The Decomposition of Nitroamine (NH_2NO_2) in Concentrated Mineral Acids

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The decomposition of nitroamine has been studied in concentrated aqueous perchloric acid, sulphuric acid, and hydrochloric acid over a range of temperatures. In all cases there is a linear correlation between log k_1 and the Hammett acidity function H_0, with a slope of *ca.* 0.35. These results have been interpreted in terms of a rate-determining nucleophilic attack of water upon the protonated nitroamine to give hydroxylamine and nitrous acid, which then react to give dinitrogen oxide.

The decomposition of nitroamine (NH_2NO_2) to dinitrogen oxide and water is slow in cold, aqueous neutral solution but is subject to acid and base catalysis. The base-catalysed decomposition is of classical significance [1] in the development of theories of general base catalysis, and has been the subject of an enormous amount of work. Even so, additional features of this reaction have only recently been identified.[2] The acid-catalysed reaction has been studied by Marlies and La Mer [3] at acidities up to 2 mol dm^{-3}. We have studied this reaction in several acids up to *ca.* 12 mol dm^{-3}, partly because of our interest in nitroamine as an intermediate in the nitric acid–sulphamic acid reaction.[4] We have also studied [5] the acid-catalysed decomposition of nitroamine in $H_2{}^{18}O$–acid solutions and have shown that the dinitrogen oxide produced in neutral or weakly acidic solution contains zero oxygen-18, but that the dinitrogen oxide produced through the acid-catalysed pathway contains the oxygen-18 label. This indicates that the acid-catalysed pathway involves attack by solvent water on a nitroamine species.

Experimental

Nitroamine was prepared and stored as described earlier.[6] As before there was some lack of reproducibility between rate constants obtained for reactions using different batches of nitroamine, although reproducibility using nitroamine from one batch was good (3—4%). Each set of runs quoted for a particular mineral acid was obtained on a single batch of nitroamine, and test runs were repeated with new batches to ensure that reproducibility was reasonable. It appears however that experiments with perchloric acid at 35 °C involved a batch of nitroamine which gave rather higher rate constants than expected. While the dependence of rate constant upon the Hammett acidity function H_0 was exactly that found in perchloric acid at other temperatures, these runs at 35 °C have been excluded from the data used for the assessment of activation parameters. Other chemicals were the best grade available (AnalaR or Aristar), while sodium perchlorate was prepared in solution from AnalaR perchloric acid and AnalaR sodium hydroxide solution.

Kinetic runs were started by adding *ca.* 0.005 g of solid nitroamine to the mineral acid solution (20 cm^3) thermostatted at an appropriate temperature. Samples (0.1—0.5 cm^3) were removed at time intervals and run into ice-cold water (10 cm^3) to quench the reaction. The concentration of nitroamine was determined by recording the optical density at 209 nm in a Unicam SP 500 spectrophotometer. Extrapolation of the log (optical density) *vs.* time plot to zero time allowed the calculation of the nitroamine concentration for the run (ε = 6 300 dm^3 mol^{-1} cm^{-1}).

Table 1. Decomposition of nitroamine in aqueous perchloric acid

T/°C	[$HClO_4$]/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	$10^4(k_{obs.} - k_0)$/ s^{-1}
30.6	0.01	0.500	—
30.6	4.85	1.42	0.920
30.6	7.35	2.87	2.37
30.6	8.27	4.84	4.34
35.0 *	0.01	2.65	—
35.0	3.57	4.26	1.61
35.0	4.85	5.02	2.37
35.0	6.04	8.18	5.53
35.0	7.85	16.3	13.7
35.0	8.30	19.8	17.2
35.0	9.82	72.9	70.3
35.0	12.24	300	297
41.0	0.01	2.00	—
41.0	2.50	3.12	1.12
41.0	3.23	3.75	1.75
41.0	4.04	4.22	2.22
41.0	4.85	4.51	2.51
41.0	6.13	7.12	5.12
41.0	7.35	10.3	8.30
41.0	8.27	16.8	14.8
41.0	8.63	21.4	19.4
41.0	9.23	33.1	31.1
41.0	9.68	47.2	45.2
41.0	9.92	59.1	57.1
45.6	0.01	2.50	—
45.6	1.67	3.83	1.33
45.6	4.85	7.09	4.59
45.6	7.35	15.7	13.2
45.6	8.27	26.4	23.9
59.8	0.01	9.00	—
59.8	1.67	14.00	5.00
59.8	4.85	28.9	19.9
59.8	7.35	84.0	75.0

* Results at 35 °C reflect an atypical batch of nitroamine; [NH_2NO_2] usually *ca.* 2.5 × 10^{-2} mol dm^{-3}, but varied over the range 0.6 × 10^{-2} to 5 × 10^{-2} mol dm^{-3} at certain acidities.

Results

The kinetics were studied in perchloric acid solutions at five temperatures over the range 30—60 °C, and in hydrochloric acid and sulphuric acid solutions at 35 °C. In all cases the reaction was first order in nitroamine. Excellent plots of log (optical density) against time were obtained, usually for over three half-lives of reaction. The measured first-order rate constant, $k_{obs.}$, was independent of [NH_2NO_2] over a 20-fold concentration range in perchloric acid and a five-fold concentration range in the other acids. Each rate constant quoted is the mean of several determinations.

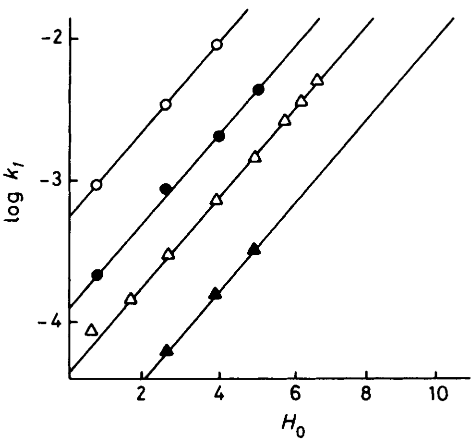

Figure 1. Dependence of log k_1 on H_0 in aqueous perchloric acid at 59.8 (○), 45.6 (●), 41.0 (△), and 30.6 (▲) °C

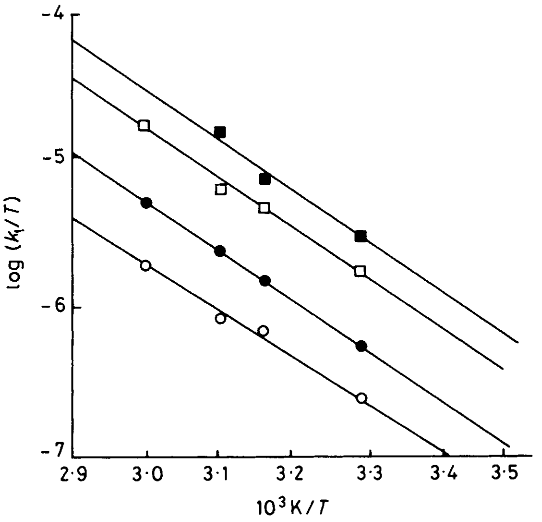

Figure 2. Dependence of log (k_1/T) on $1/T$ with [H^+] = 1.67 (○), 4.85 (●), 7.35 (□), and 8.27 (■) mol dm^{-3}

Aqueous Perchloric Acid.—Values of $k_{obs.}$ are listed in Table 1. First-order rate constants for the acid-catalysed reaction are given by $k_1 = k_{obs.} - k_0$ where k_0 is the measured first-order rate constant at very low acidity. Values of k_1 increase with [H^+], but plots of k_1 against [H^+] are non-linear. At each temperature studied there was a linear relationship between log k_1 and H_0, the Hammett acidity function, with a slope of 0.34 (Figure 1). No allowance has been made for the effect of temperature on H_0, but this will be small and usually has no effect on log k *versus* H_0 rate profiles.[7] The decomposition of nitroamine in acidic solution is thus described by the rate law (1).

$$\text{Rate} = k_0[\text{NH}_2\text{NO}_2] + k_2[\text{NH}_2\text{NO}_2]h_0^{0.34} \quad (1)$$

Figure 2 shows plots of log (k_1/T) against $1/T$ at several acidities. Values of the entropy and enthalpy of activation are -72 ± 5 J K^{-1} mol^{-1} and 82 ± 4 kJ mol^{-1} respectively, and are independent of acidity.

The effect of added sodium perchlorate on the rate was examined at [$HClO_4$] = 3.57 and 6.04 mol dm^{-3}. In both cases his resulted in an initial decrease in k_1, followed by a slight increase in k_1 with further increase in added [$NaClO_4$] (Table 2).

Table 2. Effect of ionic strength I at 35 °C in aqueous perchloric acid ($k_0 = 2.65 \times 10^{-4}$ s^{-1})

[$HClO_4$]/mol dm^{-3}	I/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
3.57	3.57	4.26
3.57	3.93	4.07
3.57	4.30	3.95
3.57	5.03	3.06
3.57	5.76	3.20
3.57	6.49	3.36
3.57	7.22	3.38
3.57	8.95	3.40
6.04	6.04	8.18
6.04	6.40	7.80
6.04	6.68	7.36
6.04	7.41	7.59
6.04	8.14	7.61

Table 3. Decomposition of nitroamine in aqueous sulphuric acid and aqueous hydrochloric acid at 35 °C

[HCl]/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	[H_2SO_4]/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
0.01	2.65	0.01	2.65
1.09	3.31	1.35	5.06
3.42	4.47	1.47	5.27
5.70	7.47	1.92	5.62
7.50	9.50	2.65	6.72
8.00	11.1	3.11	6.88
8.20	11.5	3.62	9.90
8.90	14.4	4.40	10.4
9.10	15.4	5.03	11.1
9.30	17.1	5.40	13.8
		6.37	15.7
		7.12	16.5
		7.45	19.5
		7.53	20.4
		8.00	22.0
		8.10	31.4

Aqueous Hydrochloric and Sulphuric Acids.—Similar results were found for both acids (Table 3). For both acids at 35 °C, there was a linear relationship between log k_1 and H_0, with slopes of 0.38 and 0.31 for hydrochloric acid and sulphuric acid respectively.

Discussion

The question of which acidity function should be used to describe the protonation of nitroamine is a difficult one. We have selected H_0 as there is a linear relationship between log k_1 and H_0 and it seems appropriate for the protonation of an amino-function.

A major point of interest is the slope of *ca.* 0.35 found for the log k_1 *versus* H_0 plot. Many examples are known [8] where a unit slope of H_0 is not found, for example in the hydrolysis of ethyl acetate (0.38) and isopropyl acetate (0.42). In the past the Bunnett parameters W and W^* have been used [8,9] as a guide to the way in which water is involved in the rate-determining step of reactions with intermediate slopes. These parameters are obtained as the slopes of plots of ($\log_{10} k_1 + H_0$) against $\log_{10} a_w$ (for W) and ($\log_{10} k_1 - \log_{10} C_{acid}$) against $\log_{10} a_w$ (for W^*). For the present results in perchloric acid solution, values of W(2.2) and W^* (-4.2) lie in the range for acid-catalysed reactions in which water acts as a nucleophile in the rate-determining step. However, it is recognised that, in general, a more satisfactory approach[10] involves the use of the φ parameter, given by the slope of plots of ($\log k + H_0$) or $\log k$ against ($H_0 + \log [H^+]$), where k is the observed first-order rate constant for the acid-catalysed reaction. The former plot is appropriate for reactions of weakly basic substrates and the latter for reactions of strongly basic substrates. A plot of ($\log k_1 + H_0$) against ($H_0 + \log [H^+]$) for the present results in perchloric acid at 41 °C showed distinct curvature. This probably means that nitroamine is becoming substantially protonated within the acid concentration range used in this study. This is confirmed by the fact that a plot of $\log k_1$ against ($H_0 + \log [H^+]$) is an excellent straight line with slope 0.38. This φ value lies within the range (0.22—0.56) for which water is thought[10] to act as a nucleophile in the rate-determining step. The acid-catalysed hydrolysis of sulphamic acid, NH_2SO_3H, also involves such a role for water.[11]

The involvement of water in the slow step of the acid hydrolysis of nitroamine is in accord with results obtained[5] using oxygen-18 labelled water, and also with the negative entropy of activation. In the former case it is clear that the acid-catalysed pathway gives $N_2{}^{18}O$, while decomposition in neutral solution gives unlabelled dinitrogen oxide. At high acidities the amount of oxygen-18 in the product equals that in the water. A possible mechanism involves nucleophilic attack of water on protonated nitroamine with bond cleavage to give hydroxylamine and nitrous acid. These react to give dinitrogen oxide *via* the intermediate formation of hyponitrous acid. It is assumed that the nitrous acid undergoes rapid oxygen exchange with the oxygen-18 labelled water (*via* N_2O_3) to allow for the ratio $[^{18}O \text{ in } N_2O]/[^{18}O \text{ in } H_2O] = 1$. Otherwise, the maximum value of this ratio would be 0.5. In the mechanism shown below [equations (2)—(4)] nitronic acid forms of nitroamine have not been considered. The base-

$$NH_2NO_2 + H^+ \rightleftharpoons \overset{+}{N}H_3NO_2 \tag{2}$$

$$\overset{+}{N}H_3NO_2 + H_2O \xrightarrow[\text{slow}]{} \overset{+}{N}H_3OH + HNO_2 \tag{3}$$

$$\overset{+}{N}H_3OH + HNO_2 \longrightarrow N_2O + 2H_2O + H^+ \tag{4}$$

catalysed hydrolysis of nitroamine differs from the acid-catalysed process and from the non-acid-catalysed hydrolysis of species NH_2X in that N–N bond cleavage does not occur. This results from the presence of the strongly conjugating and electron-withdrawing nitro-group in nitroamine. However, protonation of nitroamine at the amino-group enhances nucleophilic attack of water, while having little effect on the leaving of a neutral HNO_2 molecule (particularly if a nitronic acid species, $\overset{+}{N}H_2NO_2H$, is postulated). In contrast, protonation of $NH_2OSO_3^-$ at nitrogen causes a decrease in rate of nucleophilic attack, as bond breaking is hindered since the leaving group, sulphate, is charged.

The effect of added sodium perchlorate on the rate is similar at both acidities at which this effect was studied, resulting initially in a decrease in k_1, followed by a slight increase. Thus at $[H^+] = 3.57$ mol dm^{-3}, addition of *ca.* 1.5 mol dm^{-3} $NaClO_4$ caused a decrease of *ca.* 75% in the value of k_1. Subsequent addition of 3.9 mol dm^{-3} $NaClO_4$ caused only a small increase in k_1. Usually the addition of sodium perchlorate results[8,12] in a considerable increase in acidity as measured by H_0, which is clearly not the straightforward case in the present work. The decrease in k_1 brought about by added $NaClO_4$ also rules out the possibility that there is a direct dependence of k_1 on $[H^+]$ with a superimposed positive ionic strength effect. The obvious source of the decrease in k_1 brought about by added $NaClO_4$ lies in the effect on the activity of water, a_w, which will be involved in the rate law for the acid-catalysed reaction. The concentation range of $NaClO_4$ over which there is a slight increase in k_1 may then reflect the balance of these two effects, namely the decrease in a_w and the increase in H_0.

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