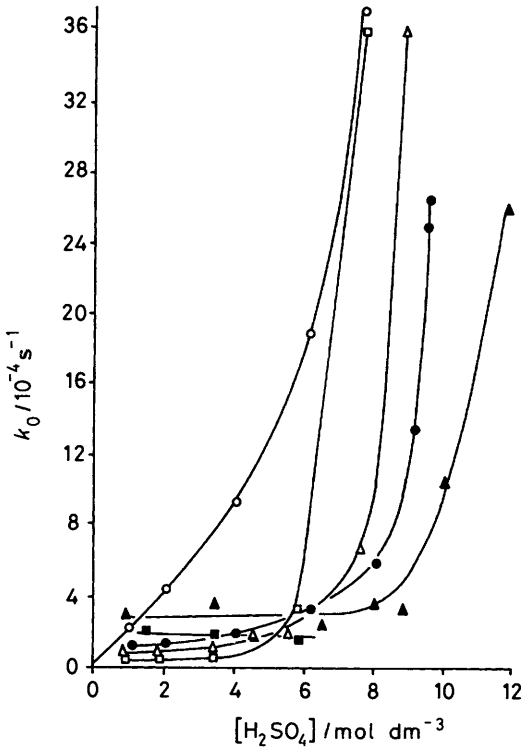


Figure 1. Hydrolysis rates of *N*-methyl-*N*-nitroamides (**1a–f**) in H_2SO_4 at 25 °C: ○, (**1a**); □, (**1b**); △, (**1c**); ●, (**1d**); ■, (**1e**); ▲, (**1f**).

^{18}O-Exchange Experiments.—Large scale hydrolyses of carbonyl ^{18}O-labelled *N*-methyl-*N*-nitrobenzamide were performed in 1 and 9 mol dm^{-3} H_2SO_4. Samples of the reaction mixture were extracted at timed intervals and, after work-up, analysed by mass spectrometry for ^{18}O content of either the substrate or the benzoic acid product.

Results and Discussion

N-Methyl-*N*-nitroamides (**1**) hydrolyse in sulphuric acid solutions to give the corresponding carboxylic acids and *N*-nitromethylamine, which undergoes subsequent decomposition to methanol and nitrous oxide [equation (2)]. Reactions show a

$$\mathrm{RCON(NO_2)Me} \xrightarrow{H^+/H_2O} \mathrm{RCO_2H} + \mathrm{MeNHNO_2} \xrightarrow{H^+} \mathrm{MeOH} + \mathrm{N_2O} + \mathrm{H_2O} \quad (2)$$

first-order dependence on [(**1**)], and pseudo-first-order rate coefficients (k_0) were obtained at several H_2SO_4 concentrations. These are summarised in Table 1 and illustrated in Figure 1. All the compounds studied exhibit an increase in rate with acidity and no rate maximum. It is clear, however, that the acetamide (**1a**) and the benzamides (**1b–f**) have different dependences upon acidity. In order to elucidate the reaction mechanisms, solvent deuterium isotope effects, temperature effects and substituent effects were also studied.

N-*Methyl*-N-*nitroacetamide.*—The hydrolysis of compound (**1a**) shows a pronounced acid catalysis that is evident even at

Table 2. Deuterium solvent isotope effects ($k_0^{H_2SO_4}/k_0^{D_2SO_4}$) for (**1a**) and (**1d**) in L_2SO_4 solution at 25 °C.

	$k_0^{H_2SO_4}/k_0^{D_2SO_4}$	
$[L_2SO_4]$/mol dm^{-3}	(**1a**)	(**1d**)
2	0.84	1.5
4	0.85	1.3
5	0.87	—
6	0.88	1.3
7	0.90	1.1
8	0.88	0.98
9	—	0.58

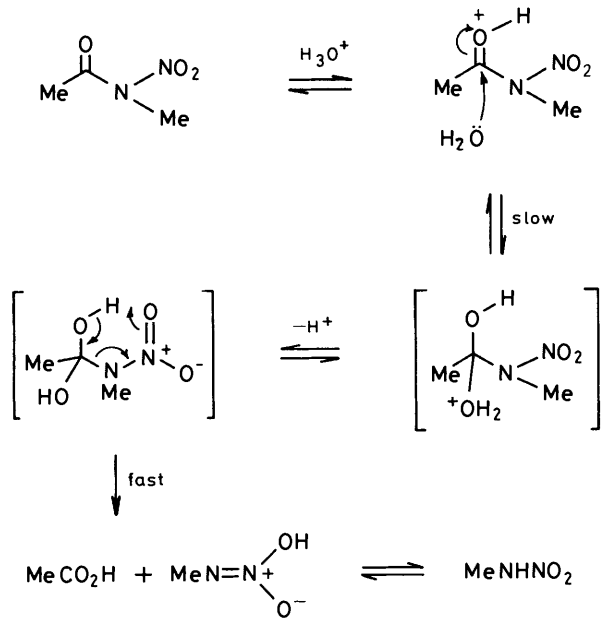
Table 3. Effect of temperature on the pseudo-first-order rate coefficients (k_0) for the decomposition of (**1a**), (**1b**), and (**1d**) in H_2SO_4. Initial [substrate] *ca.* 1 × 10^4 mol dm^{-3}.

		$k_0/10^{-4}$ s^{-1}		
$[H_2SO_4]$/mol dm^{-3}	Temp/°C	(**1a**)	(**1b**)	(**1d**)
0.1	25.0	—	—	1.04
0.1	35.0	—	—	2.1
0.1	60.0	—	—	9.5
2.0	15.0	1.4	—	0.5
2.0	25.0	4.6	—	1.5
2.0	35.0	10.2	—	3.3
2.0	44.0	21.1	—	7.2
2.0	60.0	59.3	—	15.6
3.4	25.0	—	0.86	—
3.4	30.0	—	1.11	—
3.4	36.0	—	1.20	—
3.4	45.0	—	2.50	—
6.0	15.0	8.5	—	—
6.0	25.0	18.9	—	—
6.0	35.0	43.8	—	—
7.5	15.6	—	12.0	—
7.5	19.8	—	22.0	—
7.5	22.0	—	27.0	—
7.5	25.5	—	38.0	—
9.0	11.0	—	—	2.1
9.0	16.0	—	—	3.1
9.0	25.0	—	—	13.6
9.0	35.0	—	—	52.5

Table 4. Values of the entropy of activation ($\Delta S^{\ddagger}$) for the hydrolysis of (**1a**), (**1b**), and (**1d**) in H_2SO_4.

	$\Delta S^{\ddagger}$/JK^{-1} mol^{-1}		
$[H_2SO_4]$/mol dm^{-3}	(**1a**)	(**1b**)	(**1d**)
0.1	—	—	−150 ± 10
2.0	−92 ± 10	—	−100 ± 10
3.4	—	−75 ± 10	—
6.0	−79 ± 10	—	—
7.5	—	+36 ± 10	—
9.0	—	—	+15 ± 10

low H_2SO_4 concentrations (Figure 1). The deuterium solvent isotope effect, $k_0^{H_2SO_4}/k_0^{D_2SO_4}$, was found to be independent of acidity and its mean value is 0.87 (Table 2). This value is consistent with a fast pre-equilibrium protonation of the substrate with a higher concentration of the conjugate acid in D_2SO_4 than H_2SO_4. The entropies of activation calculated for (**1a**) in 2 and 6 mol dm^{-3} H_2SO_4 from the results in Table 3 are −92 (± 10) and −79 (± 10) J K^{-1} mol^{-1} respectively (Table 4). These values are not substantially different from those obtained



Scheme 1. The acid-catalysed hydrolysis of *N*-methyl-*N*-nitroacetamide.

for an $A_{Ac}2$ ester hydrolysis.[10] Therefore, we conclude that the hydrolysis of (**1a**) proceeds *via* a rate-determining attack of water on the protonated substrate, with formation of a tetrahedral intermediate that rapidly breaks down to products (Scheme 1). The deuterium solvent isotope effect thus comprises a contribution for the pre-equilibrium protonation and one for the attack of water on the protonated substrate. The former results in an inverse isotope effect ($k^{H_2SO_4}/k^{D_2SO_4}$) whereas the latter produces a normal isotope effect ($k^{H_2SO_4}/k^{D_2SO_4}$) since D_2O is a poorer nucleophile than H_2O. These combine in the present case to yield a small inverse deuterium solvent isotope effect.

Since the *N*-nitroamide (**1a**) behaves like an ester with a good leaving group, comparison of our results with those of ester hydrolysis was made. Ionization ratios have been reported for several acetate esters and they were found to obey the linear relationship expressed in equation (3).[3] Good correlations were

$$\log \frac{[SH^+]}{[S]} = -0.62\,H_0 + c \qquad (3)$$

obtained on applying the Bunnett and Olsen[11] treatment modified by substitution of H_0 by 0.62 H_0 [equation (4)]. Since

$$\log k_0 + 0.62\,H_0 = R \log a_{H_2O} + c \qquad (4)$$

we could not determine the pK_{SH^+} for *N*-methyl-*N*-nitroamides due to their instability at high acidities, we were unable to apply this type of relationship rigorously. However, correlation of the pseudo first-order rate coefficients for (**1a**) with those for *p*-nitrophenylacetate (Figure 2) gave a straight line of slope 1.0. This strongly suggests that protonation of both compounds has a very similar dependence on acidity, and indeed a plot of the pseudo-first-order rate constants for both (**1a**) and 4-nitrophenyl acetate *versus* $\%H_2SO_4$ yields parallel lines (Figure 3). This correlation provides another argument in favour of similar mechanisms for the acid-catalysed decomposition of (**1a**) and an ester containing a good leaving group.

No evidence for a unimolecular pathway, such as changes in activation entropies or solvent isotope effects, was seen for the hydrolysis of (**1a**) in the acidity range studied. The observation that no rate maximum is attained at the acidities studied is

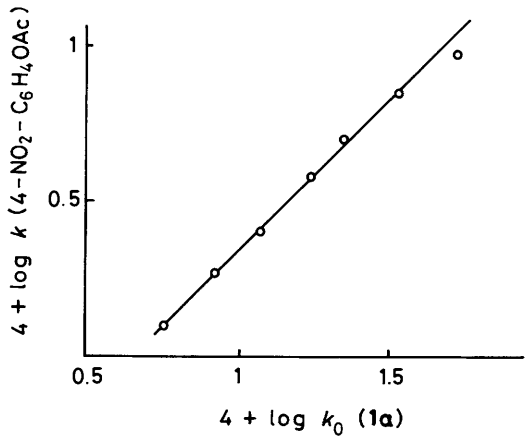


Figure 2. Correlation of hydrolysis rates of (**1a**) with 4-nitrophenylacetate.

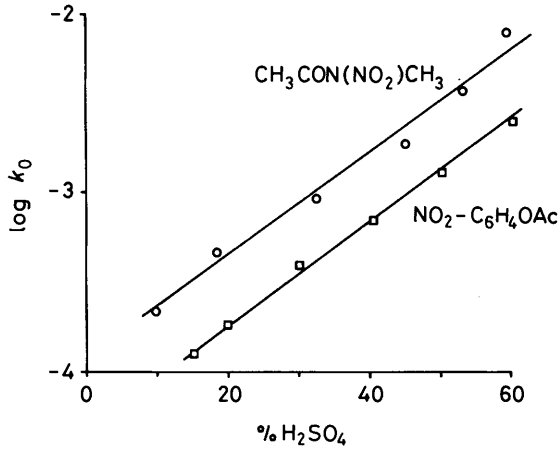


Figure 3. Correlation of hydrolysis rates of (**1a**) and 4-nitrophenylacetate with the sulphuric acid concentration.

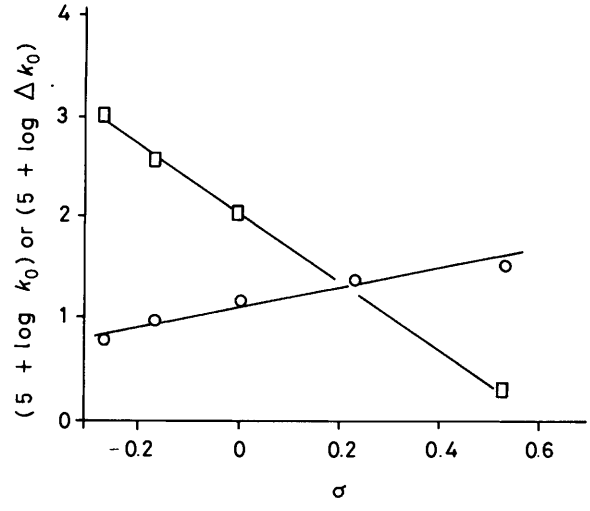


Figure 4. Hammett correlation for the hydrolysis of *N*-methyl-*N*-nitrobenzamides in 0.99 (○) and 8.8 mol dm^{-3} (□) H_2SO_4 at 25 °C.

probably due to the fact that the compound is not completely protonated since the nitro group directly attached to the amide function must lower the basicity of the compound significantly. Moreover, a unimolecular mechanism would generate an unstable acetylcation intermediate on the reaction pathway. As discussed below, this contrasts sharply with the corresponding benzamides where the benzoylcation is resonance stabilised.

Table 5. Effect of added bromide ion on the rate of hydrolysis of (**1d**) in H_2SO_4 (2 mol dm^{-3}) at 25 °C.

$[Br^-]$/mol dm^{-3}	$k_0/10^{-4}$ s^{-1}
0	1.4
1	1.8
2	1.4
3	1.2
4	1.2
5	1.3

N-*Methyl*-N-*nitrobenzamides*.—At low acidities, the rates of hydrolysis of the benzamides (**1b–f**) are virtually acidity independent, but the reaction is strongly acid catalysed at higher acidities (6 to 9 mol dm^{-3} depending on the substituent) (Figure 1). The implied change of mechanism was verified, for (**1d**), by the change in the deuterium solvent isotope effect from $k_0^{H_2SO_4}/k_0^{D_2SO_4} = 1.5$ at low acidities to $k_0^{H_2SO_4}/k_0^{D_2SO_4} = 0.58$ at higher acidities (Table 2). Further, the entropy of activation was also found to change with acidity for both (**1b**) and (**1d**); negative values were found at low H_2SO_4 concentrations and positive values at high H_2SO_4 concentrations (Table 4).

The effects of aryl substituents on the hydrolysis rates are also dependent on acidity and invert on going from dilute to concentrated H_2SO_4. Thus, electron-donating substituents produce the lowest rate at low acidity [*i.e.* (**1b**) < (**1f**)], but the highest rate at high acidity [*i.e.* (**1b**) > (**1f**)]. The substituent effects at $[H_2SO_4] = 0.99$ and 8.8 mol dm^{-3} are correlated by means of Hammett $\sigma\rho$ plots in Figure 4. At $[H_2SO_4] = 0.99$ mol dm^{-3}, the observed values of k_0 are used and these generate a value of $\rho = 1.0$. At $[H_2SO_4] = 8.8$ mol dm^{-3}, the differences between k_0 at 0.99 and 8.8 mol dm^{-3} H_2SO_4 are used (Δk_0) and these generate a value of $\rho = -3.4$. For (**1e**), reliable values of k_0 could not be obtained at $[H_2SO_4] > 5.8$ mol dm^{-3} due to very small absorbance changes caused by interference from the reaction products.

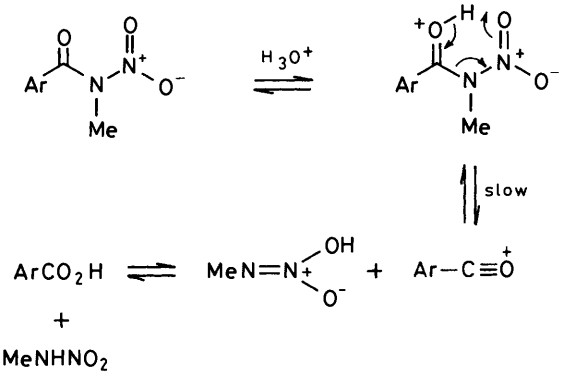
The kinetic acidity dependences, the deuterium solvent isotope effects, the entropies of activation and the aryl substituent effects all point to a change of mechanism for the hydrolysis of *N*-methyl-*N*-nitrobenzamides with increasing solvent acidity.

At very high acidities, the inverse deuterium solvent isotope effect (*e.g.* $k_0^{H_2SO_4}/k_0^{D_2SO_4} = 0.58$ for (**1d**) implies that the conjugate acid of the substrate is involved, as does the onset of acid catalysis. The positive values of $\Delta S^{\ddagger}$ for (**1b**) and (**1d**) at high acidities (Table 4) suggest that this conjugate acid decomposes *via* a unimolecular process.[10] Further, this acid-catalysed reaction is strongly facilitated by electron-donating substituents ($\rho = -3.4$). Hydrolysis by an $A_{Ac}1$ mechanism in which the conjugate acid undergoes rate-limiting cleavage to a benzoylcation and *N*-nitromethylamine (Scheme 2) is most consistent with all of these findings. Electron-donating substituents would facilitate both protonation of the substrate and stabilize the benzoylcation. The intervention of hydrolysis by an $A_{Ac}1$ mechanism with *N*-nitrobenzamides probably reflects the greater stability of the benzoylcation relative to the acetyl cation.

At low acidities, decomposition clearly involves the neutral *N*-methyl-*N*-nitrobenzamides. Electron-attracting substituents increase the rate of reaction, but the value of $\rho = 1.0$ is low for a rate-limiting attack by water on the neutral substrate. It is significantly lower than the value of $\rho = 2.8$ obtained for the HO^--catalysed hydrolysis of *N*-methyl-*N*-nitrobenzamides which is considered to involve a rate-limiting attack by the less-selective hydroxide ion on the neutral substrate.[12] Rate-limiting

Table 6. Percentage ^{18}O in *N*-methyl-*N*-nitrobenzamide (**1d**) (*m*/*z* 180) benzoic acid product (*m*/*z* 122) and their benzoyl fragment ion (*m*/*z* 105) for hydrolysis in 1 and 9 mol dm^{-3} H_2SO_4 at 25 °C.

	$[H_2SO_4]$/ mol dm^{-3}	Component	%(*m*/*z* + 2)/*m*/*z* (*m*/*z* 180 or 122)	%(*m*/*z* + 2)/*m*/*z* (*m*/*z* 105)
(**1d**)	—	—	11.6	8.3
Sample 1 (42 min)	1.0	Benzoic acid	11.3	6.0
2 (85 min)	1.0	Benzoic acid	11.6	5.5
3 (127 min)	1.0	Benzoic acid	10.9	5.8
Sample 1 (5 min)	9.0	(**1d**)	11.6	10.8
2 (10 min)	9.0	Benzoic acid	11.4	5.6



Scheme 2. $A_{Ac}1$ mechanism for the acid-catalysed hydrolysis of *N*-methyl-*N*-nitrobenzamides.

cleavage of the C–N bond in the tetrahedral intermediate derived from H_2O and the neutral *N*-methyl-*N*-nitrobenzamide is consistent with the attenuated substituent effects, but such an explanation is unlikely because this step is rapid for the HO^--catalysed hydrolysis.[12] These arguments suggest that uncatalysed hydrolysis proceeds either *via* the thermal expulsion of N_2O [equation (1)] followed by hydrolysis of the methyl benzoate product or *via* bimolecular nucleophilic cleavage of the *N*-methyl bond. The deuterium solvent isotope effects are not particularly helpful in deciding between these alternatives. Moreover, we found that the corresponding methyl ester is hydrolysed to benzoic acid under the reaction conditions and it has been reported that the unsubstituted *N*-nitrobenzamides (the products that would be produced upon *N*-methyl cleavage) themselves decompose in sulphuric acid solutions to the parent benzoic acids.[13] However, in 2 mol dm^{-3} H_2SO_4 addition of varying concentrations of Br^- has no effect on the decomposition rate of compound (**1d**) (Table 5). Thus, it is unlikely that the non-catalysed pathway involves nucleophilic cleavage of the *N*-methyl bond.

Confirmatory evidence for the proposed hydrolysis mechanisms [Scheme 2 and equation (1)] was obtained from experiments with carbonyl ^{18}O-labelled (**1d**). The ^{18}O-content of (**1d**) and the benzoic acid hydrolysis product was estimated mass spectrometrically from both the molecular ions (*m*/*z* 180 and 122, respectively) and their benzoyl fragment ions (*m*/*z* 105) (Table 6). The results confirm that insignificant ^{18}O-exchange accompanies the hydrolysis of (**1d**) at 25 °C in either 1 or 9 mol dm^{-3} H_2SO_4. These findings are entirely consistent with the $A_{Ac}1$ mechanism (Scheme 2) for hydrolysis in 9 mol dm^{-3} H_2SO_4 and the thermal rearrangement [equation (1)] in 1 mol dm^{-3} H_2SO_4.

On a different point, the acid-catalysed hydrolysis of *N*-alkyl-*N*-nitrosoamides produces concurrent deamination *via* C–N bond cleavage and denitrosation *via* N–N bond cleavage.[14] It is interesting that only deamination is found for *N*-methyl-*N*-nitroamides. This difference must reflect the different stabilities of the NO_2^+ and NO^+ moieties and is consistent with published values of $pK_a = -6.12$ for NO^+,[15] and pK_a *ca.* -15 for NO_2^+.[16]

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