THE TECHNETIUM-CATALYSED OXIDATION OF HYDRAZINE BY NITRIC ACID

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Summary

Technetium catalyses the oxidation of hydrazine by nitric acid, a reaction which is otherwise very slow except at elevated temperatures and acidities. The reaction displays an induction period followed by a rapid destruction of hydrazine. The induction period covers an initial slow reduction by hydrazine of technetium(VII) to technetium(IV) (the initiation phase) followed by a rapid technetium(IV)-catalysed reduction of technetium(VII) by hydrazine (the induction phase). The fast reaction commences when technetium(VII) has been substantially reduced to technetium(IV). The mechanism of the fast reaction is considered to be the oxidation of technetium(IV) to technetium(VI) by nitrate, followed by reduction of technetium(VI) to technetium(IV) by hydrazine; nitrite produced in the oxidation of technetium(IV) reacts with another molecule of hydrazine to produce hydrazoic acid. On completion of the reaction, technetium is present predominantly as pertechnetate. However, traces of a coloured species are produced during the reaction and this is considered to be an analogue of Eakins Pink Compound $(trans-[(NH_3)_4Tc(NO)(OH_2)]^{2+})$ which is formed by the reaction between hydrazine and technetium(IV). Hydrazoic acid is unstable in the system and is degraded, in part at least, to ammonium nitrate.

1. Introduction

In reactions with transition metal complexes, hydrazine can act as both a ligand and a redox reagent [1].

As a redox reagent hydrazine can react as both a one-electron and a twoelectron reductant. These reactions have been conveniently distinguished by their products: one-electron reduction normally leads to nitrogen and ammonia while two-electron reduction leads to nitrogen only. However, the products vary with the conditions, particularly the acidity and the transition metal present, so that one-electron reduction may produce only nitrogen and two-electron reduction may produce both hydrazoic acid and ammonia. The redox reactions between hydrazine and transition metals have been reviewed and the reaction mechanisms have been discussed by Bottomley [1].

Transition metals can also serve as catalysts for the destruction of hydrazine, *e.g.* in the oxidation of hydrazine by hydrogen peroxide where the presence of transition metals, notably copper, is necessary for the reaction to proceed [2]. The other aspect of the chemistry of hydrazine which is relevant to this work is its reactions with nitrous acid in acid media:

 $HNO_2 + N_2H_5^+ \rightarrow HN_3 + 2H_2O + H^+$

$$\rightarrow NH_4^+ + N_2O + H_2O$$

The relative rates of these reactions are acid dependent and the ratio of the products is given by the expression

 $\frac{[HN_3]}{[NH_4^+]} = 0.44 + 25[H^+]$

These reactions have been extensively investigated by Stedman and coworkers [3–5] and Phelan [6].

In the reprocessing of nuclear fuels, hydrazine can be used as a nitrite scavenger in the reductive separation of plutonium from uranium. Technetium (a major fission product) can catalyse the destruction of hydrazine to a considerable extent under these conditions [7]. A study of the reaction, with technetium concentrations of 6.4×10^{-4} - 3.2×10^{-3} M, hydrazine concentrations of 0.05-0.244 M and nitric acid concentrations of 1.2-6 M, is described in this paper. A mechanism is proposed to account for the kinetics of the principal reactions.

2. Experimental details

2.1. Materials

Ammonium pertechnetate in hydroxylamine hydrochloride was obtained from Amersham International. It was evaporated to dryness, redissolved in 8 M nitric acid and refluxed for several hours to ensure that technetium was present only as pertechnetate [8]. The concentration of technetium was determined radiometrically.

A technetium(V) standard was prepared by diluting 1 ml of standard pertechnetate solution with 9 ml of concentrated hydrochloric acid in a 10 ml flask. This treatment rapidly and completely reduces pertechnetate to technetium(V) [9]. Technetium(IV) was prepared by the reduction of a known concentration of pertechnetate by stannous chloride in the presence of ammonium thiocyanate to stabilize technetium(IV) (see below).

Commercial hydrazine nitrate was used without further purification. Nitric acid was of AnalaR quality.

2.2. Apparatus

To prevent loss of hydrazoic acid by volatilization (which is rapid at the

normal experimental temperature of 35 °C) experiments were conducted in closed 50 ml centrifuge tubes from which the evolved gases were vented through a solution of 0.1 M sodium hydroxide.

In certain experiments hydrazoic acid was deliberately vaporized by a nitrogen sparge, from which it was recovered by passage through 0.1 M sodium hydroxide. The efficiency of this recovery was determined to be about 96%.

Mixed phase experiments were carried out in a stoppered 50 ml flask with magnetic stirring.

A Pye-Unicam SP6 single-beam spectrophotometer was used for the analyses.

2.3. Procedures

Solutions of hydrazine in nitric acid were brought to the desired temperature, and concentrated pertechnetate solution was added to start the reaction. The concentrations of hydrazine, hydrazoic acid and ammonium nitrate were determined colorimetrically [10–12]. The concentration of nitrate was measured spectrophotometrically.

The concentrations of technetium(IV) and technetium(V) were determined by a modification of the thiocyanate colorimetric analysis for technetium [13]. An aliquot, normally 0.5 ml, of the reaction solution was mixed with 4.5 ml of 0.33 M ammonium thiocyanate. Under these conditions technetium(IV) forms a yellow complex, technetium(V) forms a red complex, and technetium(VI) and technetium(VII) do not react. The technetium(IV) and technetium(V) complexes mutually interfere, but can readily be separated by complete solvent extraction of the technetium(V) complex into 4 ml of butyl acetate. The separated phases were diluted to 10 ml with acetone and the absorbance of the complex was measured at 430 nm for technetium(IV) and at 513 nm for technetium(V).

The extinction coefficient of the technetium(V) complex was found to be 47700 l mol⁻¹ cm⁻¹, which is similar to that measured in the standard thiocyanate method (50000 l mol⁻¹ cm⁻¹) in which ascorbic acid is used to produce technetium(V) in situ [12]. The extinction coefficient for technetium(IV) was found to be $10000 \, \text{l} \, \text{mol}^{-1} \, \text{cm}^{-1}$.

2.4. Nitrogen balance

The gas evolved in the technetium-hydrazine reaction was collected and its volume was measured in an inverted water-filled burette. The composition of the gas was determined mass spectrometrically.

3. Results

The destruction of hydrazine by technetium in nitric acid ([Tc] = 1.6×10^{-3} M; [N₂H₅NO₃] = 0.1 M; [HNO₃] = 1.2 M; T = 35 °C) is

shown in Fig. 1. There is clearly an induction period followed by a rapid destruction of hydrazine. This latter phase, which is termed the "fast reaction", is accompanied by copious evolution of nitrogen and the development of a pale yellow colour in the solution. The reaction does not, however, continue to complete destruction of hydrazine, which remains in a small residual concentration. There is no destruction of hydrazine in the absence of technetium.

The effect of varying the initial concentration of hydrazine is shown in Fig. 2. There is no effect on the induction period, but the rate of the fast reaction, whilst insensitive to the proportion of hydrazine remaining, does increase with the initial concentration of hydrazine although in a non-linear way (Table 1).

The effects of increasing concentrations of nitric acid are shown in Fig. 3. Increasing acidity shortens the induction period and may accelerate the fast reaction, but it increases the residual concentration of hydrazine to such an extent that the reaction is totally inhibited in 6 M nitric acid. Experiments in which nitric acid is partially replaced by ammonium or sodium nitrate indicate that the rate accelerating effects on the induction period and the fast reaction



Fig. 1. Destruction of hydrazine ([Tc] = 1.6×10^{-3} M; [HNO₃] = 1.2 M; [N₂H₅NO₃] = 0.1 M; temperature, 35 °C): —, observed [N₂H₅NO₃] remaining; ---, simulated [N₂H₅NO₃] remaining. Fig. 2. The effects of varying the hydrazine concentration ([Tc] = 1.6×10^{-3} M; [HNO₃] = 1.2 M; temperature, 35 °C): \bigcirc , 0.244 M; \triangle , 0.200 M; \square , 0.145 M; \bigtriangledown , 0.094 M; \diamondsuit , 0.050 M.

$[N_2H_5NO_3]_0$ (mol l ⁻¹)	k (mol l ⁻¹ h ⁻¹)
0.050	2.5×10^{-2}
0.094	3.9×10^{-2}
0.145	$5.5 imes 10^{-2}$
0.200	6.0×10^{-2}
0.244	7.1×10^{-2}

 TABLE 1

 Effect of the initial hydrazine concentration on the rate of the fast reaction

are mainly due to the nitrate ion, while the inhibiting effect at high acidities is due to the acidity alone.

The extensive destruction of hydrazine by technetium (Fig. 1) has so far only been observed in nitric acid media (in hydrochloric acid, for example, technetium is completely reduced by hydrazine over 3-4 h to a stable intensely red species, with the consumption of less than 5% of the hydrazine). Indeed, nitrate ions are consumed during the reaction, typically to the extent of about 0.05 M, with, however, an equivalent increase in the acidity attributed to the destruction of twice as many hydrazinium ions.

The effect of temperature is shown in Fig. 4. A plot of $\ln k$ (for the fast reaction) against 1/T (where T is in kelvins) is linear, corresponding to an activation energy of 71 ± 6 kJ mol⁻¹ (1 σ) for the rate-determining step.

Increasing concentrations of technetium lead to a roughly proportional increase in the rate of the fast reaction (Fig. 5 and Table 2 (for clarity the results of several experiments are omitted from Fig. 5)). A similar effect is observed in the induction phase (Fig. 5) but no quantitative information was obtained.

Technetium is initially present only as pertechnetate (technetium(VII)), but is substantially reduced to technetium(IV) with traces of technetium(V) during the reaction (Fig. 6). Technetium(IV) is clearly a key intermediate in the fast reaction, and there is a close correlation (Fig. 7) between its highest observed concentration and the rate of reaction with varying initial concentrations of hydrazine (Fig. 2).

The induction period appears to be the time taken to reduce sufficient technetium(VII) for the fast reaction to become established. Indeed there is no induction period if another reductant is present, *e.g.* uranium(IV) or $SnCl_2$, which very rapidly reduces technetium(VII). The length of the induction period is insensitive to the concentration of hydrazine (Fig. 2), indicating that reduction of technetium(VII) by hydrazine is not the rate-determining step in the process. However, the length of the induction period is greatly reduced by the addition of small amounts of technetium(IV) recycled from the fast reaction (Fig. 8). It should be noted that the overall concentration of technetium was kept constant in these experiments.

No information is available on technetium(VI) and technetium(VII) during the reaction, but polarographic studies indicate that technetium is present essentially only as pertechnetate on completion of the reaction. Indeed the



Fig. 3. The effects of varying the acidity ([Tc] = 1.6×10^{-3} M; [N₂H₅NO₃] = 0.1 M; temperature, 35 °C): \bigtriangledown , 6 M nitric acid; \square , 5 M nitric acid; \triangle , 3.5 M nitric acid; \bigcirc , 1.2 M nitric acid.

Fig. 4. The effects of varying the temperature ([Tc] = 1.6×10^{-3} M; [HNO₃] = 1.2 M; [N₂H₅NO₃] = 0.1 M): \triangle , 29.5 °C; \bigcirc , 35 °C; \bigcirc , 46 °C; \heartsuit , 55 °C.

TABLE 2

Effect of technetium on	the rate of the fast reaction
[Tc]	k

	(11011 11)
6.4×10^{-4}	1.4×10^{-2}
7.1×10^{-4}	1.9×10^{-2}
1.4×10^{-3}	3.6×10^{-2}
1.6×10^{-3}	3.9×10^{-2}
2.1×10^{-3}	4.8×10^{-2}
2.8×10^{-3}	6.2×10^{-2}
3.2×10^{-3}	7.7×10^{-2}

reaction can be exactly repeated (within experimental error) by the addition of fresh hydrazine.

The products from the destruction of hydrazine and nitrate ions are principally nitrogen, ammonium nitrate and hydrazoic acid. The yields of these



Fig. 5. The effects of varying the technetium concentration ([HNO₃] = 1.2 M; [N₂H₅NO₃] = 0.1 M; temperature, 35 °C): ∇ , 6.4 × 10⁻⁴ M Tc; \square , 7.1 × 10⁻⁴ M Tc; \bigcirc , 1.6 × 10⁻³ M Tc; \triangle , 3.2 × 10⁻³ M Tc. Fig. 6. Evolution of technetium(IV) (\triangle , observed; ----, simulated) and technetium(V) (\diamondsuit , observed; -----, simulated) ([Tc] = 1.6 × 10⁻³ M; [HNO₃] = 1.2 M; [N₂H₅NO₃] = 0.1 M; temperature, 35 °C): ..., percentage of hydrazine remaining.

species relative to the amount of hydrazine destroyed are shown in Table 3. The amount of nitrate destroyed is also shown on the same basis.

The nitrogen mass balance MB is calculated from the formula

$$MB = \frac{3[HN_3] + 2[N_2] + [NH_4NO_3]}{2[N_2H_4] + [NO_3]}$$

to be about 0.92. The deficit is attributed to nitrous oxide. This gas is very soluble in water (130 cm³ per 100 ml [14]) and the volume (about 7 cm³) required to account for the nitrogen deficit would either remain in solution in the reaction vessel or dissolve into the water around the burette.

A closer study of the production of hydrazoic acid indicates that a steady concentration of this compound is attained during the reaction, indicating the existence of reactions both producing and consuming it. The destruction of hydrazoic acid is confirmed by its net loss from solutions doped with 0.05 M sodium azide.

Now Table 4 indicates an inverse relationship between the yields of



Fig. 7. Reaction rate vs. percentage of technetium(IV).

Fig. 8. Initiation with technetium(IV) (total $[Tc] = 1.6 \times 10^{-3}$ M; $[HNO_3] = 1.2$ M; $[N_2H_5NO_3] = 0.1$ M; temperature, $35 \degree C$): \Box , 8×10^{-4} M technetium(IV) added; \triangle , 3×10^{-4} M technetium(IV) added; --, no technetium(IV) added.

TABLE 3

Nitrogen bala	nce in the	technetium-h	ydrazine	reaction
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Ratio	Values	Average
[N ₃ ⁻] _{produced} /[N ₂ H ₄] _{destroyed}	0.149	0.153
	0.157	
[NH4 ⁺]produced/[N2H4]destroyed	0.235	0.238
•	0.243	
	0.235	
[N ₂] _{produced} /[N ₂ H ₄] _{destroved} ^a	0.76	0.81
,	0.83	
	0.83	
[NO ₃ ⁻] _{destroyed} /[N ₂ H ₄] _{destroyed}	0.60	0.51
,,	0.45	
	0.49	

 a The gas evolved was 97.2% N_2 and 2.8% N_2O and for nitrogen balance calculations can be assumed to be 100% $N_2.$

Experimental conditions	$[HN_3]_{produced}/$ $[N_2H_5NO_3]_{destroyed}$	$[\mathrm{NH_4}^+]_{\mathrm{produced}}/$ $[\mathrm{N_2H_5NO_3}]_{\mathrm{destroyed}}$
Standard	0.15	0.24
Standard + gentle N_2 sparging	0.21	0.24
Standard + vigorous N ₂ sparging	0.37	0.13
Standard + 30% TBP-OK*	0.41	0.05
Standard $+0.05$ M NaN ₃	-0.28	0.56

TABLE 4 Production of ammonium nitrate and hydrazoic acid

Standard conditions: 1.2 M HNO₃; [Tc] = 1.6×10^{-3} M; [N₂H₅NO₃] = 0.1 M; T = 35 °C. ^aTBP-OK, tributylphosphate-odourless kerosene.

hydrazoic acid and ammonium nitrate, and it is concluded that hydrazoic acid is broken down to produce, in part at least, ammonium nitrate. This reaction appears to occur predominantly in the aqueous phase, since if hydrazoic acid is removed, whether by solvent extraction or by volatilization, high yields of hydrazoic acid are obtained with low yields of ammonium nitrate. The maximum yield of hydrazoic acid (*i.e.* if no degradation to ammonium nitrate occurred) can be determined by extrapolation from the data in Table 4 as about 0.5 mol per mole of hydrazine destroyed.

4. Discussion

Technetium clearly acts as a catalyst to promote the oxidation of hydrazine by nitrate, which is otherwise very slow except at elevated temperatures and acidities [6]. The mechanism, which is shown in Table 5, can conveniently be discussed in several sections. (The exact formulae of the technetium intermediates are unknown, and conventional formulae are adopted in this discussion.)

Equation		Best-fit rate constant $(l \mod^{-1} h^{-1})$
$Tc^{VII} + N_2H_4 \rightarrow Tc^{VI} + N_2H_4(ox)$	(1)	0.02
$Tc^{V} + N_{2}H_{4} \rightarrow Tc^{IV} + N_{2}H_{4}(ox)$	(2)	750
$Tc^{1V} + Tc^{V1} \rightarrow Tc^{V} + Tc^{V1}$	(3)	10 000
$Tc^{IV} + NO_{3}^{-} \rightarrow Tc^{VI} + NO_{3}^{-}$	(4)	30
$Tc^{V1} + N_2H_4 \rightarrow Tc^{IV} + N_2H_4(ox)$	(5)	750
$Tc^{VI} + NO_3^- \rightarrow Tc^{VII} + NO_2^-$	(6)	2
$Tc^{v} + NO_{3}^{-} \rightarrow Tc^{vII} + NO_{3}^{-}$	(7)	10
$NO_2 + N_2H_4 \rightarrow HN_3 + 2H_2O$	(8)	500
1 1 4 0 1		

TABLE 5 Equations used in the simulation of the Tc–N₂H₅NO₃–HNO₃ reaction

4.1. Induction period

The kinetic data strongly indicate that the induction period, in which technetium(VII) is reduced to technetium(IV), can be divided into two phases.

(1) The initiation phase is the very slow reduction of technetium(VII) by hydrazine to either technetium(VI) or technetium(V), which is then rapidly reduced by hydrazine to technetium(IV). Once a trace of technetium(IV) is present, the induction phase commences and is the major reaction reducing technetium(VII).

(2) In the induction phase it is proposed that technetium(IV) comproportionates with technetium(VII) (Table 5, reaction (3)):

 $Tc^{1v} + Tc^{v1} \rightarrow Tc^{v} + Tc^{v1}$

Technetium(V) and technetium(VI) are rapidly reduced to technetium(IV). Thus the reaction is the technetium(IV)-catalysed reduction of technetium(VII) by hydrazine. Reaction (3) is rapid, and the competing oxidation of technetium(IV) by nitrate, which is an essential part of the fast reaction, does not become significant until technetium(VII) has been substantially reduced to technetium(IV).

4.2. Fast reaction

The kinetic data indicate that the rate-determining step in the fast reaction is the nitrate oxidation of technetium(IV), probably to technetium(VI) (Table 5, reaction (4)):

$$TcO_2 + NO_3^- \rightarrow TcO_3 + NO_2^-$$

where TcO_2 and TcO_3 represent appropriately oxidized species and not necessarily the true simple oxides. Indeed, the fast destruction of hydrazine may be inhibited by complexing technetium(IV) with ligands such as thiourea or thiocyanate to form species which are resistant to oxidation by nitrate.

The nitrite produced in reaction (4) reacts rapidly with hydrazine at the experimental acidity of 1.2 M nitric acid to produce hydrazoic acid (Table 5, reaction (8)):

$$NO_2^- + N_2H_5^+ \rightarrow HN_3 + 2H_2O$$

To complete the cycle of steps comprising the fast reaction, technetium(VI) is reduced by hydrazine to technetium(IV). This can be either a two-electron or a one-electron reduction. However, to give the experimentally observed value of 0.5 for the ratio $[NO_3^-]_{destroyed}/[N_2H_4]_{destroyed}$ (Table 3), it must be predominantly two-electron reduction (Table 5, reaction (5)):

$$TcO_3 + N_2H_5^+ \rightarrow TcO_2 + H_2O + N_2H_3^+$$

The overall stoichiometry of the fast reaction (Table 5, reactions (4), (5) and (8)) is then

$$2N_2H_5^+ + NO_3^- \rightarrow HN_3 + 3H_2O + N_2H_3^+$$

in agreement with the experimental observations. Technetium(V) is not considered to play a significant role in the fast reaction.

The reactions leading to the destruction of hydrazoic acid are unknown. However, one possibility is the reaction with the diimine produced in reaction (5):

 $N_2H_3^+ + HN_3 \rightarrow NH_4^+ + 2N_2$

4.3. Termination reaction

Since technetium is present as pertechnetate on completion of the reaction, there are clearly reactions oxidizing the lower valence states to technetium(VII). The kinetic data indicate that the rate-determining step is the acid-accelerated oxidation of technetium(VI). This reaction competes with reaction (5) and only becomes significant when the $[HNO_3]/[N_2H_5NO_3]$ ratio is high, *i.e.* towards the end of a reaction, or at high acidities.

4.4. Reaction mechanism

The proposed mechanism for the technetium-hydrazine reaction is shown in Fig. 9. The reaction was computer simulated using the equations given in Table 5, and an excellent fit to the destruction of hydrazine was obtained (see Fig. 1). The "best-fit" rate constants, which apply only to these particular conditions, are included in Table 5. The fit to technetium(IV) and technetium(V) is poorer (Fig. 6) but still adequate in view of the larger errors involved in the measurement of these species and the fact that the mechanism does not include such reactions as the disproportionation of technetium(VI) and technetium(V).



Fig. 9. Proposed scheme for the reaction of technetium with hydrazine and nitric acid.

4.5. Colour formation

In the technetium-hydrazine reaction the solution develops a pale yellow colour, which becomes an intense red if the concentration of hydrazine is very high (1-2 M). If hydroxylamine is present (0.03-0.2 M), or if nitric acid is replaced by hydrochloric acid, technetium is completely converted to a stable intensely red species. It has not been possible to identify these

compounds; however, they are considered to be analogues of Eakins Pink Compound [15], which has been reported to be a nitrosyl technetium(I) or technetium(II) species with the formula trans-[(NH₃)₄Tc(NO)(OH₂)]²⁺.

Eakins Pink Compound is formed by the reaction between technetium(IV) and hydroxylamine, and a similar reaction would be expected between technetium(IV) and hydrazine. However, in the presence of nitrate the oxidation of technetium(IV) is rapid compared with the reaction with hydrazine, so that significant amounts of the coloured species are formed only at high concentrations of hydrazine. The reaction of technetium(IV) with hydroxylamine appears to be much more rapid and there is no competing oxidation reaction in hydrochloric acid so that in these systems large yields of the coloured species are obtained.

The amount of technetium reduced to the coloured species at 0.1 M hydrazine is estimated from the intensity of the colour to be about 2%-3%.

5. Conclusions

The fast destruction of hydrazine by technetium in nitric acid is a cyclic process, with the rate determined by the oxidation of a reduced technetium species by nitrate. The hydrazine is oxidized partly by concomitantly produced nitrous acid and partly by the higher oxidation state of technetium. The technetium valencies mainly involved are probably 4 and 6.

The induction mechanism is the technetium(IV)-catalysed reduction of technetium(VII) by hydrazine, which is initiated by the slow reduction of technetium(VII) by hydrazine. Termination is the acid-dependent oxidation, probably by nitrate, to pertechnetate.

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