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The Chemistry of the Hydrazine–Hydroxylamine–Nitric Acid System at High Temperatures†

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The kinetics of decomposition of hydrazine and hydroxylamine in concentrated nitric acid at 70 °C establish a critical concentration [hydrazine] $\approx 5 \times 10^{-4}$ mol dm^{-3} below which a rapid autocalalytic decomposition of hydroxylamine occurs; this corresponds to the rate of nitrite scavenging by hydrazine balancing the rate of N_2O_4 formation.

Modern developments in the Purex Process for nuclear fuel reprocessing involve the use of hydroxylamine as a reducing agent in place of Fe^{II} and hydrazine in place of sulfamic acid as a nitrite scavenger. The nitrite scavenger is necessary because even traces of nitrous acid caused a rapid autocatalytic decomposition of hydroxylamine in nitric acid, eqn. (1), and there have been several studies[1,2] of this reaction. Hydrazine is a powerful nitrite scavenger, eqn. (3), and decomposes only very slowly in nitric acid, eqn. (2).

$$NH_3OH^+ + 0.5(x+1)HNO_3 \rightarrow xHNO_2 + 0.25(3-x)N_2O + H_3O^+ \qquad (1)$$

The rate of reaction (1) increases rapidly with increase in $[HNO_3]$ and temperature. The object of the present study was to examine quantitatively the ability of hydrazine to stabilise hydroxylamine in nitric acid under much more demanding conditions of temperature and acid concentration. Experiments were carried out at 70 °C in nitric acid solution (9.1–13.2 mol dm^{-3}) with $10^3[NH_3OH^+]_0 = 6.7-16.7$ and $10^3[\text{hydrazine}]_0 = 3.3 - 16.7$ mol dm^{-3}. At high acidities hydrazine probably exists as a mixture of $N_2H_5^+$ and $N_2H_6^{2+}$, but values for pK_1 of $N_2H_6^{2+}$ under our conditions are not available. The reaction solution was continuously sparged with a flow of N_2 (500 cm^3 min^{-1}) to sweep away volatile HN_3 which is formed in both reactions (2) and (3). Hydrazoic acid is also destroyed according to eqn.(4).

$$17\,N_2H_5^+ + 16\,HNO_3 \rightarrow 4\,NH_4NO_3 + 4\,HN_3 + 4\,N_2O + 11\,N_2 + 32\,H_2O + 17\,H^+ \qquad (2)$$

$$N_2H_5^+ + HNO_2 \rightarrow HN_3 + 2\,H_2O + H^+ \qquad (3)$$

$$HN_3 + HNO_2 \rightarrow N_2 + N_2O + H_2O \qquad (4)$$

The stoichiometry of eqn. (2) is complex, but studies by Koltunov *et al.*[3] and Karraker[4] are in basic agreement. The stream of sparging gas was passed through NaOH solution and samples were analysed for NO_2^- and N_3^-. During each run a series of aliquots were removed from the reaction solution, quenched in water, and analysed for hydroxylamine and hydrazine. Typically a run might last for *ca.* 1 h and around 10 aliquots might be sampled.

The pattern of behaviour was very consistent. The hydrazine concentration decreased steadily, obeying good first order kinetics for most runs for around two half-lives, k_1/min^{-1}; in a typical run K2, Table 1, the first two half-lives were 22.2 and 22.6 min. In the later stages of reaction the rate was somewhat *greater* than calculated from k_1 [hydrazine]. For most runs $[NH_3OH^+]$ remained essentially constant during the first stage. The end of reaction at time t_f was marked by the sudden appearance of a puff of brown fumes above the surface of the solution, presumably NO_2, and samples taken after this time gave zero concentration for both hydrazine and hydroxylamine. Samples from the alkali trap showed a sharp increase in $[NO_2^-]$ but not in $[N_3^-]$ after time t_f. A typical run is shown in Fig. 1 and the results are summarised in Tables 1 and 2.

The k_1 values are in close agreement with the rate constants reported[3] for reaction (2). Extrapolation from 97 to 70 °C and to $[HNO_3] = 10$ mol dm^{-3} gives $k_1 = 0.036$ min^{-1}, close to the values in Table 1. For concentrations above $[\text{hydrazine}]_0 > 10^{-2}$ mol dm^{-3} there was essentially no detectable lOss of hydroxylamine over a 50 min timescale. However, for the lowest scavenger concentration, $[\text{hydrazine}]_0 = 3.3 \times 10^{-3}$, K4, there was clear evidence of a slow and steady decrease in $[NH_3OH^+]$ over the course of the run; some 19% of the initial NH_3OH^+ had decomposed up to the moment when the autocatalytic reaction rapidly destroyed the remainder. The fact that k_1 is markedly greater than normal strongly suggests that the concentration of hydrazine was not sufficient to efficiently suppress the formation of HNO_2, and the nitrous acid generated by reaction (1) consumed

Table 1 Reaction data for $N_2H_5^+$ and NH_3OH^+ in 10 mol dm^{-3} HNO_3 at 70 °C

Run	$10^3[N_2H_5^+]_0$/ mol dm^{-3}	$10^3[NH_3OH^+]_0$/ mol dm^{-3}	t_f/min	10^2k_1/min^{-1}	$10^5([NH_3OH^+]/dt)$/ mol dm^{-3} min^{-1}
K4	3.33	16.7	24	5.0	17
K6	6.67	16.7	45	3.3	7
K1	8.33	16.7	53	2.8	4
K1R	8.33	16.7	57	2.6	2
K2	10.0	16.7	75	3.1	
K3	11.7	16.7	66	3.3	
K8	16.7	16.7	59	3.1	
K9	16.7	13.3	58.5	3.5	
K10	16.7	10.0	54.5	3.0	
K11	16.7	6.67	—	3.0	
K17	8.33	0.0	—	2.7	

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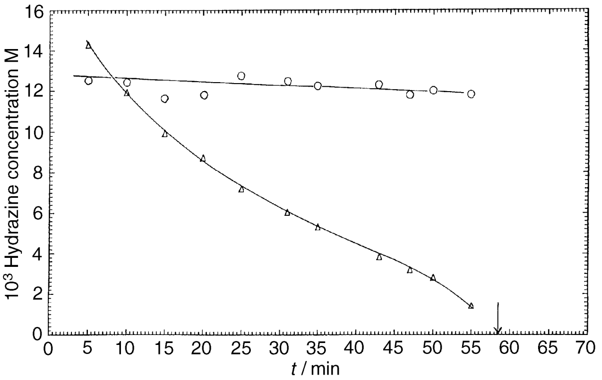

Fig. 1 Variation of hydrazine and hydroxylamine concentrations in run K9. $[HNO_3] = 10$, $[NH_3OH^+]_0 = 0.0133$, $[N_2H_5^+]_0 = 0.0167$ mol dm^{-3}; (△) hydrazine, (○) hydroxylamine; ↓ t_f

Table 2 Effect of $[HNO_3]$ on reaction data at 70 °C[a]

Run	K16	K8	K15	K14
$[HNO_3]$/mol dm^{-3}	9.1	10.0	11.1	12.0
t_f/min	127	59	52	30
$10^2 k_1$/min^{-1}	1.4	3.1	5.8	12.0

[a] $[N_2H_5^+]_0 = [NH_3OH^+]_0 = 0.0167$ mol dm^{-3}.

additional hydrazine by reaction (3). The same effect can be seen in K6 with twice the [hydrazine]$_0$. This should be twice as effective a scavenger in reducing $[HNO_2]$, and the rate of loss of NH_3OH^+ is about half that of K4. Slight signs of this can also be seen in the values of $-(d[NH_3OH^+]/dt)$ for K1 and K1R with a still higher [hydrazine]$_0$. As such effects show up in the range [hydrazine]$_0 = 3-6 \times 10^{-3}$ mol dm^{-3} they should appear in the later stages of runs such as K8–K11 with [hydrazine]$_0 = 0.0167$ mol dm^{-3}. Presumably this is the explanation of the increase in rate of consumption of hydrazine above k_1[hydrazine] after two half-lives referred to earlier. Our analytical method for hydroxylamine is not sufficiently precise to detect this effect with certainty in hydroxylamine consumption.

The sudden appearance of brown fumes at the end of reaction and the large and rapid drop in $[NH_3OH^+]$ to zero implies that there is a critical value of [hydrazine] below which the autocatalytic reaction 'takes off'. In runs K3 and K6 the final aliquot was sampled very shortly before the appearance of brown fumes, and [hydrazine] was 0.73×10^{-3} and 0.5×10^{-3} mol dm^{-3} in $[HNO_3] = 10$ mol dm^{-3}, respectively. For K15 and K14 [hydrazine] was 0.32×10^{-3} and 0.55×10^{-3} for $[HNO_3] = 11$ and 12 mol dm^{-3}. These figures suggest a critical hydrazine concentration of *ca.* 5×10^{-4} mol dm^{-3}. The results show, however, that significant amounts of decomposition of hydroxylamine occur at higher hydrazine concentrations, albeit in a slow, controlled manner. The nitrous acid that is generated in reaction (1) will rapidly destroy the residual hydrazine together with any hydrazoic acid present. The NO_2 fumes that appeared at time t_f were swept into the alkali trap, resulting in the formation of nitrite and nitrate by reaction (5).

$$2NO_2 + 2OH^- \rightarrow NO_2^- + NO_3^- + H_2O \qquad (5)$$

It is desirable to see if these results can be rationalised. The autocatalytic oxidation of hydroxylamine, reaction (1), is suggested[1,2] to involve N_2O_4 as the active nitrite species, oxidising NH_2OH. An estimate of the rate of formation of N_2O_4 in 9 mol dm^{-3} nitric acid at 0 °C can be obtained from the work of Bunton *et al.*[5] on the nitrite catalysed exchange of oxygen-18 tracer between nitric acid and water. Using an activation energy of 71.9 kJ mol^{-1} the estimated rate of formation of N_2O_4 at 70 °C is 1100[nitrite] mol dm^{-3} s^{-1}, where [nitrite] is the total concentration of all species analysed by a diazotisation/coupling analytical method. The rate of nitrite scavenging by hydrazine has been measured[6] from 4 to 15 mol dm^{-3} nitric acid at 0 °C and for 9 mol dm^{-3} it is 35600[nitrite][hydrazine] mol dm^{-3} s^{1}. Using an activation energy[7] of 46.9 kJ mol^{-1} this gives a rate at 70 °C of 3.0×10^6[nitrite][hydrazine]. If the critical condition corresponds to the rate of nitrite scavenging ≈ rate of formation of N_2O_4 then this gives [hydrazine] $\approx 5 \times 10^{-4}$ mol dm^{-3}. These calculations involve long temperature extrapolations using activation energies obtained in much more dilute acid media and so the close agreement is fortuitous. The calculation has been made for 9 mol dm^{-3} nitric acid because the oxygen exchange work of Bunton *et al.*[5] showed kinetic orders with respect to [nitrite] between 1 and 2 due to parallel paths involving N_2O_4 and N_2O_3. At 10 mol dm^{-3} nitric acid, the chosen concentration for most of our work, the second order path dominates and estimation of the first order component due to N_2O_4 is much more uncertain than for 9 mol dm^{-3} nitric acid. The calculation does not work so well at higher nitric acid concentrations where a large fraction of nitrite is present as N_2O_4 (and NO_2); the activation energies used were measured at much lower acidities where nitrite was mainly HNO_2. We conclude that the critical condition for hydrazine to stabilise hydroxylamine in nitric acid is for the rate of nitrite scavenging to be greater than the rate of formation of N_2O_4.

Experimental

The reaction vessel was a modified Drexel bottle with a sintered glass frit to disperse small bubbles of preheated N_2 through the solution. A double internal coil condenser was fitted to prevent losses of water and nitric acid vapour.

Analytical Methods.—Hydroxylamine was analysed by a flow injection method[8] and hydrazine by a standard colourimetric method[9] using *p*-dimethylaminobenzaldehyde. Nitrite ion was measured spectrophotometrically at 355 nm. Azide was measured volumetrically by reaction with Ce^{4+}, the nitrite having previously been destroyed by reaction with sulfamic acid.

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