The Role of Intermediate Oxidation States of Technetium in Catalysis of the Oxidation of Hydrazine by Oxo-anions. Part 1. Nitrate Ions†

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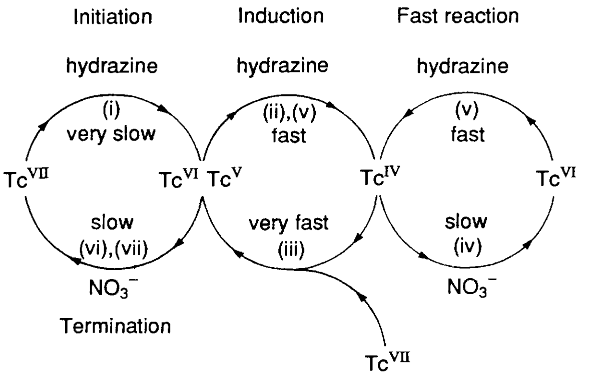
The catalysis by technetium of the oxidation of hydrazine by nitric acid has been studied over a wide range of concentrations of hydrazine and nitric acid and also in media where HNO_3 is replaced by HBF_4. The reaction is confirmed as a chain process, exhibiting a higher turnover number of hydrazine molecules per atom of Tc and a kinetic profile consisting of an initial slow stage, a very fast stage and a termination stage characterised by a high residual concentration of unreacted hydrazine and the existence of all Tc in the form of the initial pertechnetate ion. A model of the reaction which is an elaboration of that devised earlier by Garraway and Wilson, reproduces the main characteristics of reaction over a much wider range of reactants than before. The strong effects of increasing the acid concentration are in the opposite direction for HNO_3 and HBF_4.

The reaction between TcO_4^- ion and hydrazine in acidic nitrate-ion media has attracted interest both as a technologically highly significant reaction occurring in the reprocessing of spent nuclear fuel[1] and as an example of an inorganic chain reaction of high efficiency but of considerable complexity,[2] marked by conflicting accounts of its kinetics in the largely, but not exclusively, Russian literature.[3-7]

Its involvement in reprocessing[8] stems from the use of hydrazine as nitrite-ion scavenger in the uranium(IV) solution employed to backwash plutonium as the virtually inextractable Pu^{III}, from the solvent loaded with U^{VI} and Pu^{IV} in the first cycle of fuel reprocessing. Without this provision, nitrite inevitably formed by radiolysis would reoxidise Pu^{III} to Pu^{IV} and so frustrate the separation. The presence of Tc as a fission product of *ca.* 6% abundance in its preferred form of TcO_4^-, in the oxidising medium of aqueous HNO_3 (1.6 mol dm^{-3}), results in the destruction of hydrazine with an efficiency tens or hundreds of times greater than indicated by simple stoichiometry. This high turnover clearly implies the operation of a chain reaction involving the only other oxidant present, namely the anion of the reprocessing medium, *i.e.* NO_3^-. This is regarded as the oxidant of reduced Tc, which on reoxidation to a higher state, namely Tc^{VI}, attacks fresh hydrazine to yield NH_4^+, N_2 and other nitrogeneous products, reforming the reduced state of Tc, namely Tc^{IV}, capable of reducing fresh nitrate ion.

These reactions are summarised in Scheme 1 from Garraway and Wilson[2] (GW). The reaction displays an *induction period* which comprises an initial slow reduction of hydrazine to give Tc^{VI}, which is further reduced by hydrazine *via* a two-electron step to give Tc^{IV}. The Tc^{IV} and Tc^{VII} then react *via* a comproportionation reaction to give Tc^{VI} and Tc^{V}. Both these species then react rapidly with hydrazine to produce Tc^{IV} in increasing concentrations. The *fast reaction* commences when the Tc^{VII} has been substantially reduced to Tc^{IV}. At each stage of the reaction the reduced states of technetium are oxidised by nitrate, the *termination reaction* being the acid-catalysed oxidation of Tc^{VI} by nitrate, when reduction by hydrazine can no longer compete effectively. The values of the rate constants of the individual steps of Scheme 1 are discussed below.



Scheme 1 Reaction steps correspond to those in Table 3

In this paper and Part 2,[9] we present data generally supporting the GW scheme which, in Part 1, extends the ranges of acidity and nitrate ion concentration and in Part 2 describes an exactly parallel situation in perchlorate media, where ClO_4^- plays essentially the same role as NO_3^-.

Experimental

Materials.—Technetium-99 was obtained in the form of concentrated aqueous ammonium pertechnetate (1 mCi) in ammonium hydroxide (0.01 mol dm^{-3}) from Amersham International. The solution was evaporated to dryness, redissolved in nitric acid (8 mol dm^{-3}) and refluxed for several hours to convert all Tc to pertechnetate. The concentration of Tc was determined by liquid scintillation spectrometry using LKB Optiphase 'Safe' cocktail after calibration with a Tc standard, due allowance being made for internal quenching.

Other materials were of AnalaR quality.

Analytical Methods.—The concentrations of Tc^{IV} and Tc^{V} were determined by the modification due to Garraway and Wilson[2] of the thiocyanate colorimetric method of Howard and Weber[10] for Tc^{V}.

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† *Non-SI unit employed:* Ci = 3.7×10^{10} Bq.

A Tc^{V} standard was prepared by adding standard TcO_4^- solution (1 cm^3) to concentrated HCl (9 cm^3), which reduces all Tc^{VII} to $[TcOCl_4]^-$. Aliquots of the $[TcOCl_4]^-$ solution (0.5 cm^3) were added to 4.5 cm^3 portions of aqueous ammonium thiocyanate (0.33 mol dm^{-3}) to yield, over 40 min, the red $[Tc^{V}O(NCS)_5]^{2-}$, which was stable for at least several hours. This complex was extracted into *n*-butyl acetate (4 cm^3) and the two phases separated using a Pasteur pipette containing a cotton wool plug to act as a moisture filter. The absorbance at 513 nm was measured and a molar absorption coefficient of 5.0×10^4 dm^3 mol^{-1} cm^{-1} obtained, the same value as Howard and Weber.[10] [Garraway and Wilson[2] record $\varepsilon = 4.77 \times 10^4$ dm^3 mol^{-1} cm^{-1} in 40% *n*-butyl acetate–60% acetone (v/v).]

A Tc^{IV} standard was prepared by reducing TcO_4^- with a 50% excess of tin(II) chloride in the presence of nitric acid (1.0 mol dm^{-3}), followed by addition of ammonium thiocyanate (0.33 mol dm^{-3}). The sequence of reactions is given by equation (1).

$$TcO_4^- \xrightarrow{SnCl_2} [Tc^{IV}Cl_6]^{2-} \xrightarrow{NH_4NCS} [Tc^{III}(SCN)_6]^{3-} \quad (1)$$

An aliquot (0.5 cm^3) of the red-brown product obtained from the reduction of TcO_4^- by hydrazine, which contains Tc^{IV} and Tc^{V}, was added to a 4.5 cm^3 portion of aqueous ammonium thiocyanate solution (0.33 mol dm^{-3}) and, after removal of the by-product Tc^{V} by extraction with *n*-butyl acetate, the absorbance of the (yellow) aqueous phase was measured at 430 nm, to give an absorption coefficient of 9500 dm^3 mol^{-1} cm^{-1}, agreeing quite well with the value of 10 000 dm^3 mol^{-1} cm^{-1} of Garraway and Wilson.[2] [The assignment of this species as a technetium(III) complex follows Grases *et al.*[11]]

A technique for the estimation of Tc^{VII} was devised based on the spot test of Jasim *et al.*[12] utilising the colour reaction between TcO_4^- and thiourea, equation (2). Pertechnetate

$$TcO_4^- \xrightarrow[HNO_3]{thiourea} [Tc^{III}\{CS(NH_2)_2\}_6][NO_3]_3 \quad (2)$$

solution (1 cm^3) was added to nitric acid (4 mol dm^{-3}, 0.5 cm^3) and 10% aqueous thiourea (0.5 cm^3) and the mixture heated for 5–6 min on a water-bath at 80 °C to produce a deep orange solution with λ_{max} 425 (ε 2900 ± 200) and 490 nm ($\approx$2650 dm^3 mol^{-1} cm^{-1}), which was stable for at least a few hours.

Hydrazine assay was by the colorimetric method of Watt and Chrisp[13] as successively modified by Martin[14] and Embleton and Wilson.[15] This depends on the condensation between hydrazine and two molecules of *p*-dimethylaminobenzaldehyde to give the yellow-orange quinoidal azine $Me_2NC_6H_4CH{=}N{-}N{=}CHC_6H_4NMe_2$ (λ_{max} 468 nm, ε_{max} 60 400 dm^3 mol^{-1} cm^{-1}). An aliquot of the test hydrazine solution (0.5 cm^3) was placed in a volumetric flask (50 cm^3) and the contents made up to the mark with the following mixture: 2% *p*-dimethylaminobenzaldehyde in methylated spirit (10 cm^3), HCl (0.4 mol dm^{-3}, 10 cm^3) and methylated spirit. The colour took 45 min to develop fully at room temperature.

The nitrogen evolution was monitored by capturing the evolved gas in an inverted water-filled burette.

Kinetic Studies.—Reactions were carried out in Quickfit conical flasks (50 cm^3) immersed in the water of a thermostatted tank. A Tc^{VII} concentration of 1.6×10^{-3} mol dm^{-3} was chosen following Garraway and Wilson.[2] Unless stated otherwise all reactions were performed at 35.0 ± 0.1 °C. Evolved gases were passed through a solution of sodium hydroxide (0.1 mol dm^{-3}) and then collected as described above. For reactions carried out in tetrafluoroborate ion media, conical flasks made of polymethylpentene (Nalgene Labware Ltd.) were used. Aliquots of 0.5 cm^3 were withdrawn from time to time and subjected to analysis for N_2H_4, Tc^{IV} and Tc^{V}.

Kinetic Curve Fitting.—Computer fits to the experimental curves for the time dependences of the concentration of N_2H_4 and Tc^{VII} were achieved using a specially written program adapted from that of Garraway and Wilson used in ref. 2, but including certain additional features.

Results

General Course of Reaction.—In agreement with GW,[2] we find the reaction between TcO_4^- and hydrazine in a nitrate ion–nitric acid medium displays the following characteristics: (*a*) an induction period of from several tens of minutes up to hours, depending on reactant concentrations, temperature, *etc.*, (*b*) a fast reaction stage, during which most (but by no means all) of the hydrazine is destroyed with the visible evolution of N_2, (*c*) a termination stage, covering the marked slowing up and then cessation of hydrazine destruction, even when considerable amounts of hydrazine remain. These three stages are clearly evident in some of the reaction profiles illustrated in Fig. 1 which are based on assays of residual hydrazine.

Attempts to control the reaction by systematic variation of the concentration of one particular reactant affected all three stages of reaction.

Effect of Acidity.—Variation of the nitric acid concentration (at constant total nitrate ion concentration) exercised the most fundamental changes in the reaction profile. From Fig. 1 it is clear that at $[HNO_3] > 6.0$ mol dm^{-3} and $[Tc] = 1.6 \times 10^{-3}$ mol dm^{-3}, reaction fails to commence. As $[HNO_3]$ is gradually reduced, *e.g.* to 3.0 mol dm^{-3}, reaction takes place but (*i*) the induction period is relatively long, (*ii*) the rate of the fast stage is slow and (*iii*) the residual concentration of hydrazine is relatively high. Further lowering of $[HNO_3]$, *e.g.* to 0.5 mol dm^{-3}, results in (*i*) much shortening of the induction period, (*ii*) great acceleration of the fast stage and (*iii*) more extensive destruction of hydrazine, although under the reaction conditions of Fig. 1 this never exceeds 60%, *i.e.* 0.06 mol dm^{-3}, for $[TcO_4^-] = 1.6 \times 10^{-3}$ mol dm^{-3}; even so the stoichiometry for $[N_2H_4]:[Tc^{VII}]$ is *ca.* 38. At $[TcO_4^-] = 7.15 \times 10^{-4}$ mol dm^{-3}, $[HNO_3] = 4.0$ mol dm^{-3} and $[N_2H_5NO_3] = 0.1$ mol dm^{-3}, 35% of the hydrazine was ultimately destroyed, implying a stoichiometry for $[N_2H_4]:[Tc^{VII}]$ of *ca.* 49.

The effect of acid in retarding the rate of the fast stage, which displays approximately zero-order kinetics for much ($\approx$80%) of its duration, is shown in Fig. 2.

Effect of Acidity using HBF_4 *as Source of Protons.*—The difficulty with using an all-nitrate system is that added nitrate ions act both as a contributor to the ionic strength and an oxidant, while the scope for varying acidity independently is limited. Accordingly, at a fixed nitrate ion concentration of 0.6 mol dm^{-3}, HBF_4 was added to the system, the total ionic strength being maintained at 5.1 mol dm^{-3} by $NaBF_4$. Fig. 3 shows that, in contrast to the effect of nitric acid, increase of acidity reduces the induction period and increases the rate of the fast stage.

The effect of added HBF_4 in the same reaction mixture on the production of Tc^{IV} and Tc^{V} is intriguing. As in the all-nitrate ion system, both Tc^{IV} and Tc^{V} build up in concentration to a well defined peak, and then decline (Fig. 4). However, the peak in the NO_3^-–HBF_4 system is found to be both greater and steeper at high acidities at constant ionic strength. At all acidities there is a residual plateau concentration of Tc^{IV} representing *ca.* 15–20% of all Tc. There is an approximately linear relation between the percentage of Tc present as Tc^{IV} at the peak and rate of destruction of hydrazine in the fast stage. The yield of ammonium ions based on hydrazine destroyed was also found to decrease with increasing acidity (Table 1) in line with the results in an all-nitrate medium. It appears that high acidities promote reaction (3) at the expense of reaction (4).

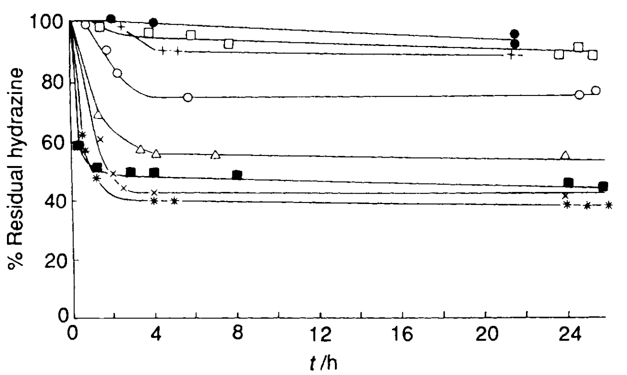

Fig. 1 Time dependence of the destruction of hydrazine with varying nitric acid concentrations; 0.1 (■), 0.5 (✱), 1.0 (×), 2.0 (△), 3.0 (○), 4.0 (+), 5.0 (□) and 5.9 mol dm^{-3} (●). Initial reactant concentrations (mol dm^{-3}): $[TcO_4^-]$ = 1.6 × 10^{-3}, $[N_2H_5NO_3]$ = 0.1, $[NO_3^-]_{total}$ = 7.0, T = 308 K

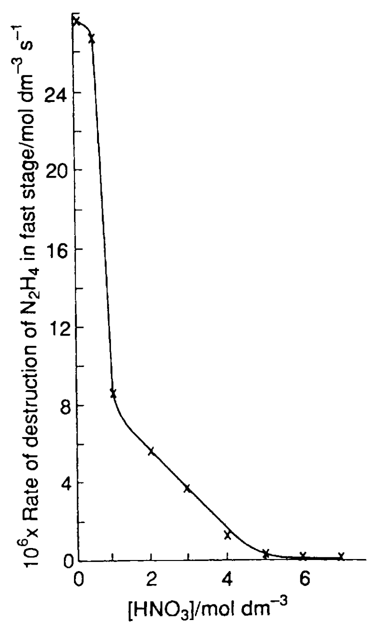

Fig. 2 Dependence of rate of destruction of hydrazine during the fast stage on nitric acid concentration. Reactant concentrations as for Fig. 1. T = 308 K

$$HNO_2 + N_2H_5^+ \longrightarrow HN_3 + 2H_2O + H^+ \quad (3)$$

$$HNO_2 + N_2H_5^+ \longrightarrow NH_4^+ + N_2O + H_2O \quad (4)$$

Effect of Nitrate Ion at Constant Ionic Strength.—In an initial series of experiments, $NaClO_4$ was used as the inert electrolyte. It was found, however, that this salt was far from inert (see Part 2[9]) and $NaBF_4$ was substituted. The rate of hydrazine destruction in the fast stage increases monotonically with nitrate ion concentration (Fig. 5): a rather sharper dependence of the rate of production of ammonium ions on nitrate ion concentration is apparent (Fig. 6). The overall yield of NH_4^+ ions falls with increasing nitrate ion concentration (Table 2), as the higher rate is evidently outweighed by the shorter reaction time.

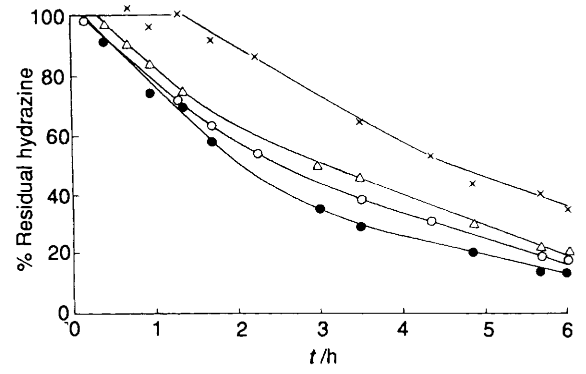

Fig. 3 Time dependence of the destruction of hydrazine with varying tetrafluoroboric acid concentrations; 1.0 (×), 2.0 (△), 3.0 (○) and 4.0 mol dm^{-3} (●). Initial reactant concentrations (mol dm^{-3}): $[TcO_4^-]$ = 1.6 × 10^{-3}, $[N_2H_4{\cdot}H_2O]$ = 0.1, $[NaNO_3]$ = 0.6, $[HNO_3]$ = 0.05, $[BF_4^-]_{total}$ = 5.0, T = 308 K

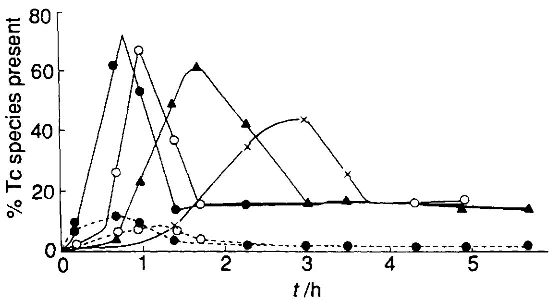

Fig. 4 Evolution of Tc^{IV} (full line) and Tc^{V} (broken line) over time at varying tetrafluoroboric acid concentrations; 1.0 (×), 2.0 (▲), 3.0 (○) and 4.0 mol dm^{-3} (●). Other conditions as for Fig. 3

Table 1 Variation in the production of ammonium ions with increasing tetrafluoroboric acid concentration

$[HBF_4]$/mol dm^{-3}	1.0	2.0	3.0	4.0
$[NH_4]^+$ produced/ mol dm^{-3}	0.0257	0.0262	0.0282	0.0249
$[N_2H_5]^+$ oxidised/ mol dm^{-3}	0.0660	0.0813	0.0843	0.0873
Yield of NH_4^+ per mol percent based on hydrazine loss	38.9	32.2	33.3	28.5

Discussion

The existence of an induction period, a fast stage and a termination stage (leaving sizeable quantities of unreacted hydrazine) coupled with a very high figure for $[N_2H_4]/[Tc^{VII}]$ all point to a chain mechanism which must ideally accommodate the following features: (*i*) the duration of the induction period, (*ii*) the rate of the fast stage and (*iii*) the residual level of hydrazine.

The GW model,[2] summarised in Scheme 1, copes with all three major requirements. The individual steps in the model, together with appropriate rate constants, are given in Table 3. While these constants give an excellent fit to the data of ref. 2, they are rather limited insofar as they refer only to one set of reactant concentrations,[2] namely $[TcO_4^-]$ = 1.6 × 10^{-3} mol dm^{-3}, $[N_2H_5NO_3]$ = 0.1 mol dm^{-3} and HNO_3 = 1.2 mol dm^{-3}. One of our aims was to extend the GW model to cover much wider ranges of concentrations. The major modification found to be necessary was to introduce a rather complex acid dependence for the oxidation of Tc^{VI} by NO_3^- [reaction (vi), Scheme 1], to account for the sharp inhibition of the fast reaction at high nitric acid concentrations. This is summarised in Table 4 but in explicit form, step (vi) of Scheme 1 takes the form $k_{vi} = (5 \times 10^{-4}) + K(12)$, where $K(12) = f[H_3O^+]$. The (very slow) initiation rate k_i also needed much adjustment, but other changes are minor. Our proposed set of rate constants also appears in Table 3. These were reached after attempted fits to a very large number of runs under a

Table 2 Variation in the yield of ammonium ions with increasing nitrate ion concentration at constant ionic strength

$[NO_3^-]$/mol dm^{-3}	0.55	1.05	1.55	2.55	3.55	4.55
$[NH_4^+]$ produced/mol dm^{-3}	0.0265	0.0280	0.0238 0.0220	0.0238	0.0201	0.0190
$[N_2H_5]^+$ oxidised /mol dm^{-3}	0.0693	0.0733	0.0774 0.0646	0.0605	0.0626	0.0666
Yield of NH_4^+ per mol percent based on hydrazine loss	38.2	38.2	30.7 34.1	39.3	32.1	28.5

Table 3 Equations used by GW (ref. 2) in their simulation of the Tc–$N_2H_5NO_3$–HNO_3 reaction together with the GW rate constants and ours

	Best-fit rate constant/dm^3 mol^{-1} s^{-1}	
Reaction	GW (ref. 2)	Present work
(i) $Tc^{VII} + N_2H_5^+ \longrightarrow Tc^{VI} + N_2H_3^{\cdot} + H^+$	5.55×10^{-6}	2.22×10^{-3}
(ii) $Tc^{V} + N_2H_5^+ \longrightarrow Tc^{IV} + N_2H_3^{\cdot} + H^+$	0.208	0.25
(iii) $Tc^{IV} + Tc^{VII} \longrightarrow Tc^{V} + Tc^{VI}$	2.78	3.056
(iv) $Tc^{IV} + NO_3^- \longrightarrow Tc^{VI} + NO_2^-$	8.3×10^{-3}	1.25×10^{-3}
(v) $Tc^{VI} + N_2H_5^+ \longrightarrow Tc^{IV} + N_2H_2 + 3H^+$	0.208	0.236
(vi) $Tc^{VI} + NO_3^- \xrightarrow{H^+} Tc^{VII} + NO_2^-$	5.55×10^{-4}	$5 \times 10^{-4} + K(12)$[a]
(vii) $Tc^{V} + NO_3^- \longrightarrow Tc^{VII} + HNO_2$	2.78×10^{-3}	1.389×10^{-3}
(viii) $HNO_2 + N_2H_5^+ \longrightarrow HN_3 + 2H_2O + H^+$	0.139[b]	0.139[b]
(ix) $HN_3 + HNO_2 \longrightarrow N_2 + N_2O + H_2O$	—	1.389×10^{-2}[c]

[a] $K(12)$ is an acid-dependent rate constant (see text and Table 4). [b] This figure is much lower than the literature value[16] and represents the highest figure we could use within the constraints of operating the computer; the kinetic curves are insensitive to the magnitude of k_{viii} at or above this value. [c] Units of dm^6 mol^{-2} s^{-1}. This is a 'fitting' value of k_{ix}, variation in which barely affects the simulation.

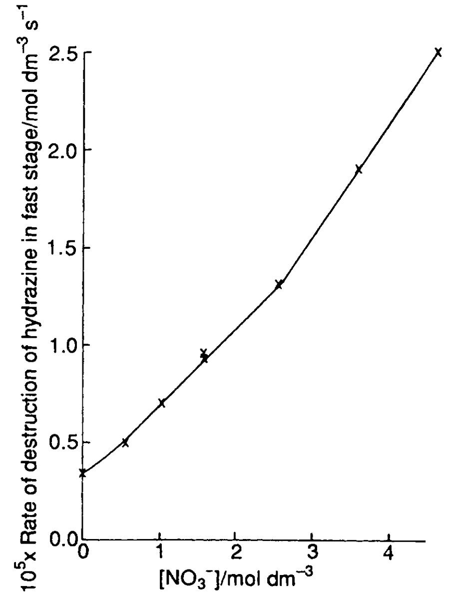

Fig. 5 Variation of rate of oxidation of hydrazine during the fast stage with nitrate ion concentration at constant acidity and ionic strength. Initial reactant concentrations (mol dm^{-3}): $[TcO_4^-] = 1.6 \times 10^{-3}$, $[N_2H_4{\cdot}H_2O] = 0.1$, $[HNO_3] = 0.55$ mol dm^{-3}; $[NaNO_3]$, $[NaBF_4]$ varied to give total I of 6.05 mol dm^{-3}, $T = 308$ K

Table 4 Variation in the value of $K(12)$ with $[HNO_3]$

$[HNO_3]$/mol dm^{-3}	5	4	3	2	1	0.5	0.1
$10^4K(12)$/dm^3 mol^{-1} s^{-1}	1.11	1.32	1.43	1.75	2.92	3.12	30.1

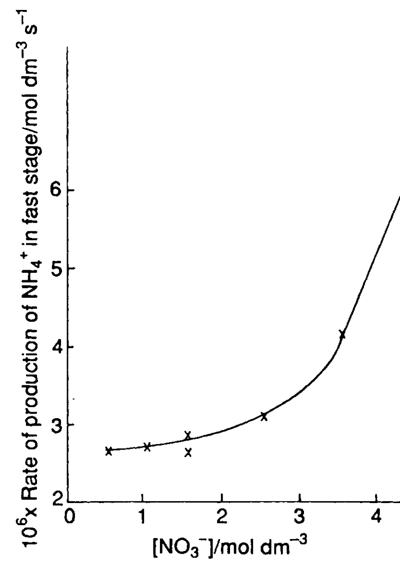

Fig. 6 Dependence of rate of production of NH_4^+ ions in the fast stage upon nitrate ion concentration at fixed ionic strength. Initial reaction concentrations as for Fig. 5

variety of conditions. The rate constants used are largely those of GW; one should note that certain rate constants, *e.g.* k_{viii} and k_{ix}, represent the largest figure one could use while still running the program. These therefore represent lower limits. Accurate figures for k_{viii} are given in ref. 16. Our set of rate constants reproduce the essential features of the GW model, *i.e.* that (*i*) the very slow initiation step is the attack of Tc^{VII} upon N_2H_4 to give Tc^{VI}, step (i), which subsequently attacks N_2H_4 to give Tc^{IV}, step (ii); Tc^{IV} then comproportionates with Tc^{VII} to give Tc^{V} and Tc^{VI} in step (iii). Reaction (iii) is rapid and attack of Tc^{IV} on NO_3^-, reaction (iv), does not become significant until virtually all Tc^{VII} has been reduced.

(*ii*) The fast stage consists of the cycle of steps (iv), (v) and (xi) (Table 3).

$$Tc^{IV} + NO_3^- \longrightarrow Tc^{VI} + NO_2^- \qquad \text{(iv)}$$

$$Tc^{VI} + N_2H_5^+ \longrightarrow Tc^{IV} + N_2H_2 + 3H^+ \qquad \text{(v)}$$

$$2N_2H_2 \longrightarrow N_4H_4 \longrightarrow NH_3 + HN_3 \qquad \text{(xi)}$$

(*iii*) Termination consists of the reoxidations of Tc^{V}, and especially Tc^{VI} in step (vi), to Tc^{VII}, which is the sole technetium

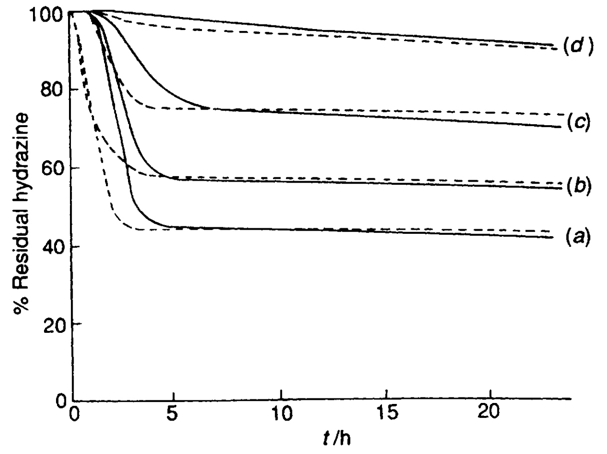

Fig. 7 Computer simulation based on modified GW scheme of the effect of changing nitric acid concentration on the reaction profile of the TcO_4^--N_2H_4-HNO_3 reaction; (*a*) 1.0, (*b*) 2.0, (*c*) 3.0 and (*d*) 5.0 mol dm^{-3} HNO_3, (– – – –) experimental profile, (——) simulated profile. Initial reactant concentrations (mol dm^{-3}): $[TcO_4^-] = 1.6 \times 10^{-3}$, $[N_2H_4 \cdot H_2O] = 0.1$

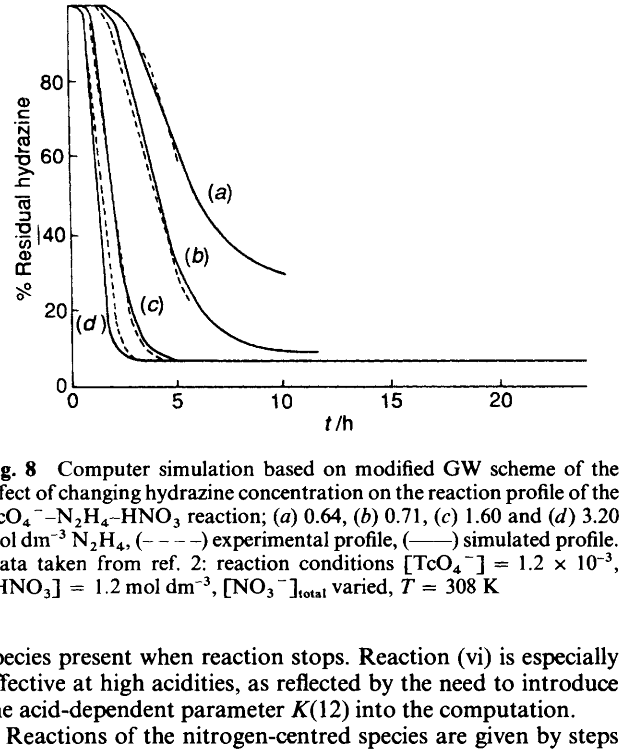

Fig. 8 Computer simulation based on modified GW scheme of the effect of changing hydrazine concentration on the reaction profile of the TcO_4^--N_2H_4-HNO_3 reaction; (*a*) 0.64, (*b*) 0.71, (*c*) 1.60 and (*d*) 3.20 mol dm^{-3} N_2H_4, (– – – –) experimental profile, (——) simulated profile. Data taken from ref. 2: reaction conditions $[TcO_4^-] = 1.2 \times 10^{-3}$, $[HNO_3] = 1.2$ mol dm^{-3}, $[NO_3^-]_{total}$ varied, $T = 308$ K

species present when reaction stops. Reaction (vi) is especially effective at high acidities, as reflected by the need to introduce the acid-dependent parameter $K(12)$ into the computation.

Reactions of the nitrogen-centred species are given by steps (viii)–(x) (Table 3, Scheme 1).[16,17]

$$HNO_2 + N_2H_5^+ \longrightarrow HN_3 + 2H_2O + H^+ \quad \text{(viii)}$$

$$2N_2H_3^{\bullet} \longrightarrow N_4H_6 \longrightarrow 2NH_3 + N_2 \quad \text{(x)}$$

$$HN_3 + HNO_2 \longrightarrow H_2O + N_2O + N_2 \quad \text{(ix)}$$

As regards the effectiveness of the simulation of these various stages, this was reasonably good at 5.0 mol dm^{-3} > $[HNO_3]$ > 3.0 mol dm^{-3} (Fig. 7) but at $[HNO_3]$ < 3.0 mol dm^{-3}, while the rate of the fast reaction stage and the level of residual hydrazine could be predicted accurately, the estimate of the initiation–induction period was very poor. Since the initiation must be a positive feedback mechanism of inherent instability, any prediction is bound to be highly sensitive to the precise conditions.

It was found possible to obtain reasonably good simulations of the induction period for a series of runs with wide variation in the hydrazine concentration by parameterising the rate constant of reaction (i), Fig. 8 and Table 3. However, the very strong hydrazine concentration dependence of reaction (i) is difficult to account for in a simple chemical way. It simply means that there are probably further minor steps in the total scheme which have not been accounted for. Zelverte,[6] for example, has proposed the involvement of the strongly reducing Tc^{III}.

Tetrafluoroboric acid offers contrasts with HNO_3 in the overall reaction, especially in that, at a given sodium nitrate concentration, whereas addition of nitric acid preserves the hydrazine against destruction, the addition of HBF_4 (*i*) greatly shortens the initiation–induction period, (*ii*) slightly increases the rate of the fast stage, (*iii*) gives a more gradual transition from the fast stage to the near-plateau stage and (*iv*) destroys more hydrazine. Tetrafluoroboric acid is a stronger acid than HNO_3 and all the technetium species are likely to be more extensively protonated at high HBF_4 concentrations: this may have the effect of promoting attack of technetium species on hydrazine in both the initial period and, less conspicuously, in the fast stage, more than on the reoxidation of technetium species to Tc^{VII}.

Acknowledgements

One of us (A. M. T.) thanks SERC and British Nuclear Fuels for financial support through a CASE studentship.

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Received 20*th April* 1993; *Paper* 3/02271D