# The Role of Intermediate Oxidation States of Technetium in Catalysis of the Oxidation of Hydrazine by Oxo-anions. Part 2.[1] Perchlorate Ions

**Terence J. Kemp,**[*,a] **Aubrey M. Thyer**[a] **and Peter D. Wilson**[b]
[a] *Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK*
[b] *Building 229, Research and Development Department, British Nuclear Fuels, Sellafield, Seascale CA20 1PG, UK*

The oxidation of hydrazine by an aqueous acid perchlorate medium is catalysed very efficiently by $TcO_4^-$ ions in a manner recalling the nitrate ion system. The reaction shows an induction period followed by a fast stage of evolution of $N_2$, and a high turnover number ( > 60) but no residue of unreacted hydrazine is left in contrast to the nitrate system, especially under strongly acid conditions. The concentration of $Tc^{IV}$ in the system goes through two maxima as reaction proceeds, the first being extremely sharp, the second much broader. This complex kinetic behaviour has been computer-modelled reasonably successfully. The colour changes depend on the acidity of the system, but some coloured products have been characterised by UV/VIS and/or ESR spectroscopy.

The role of technetium in the catalysis of the oxidation of hydrazine by nitrate ions is a serious consideration in the reprocessing of nuclear fuel. As described in Part 1,[1] this reaction has all the hallmarks of a classical chain reaction, *i.e.* an induction period, a period of fast reaction and a termination step which leaves high residual concentrations of hydrazine, all coupled with a high turnover number. A mechanism has been devised, involving the oxidation of hydrazine by Tc in a high oxidation state followed by the reduction of nitrate ion by the reduced states of Tc, to regenerate the high oxidation state of Tc needed to attack fresh hydrazine. This mechanism accounts for all the observed chain characteristics of the reaction, and gives good quantitative accounts of the rate of the fast stage and the residual level of hydrazine: it is somewhat less successful in predicting the induction period.

It was shown by Spitsyn *et al.*,[2] that this reaction also proceeds in a perchlorate ion medium, although these studies were based on UV/VIS spectrophotometric studies of the reduced states of Tc and no analysis of the reaction profile of hydrazine was attempted. However an induction period and a fast stage were noted. We report here that the oxidation of hydrazine by perchlorate ion is highly efficient in the presence of low concentrations of pertechnetate ion, and that this reaction also shows chain behaviour, particularly an induction period and a high turnover number. In this reaction, however, reaction proceeds to complete destruction of a large excess of hydrazine, in contrast to the situation with nitrate ion when a termination step led to large residual amounts of hydrazine. A model is proposed, based on that of Garraway and Wilson [3] for the $N_2H_4$–$Tc^{VII}$–$NO_3^-$ system, which accounts for all the main features of the reaction (loss of hydrazine, behaviour of intermediate oxidation states of Tc) including the remarkable oscillatory behaviour in the technetium concentration.

## Experimental

All materials, and analytical and kinetic procedures have been described in Part 1. Except where stated otherwise, all reactions were carried out in a bath thermostatted to 35.0 ± 0.1 °C. Spectrophotometric kinetic runs were carried out by monitoring the concentration of $TcO_4^-$ ion at the 244.5 nm component of its doublet absorption band. ESR spectra were measured in a flat cell in an X-band spectrometer (Bruker model ER 200tt).

## Results

*Products of Reaction.*—The principal products of the reaction were, as for the nitrate system, nitrogen gas (detected by gas chromatography–mass spectrometry, together with minor amounts of nitric oxide), ammonia (see Fig. 2) and hydrazoic acid. Gravimetric analysis for chloride ion revealed that oxidation of 0.1 mol dm$^{-3}$ hydrazine in $HClO_4$ (2 mol dm$^{-3}$) yielded a chloride ion concentration of 0.032 mol dm$^{-3}$. The $N_2H_5^+$–$TcO_4^-$–$HClO_4$ reaction mixture developed a UV band during reaction in the region 190–230 nm identical in character with that of a solution of $KClO_3$: we estimate that a solution containing $TcO_4^-$ ($1.6 \times 10^{-3}$ mol dm$^{-3}$), $N_2H_5^+$ (0.1 mol dm$^{-3}$), $HClO_4$ (6.0 mol dm$^{-3}$) and $NaClO_4$ (0.9 mol dm$^{-3}$) develops a chlorate ion concentration of *ca.* 0.018 mol dm$^{-3}$ in the first 35 min of reaction at 35.0 °C. No spectral evidence could be adduced indicating formation of detectable levels of $ClO^-$ or $ClO_2^-$.

*Weakly Acid Solution* ($I$ = 1.1 mol dm$^{-3}$).—The general profile of the reaction, based on analysis for residual hydrazine, is shown in Fig. 1 from which the regions of the induction

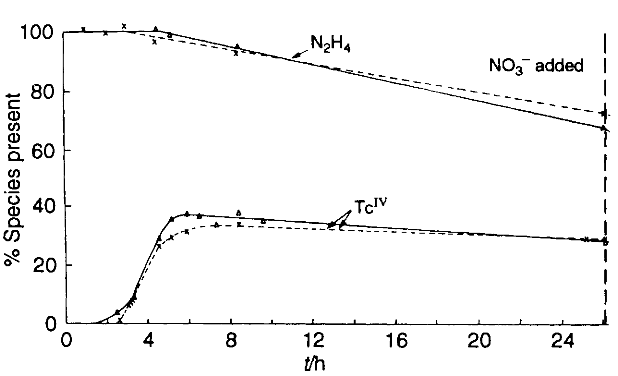


**Fig. 1** Destruction of hydrazine and evolution of $Tc^{IV}$ and $Tc^V$ in a $HClO_4$–$N_2H_4$–$TcO_4^-$ system at low acidity. Initial reaction conditions: $[TcO_4^-] = 1.6 \times 10^{-3}$, $[N_2H_4] = 0.1$, $[HClO_4] = 1.0$, $[NaNO_3]$ (after injection at 26 h) = 0.29 mol dm$^{-3}$, $T$ = 308 K; –△– and –×– refer to duplicate runs

period and the fast reaction can be seen: the reaction does not proceed at all rapidly compared with the nitrate system at the same acidity.[1] Of particular interest are the rather sudden appearance of $Tc^{IV}$ in the later part of the induction period and the strongly accelerative effects of adding nitrate ion after 26 h. In Fig. 2 is shown the relation between the destruction of $N_2H_4$ and the emergence of ammonia. The development of $Tc^{IV}$ became, in some runs, manifest through formation of a dark brown precipitate of $TcO_2$.

*Strongly Acid Solutions* ($I = 7.0$ mol dm$^{-3}$).—The strongly accelerating effect of adding acid at constant ionic strength is evident from Fig. 3. At $[HClO_4] = 1.0$ mol dm$^{-3}$ the reaction shows three clearly defined stages as in the nitrate system,[2] but as the acidity is raised, the induction period shortens, the rate of the fast stage increases and the clear distinction between the fast stage and the termination stage disappears. In all systems, in contradistinction to the nitrate system, the hydrazine is totally destroyed. The time dependence of the concentrations of both $Tc^{IV}$ and $Tc^{V}$ were determined and that for $Tc^{IV}$ is shown in Fig. 4. The reaction profile for $Tc^{V}$ was very similar in shape to that of $Tc^{IV}$ but only a maximum of 10% of Tc appeared as $Tc^{V}$ (in 6.0 mol dm$^{-3}$ acid) whilst in 1.0 mol dm$^{-3}$ acid this was reduced to only 2–3%.

The dependence of the rate of oxidation of hydrazine in the fast stage upon acidity is shown in Fig. 5 and indicates a clear first-order dependence. This contrasts strongly with the *inhibiting* effect of nitric acid on the fast stage in the nitrate system.

The acid dependence of the initiation reaction was determined from loss of the $TcO_4^-$ absorption at 244.7 nm: it is shown in Fig. 6 along with the rate of the fast stage measured in the same way. The rate during the fast stage depends on $[H_3O^+]^2$ while that during initiation is acid-independent below $[H_3O^+] = 2.5$ mol dm$^{-3}$ but depends on $[H_3O^+]^2$ above this. This offers another contrast to the nitrate system in which virtually all $Tc^{VII}$ disappears before the fast stage begins: with the perchlorate medium, the loss of $Tc^{VII}$ proceeds throughout the fast stage.

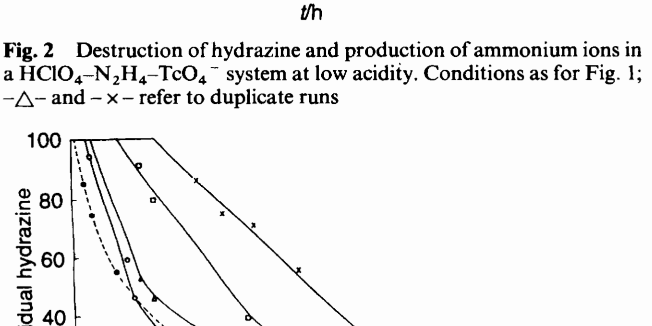


**Fig. 2** Destruction of hydrazine and production of ammonium ions in a $HClO_4$–$N_2H_4$–$TcO_4^-$ system at low acidity. Conditions as for Fig. 1; –△– and – × – refer to duplicate runs

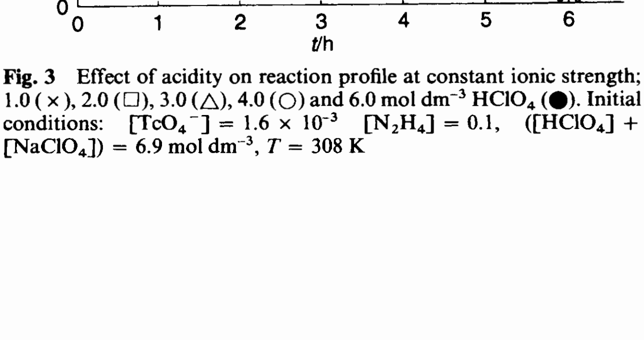


**Fig. 3** Effect of acidity on reaction profile at constant ionic strength; 1.0 ( × ), 2.0 (□), 3.0 (△), 4.0 (○) and 6.0 mol dm$^{-3}$ $HClO_4$ (●). Initial conditions: $[TcO_4^-] = 1.6 \times 10^{-3}$ $[N_2H_4] = 0.1$, $([HClO_4] + [NaClO_4]) = 6.9$ mol dm$^{-3}$, $T = 308$ K

The effect of temperature on the destruction of hydrazine is clear from Fig. 7: this picture was paralleled completely in profiles of the growth of ammonium ion concentration. Both

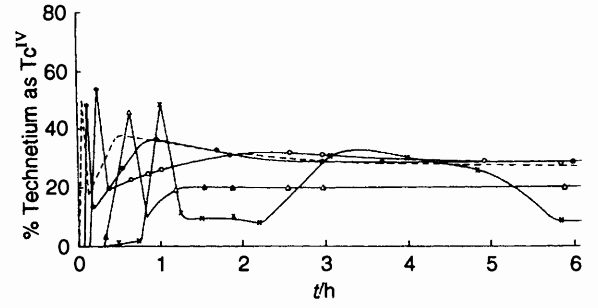


**Fig. 4** Effect of acidity on time profile of $Tc^{IV}$; 1.0 ( × ), 2.0 (△), 3.0 (○), 4.0 (●) and 6.0 mol dm$^{-3}$ $HClO_4$ (– – – –). Initial conditions as for Fig. 3. Data points for 6.0 mol dm$^{-3}$ $HClO_4$ omitted for clarity

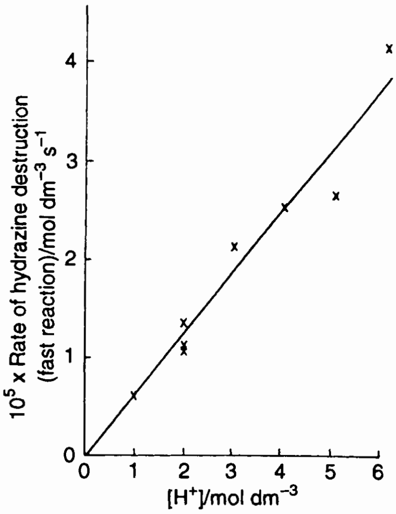


**Fig. 5** Acidity dependence of rate of oxidation of hydrazine at constant ionic strength during fast stage. Initial conditions as for Fig. 3

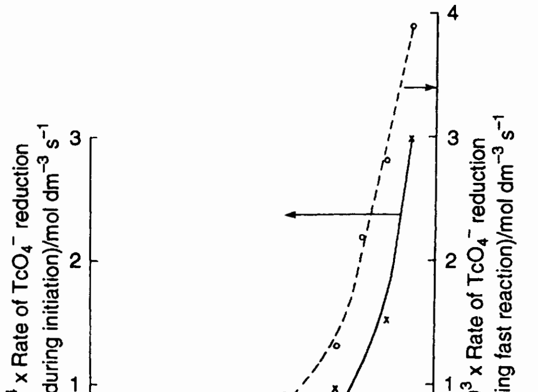


**Fig. 6** Rate of reduction of $TcO_4^-$ ion in initial ( × , ——) and fast (○, – – – –) reaction stages in the $TcO_4^-$–$N_2H_4$–$HClO_4$ system. Initial reaction conditions as for Fig. 3

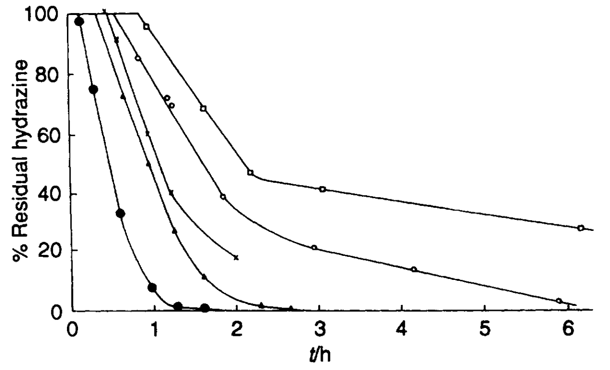


**Fig. 7** Temperature dependence of time profile of hydrazine concentration; 27.7 (□), 35.0 (○), 39.9 (×), 43.2 (△) and 40.8 °C (●). Initial conditions: $[TcO_4^-] = 1.6 \times 10^{-3}$, $[N_2H_4] = 0.1$, $[HClO_4] = 2.0$, $[NaClO_4] = 4.9$ mol dm$^{-3}$

initiation and fast stage have considerable activation energies: that for initiation based on the data of Fig. 7 is 35.5 ± 1 kJ mol$^{-1}$. The value based on the profiles for ammonia production is 83 ± 12 kJ mol$^{-1}$. The corresponding activation energy for the nitrate system is 72 ± 6 kJ mol$^{-1}$.

*Effect of adding Salts based on Reduced States of* $ClO_4^-$.—Since the turnover number, $[N_2H_4(loss)]/[Tc]$ is very high (> 60), clearly the perchlorate ion is acting as the source of oxidising equivalents in the system, *cf.* the picture in the nitrate system where $NO_3^-$ fulfils the same function. It is also obvious that $ClO_4^-$ is reduced, and we attempted to determine $ClO_3^-$, $ClO_2^-$, $ClO^-$ and $Cl^-$ ions in the system. Unfortunately, the huge excess of $ClO_4^-$ interfered with all analytical procedures tried, although $Cl^-$ was certainly present. Accordingly, to assess the role of these 'reduced states' upon the overall process, we added appropriate ions at various stages of reaction.

(*i*) *Effect of added chlorate ion.* This is clear from Figs. 8 and 9, where $ClO_3^-$ simply terminates reaction by promptly oxidising all the $Tc^{IV}$ and $Tc^V$ to $Tc^{VII}$. This conclusion was confirmed by spectrophotometric measurements on a reaction mixture. A solution of $Tc^V$ prepared separately was also found to undergo very rapid oxidation by $ClO_3^-$ (within 15 s), indicating a second-order rate constant at 298 K > 80 dm$^3$ mol$^{-1}$ s$^{-1}$.

(*ii*) *Effect of added hypochlorite ion.* This addition prompted the vigorous evolution of chlorine gas and a change in colour of the reaction mixture from red-brown to an intense yellow ($\lambda_{max}$ 344 nm). The addition also had an immediate depressant effect on the concentration of $Tc^{IV}$ and $Tc^V$ but, in contrast to the effect of $ClO_3^-$ ion, sharply accelerated the destruction of hydrazine (Fig. 10). The deep yellow solution gave an intense four-line ESR spectrum with $g = 2.0099 \pm 0.003$ and $a = 17.50 \pm 0.20$ G (G = $10^{-4}$ T) attributable to $ClO_2^{\bullet}$. We found, however, that this spectrum depended on the presence of chlorite impurities in the hypochlorite solution.

*Formation of Coloured Complexes in the* $Tc–N_2H_4–HClO_4$ *System.*—At low acidities, hydrated $TcO_2$ is precipitated, but at higher acidities the $Tc^{IV}$ remains in solution. The initially pale yellow solutions became dark yellow-brown in the fast stage, the coloration being more intense at higher acidities and persisting for several days. At lower acidities (1–2 mol dm$^{-3}$) the solutions became pale red (but remained diamagnetic) after 24 h, while at 6 molar acid, after 5–6 d, the solution became intensely yellow and paramagnetic due to formation of $[Tc^{VI}NCl_5]^{2-}$ identified by ESR spectroscopy[4] and its UV/VIS spectrum ($\lambda_{max}$ 398 nm);[5] our material showed $g_{\parallel} = 1.966$, $g_{\perp} = 1.993$, $A_{\parallel} = 326$, $A_{\perp} = 145$ G. Clearly the final reduction product, $Cl^-$, is captured by the Tc centre. A series of ESR spectral changes and colour are induced by adding $NH_4SCN$ to the deep yellow solution: these are described in detail elsewhere.[6]

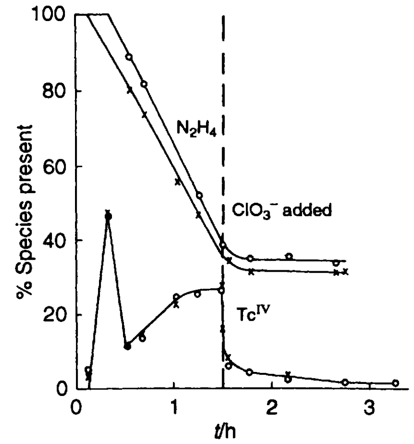


**Fig. 8** Effect of hydrazine and $Tc^{IV}$ concentrations of spiking reaction mixture during fast stage with chlorate ion. Initial conditions as for Fig. 6; $[KClO_3]$ (after spiking) = 0.01 mol dm$^{-3}$; ○ and × signify duplicate runs

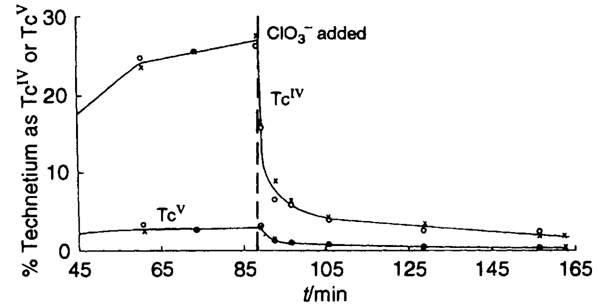


**Fig. 9** Effect on $Tc^{IV}$ and $Tc^V$ concentrations of spiking reaction mixture during the fast stage with chlorate ion. Initial conditions as for Figs. 7 and 8; ○ and × signify duplicate runs

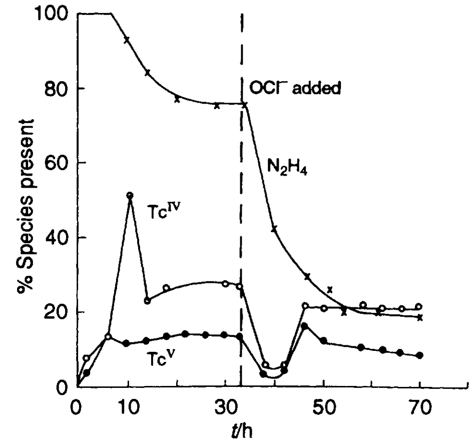
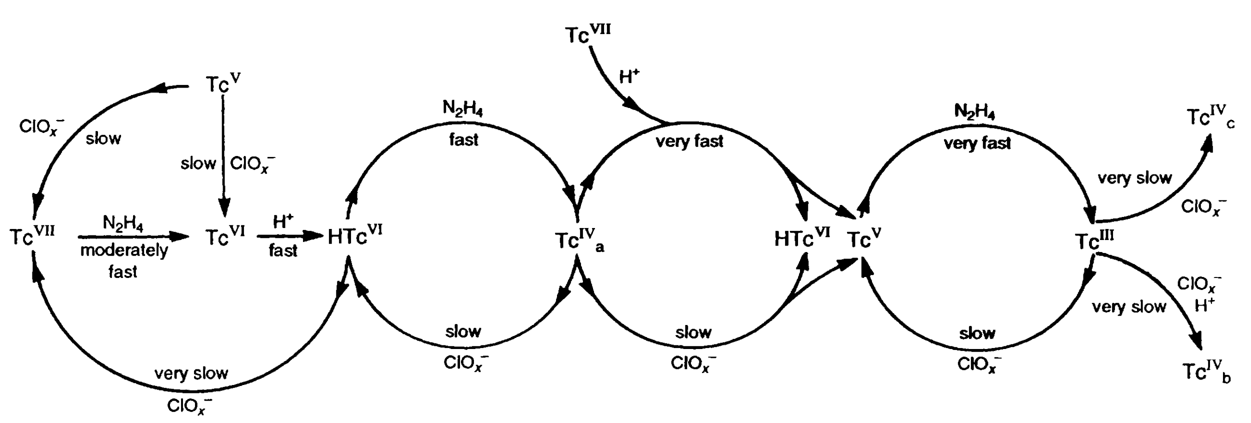


**Fig. 10** Effect on hydrazine, $Tc^{IV}$ and $Tc^V$ concentrations of spiking reaction mixture during the fast stage with hypochlorite ion. Initial conditions: $[TcO_4^-] = 1.6 \times 10^{-3}$, $[N_2H_4] = 0.1$, $[HClO_4] = 6.0$, $[NaClO_4] = 0.9$, $[NaOCl]$(after injection) = 0.03 mol dm$^{-3}$, $T = 295$ K

## Discussion

We propose a reaction scheme, set out below, for the $TcO_4^-–N_2H_4–HClO_4$ system which meets the requirements of (*i*) simulating the destruction of $N_2H_4$ and (*ii*) simulating the double maximum in the time profile of $Tc^{IV}$ (Scheme 1).

The set of equations and associated rate constants are given in Table 1. Note that a rather different rate constant is used for step (i) compared with the nitrate system: while this may be due in part to a medium effect, it must be recognised that it is a 'fitting' rate constant which may be subject to very large variation. The main difficulty in making the simulation



**Scheme 1** $x = 1–4$

**Table 1** Equations and rate constants used in the computer simulation of the technetium–hydrazine reaction in perchloric acid

| Reaction | Rate constant $k_n$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|
| (i) $Tc^{VII} + N_2H_5^+ \longrightarrow Tc^{VI} + N_2H_3^{\cdot} + 2H^+$ | 0.083 |
| (ii) $Tc^{VI} + H^+ \longrightarrow HTc^{VI\,a}$ | $5.6 \times 10^{-3}$ |
| (iii) $HTc^{VI} + N_2H_5^+ \longrightarrow Tc^{IV}{}_a{}^b + N_2H_2 + 3H^+$ | 0.241 |
| (iv) $Tc^{VII} + Tc^{IV}{}_a \longrightarrow HTc^{VI} + Tc^V$ | 5.556 |
| (v) $Tc^V + N_2H_4 + H^+ \longrightarrow Tc^{III} + N_2H_2 + 3H^+$ | 10.00 |
| (vi) $Tc^{IV}{}_a + ClO_4^- + H^+ \longrightarrow HTc^{VI} + ClO_3^-$ | $1.7 \times 10^{-3\,c}$ |
| (vii) $Tc^{III} + ClO_4^- \longrightarrow Tc^V + ClO_3^-$ | $1.1 \times 10^{-3}$ |
| (viii) $Tc^V + ClO_4^- \longrightarrow Tc^{VI} + ClO_4^{2\cdot-\,d}$ | 0.01 |
| (ix) $Tc^V + ClO_4^- \longrightarrow Tc^{VII} + ClO_3^-$ | $2.8 \times 10^{-3}$ |
| (x) $Tc^{III} + ClO_4^- + H^+ \longrightarrow Tc^{IV}{}_b + ClO_4^{2\cdot-}$ | $1.7 \times 10^{-5\,c}$ |
| (xi) $Tc^{IV}{}_a + ClO_4^- \longrightarrow Tc^V + ClO_4^{2\cdot-}$ | $1.7 \times 10^{-4}$ |
| (xii) $HTc^{VI} + ClO_4^- \longrightarrow Tc^{VII} + ClO_4^{2\cdot-}$ | $2.2 \times 10^{-3}$ |
| (xiii) $Tc^{IV}{}_b + ClO_4^- + H^+ \longrightarrow HTc^{VI} + ClO_3^-$ | $8.3 \times 10^{-7\,c}$ |
| (xiv) $Tc^{III} + ClO_4^- + H^+ \longrightarrow Tc^{IV}{}_c + ClO_4^{2\cdot-}$ | $1.4 \times 10^{-6\,c}$ |

[a] The species $HTc^{VI}$ is viewed as $HTcO_4^-$; an alternative model would present this species as in equilibrium with $TcO_4^-$. [b] The species $Tc^{IV}{}_a$, $Tc^{IV}{}_b$ and $Tc^{IV}{}_c$ are different complexes of $Tc^{IV}$. [c] Units of rate constant dm$^6$ mol$^{-2}$ s$^{-1}$. [d] $ClO_4^{2\cdot-}$ is removed by fast disproportionation to $ClO_3^-$ and $ClO_4^-$.

compared with the nitrate system[1,3] is the appearance of the double maximum: to achieve this we needed to invoke the presence of a low oxidation state such as $Tc^{III}$ (as utilised by Zelverte[7] in his scheme for the nitrate reaction). It was also necessary to involve three different complexes of $Tc^{IV}$, which are probably chloro complexes.

We have been able to simulate the rates of both the fast stage and the termination, and to mimic the double maximum, Fig. 11. The first 'spike' in the $Tc^{IV}$ profile was achieved only by 'losing' the initiation period: clearly our scheme is only part of a more complex picture involving further relatively minor reactions of lower oxidation states of chlorine, *e.g.*, $ClO_3^-$, $ClO_2^-$ and $ClO^-$. (There must be an extremely effective step of eliminating $ClO_3^-$ as it proved to be a powerful inhibitor of the overall reaction.)

Another main difference with the nitrate system is the absence of a chain termination step. In nitrate media this was the oxidation of $Tc^{VI}$ by $NO_3^-$; the oxidation of $Tc^{VI}$ in step (xii) by $ClO_4^-$ is perceived as very slow in comparison, probably because it is regarded as becoming protonated in step (ii). The common main feature in the schemes is the cycle of reduction of $Tc^{VI}$ to $Tc^{IV}$ by $N_2H_4$ [step (iii)] followed by reoxidation of $Tc^{IV}$ (in various guises) by $ClO_4^-$, steps (vi) and (xiii), giving a net oxidation of $N_2H_4$ by $ClO_4^-$.

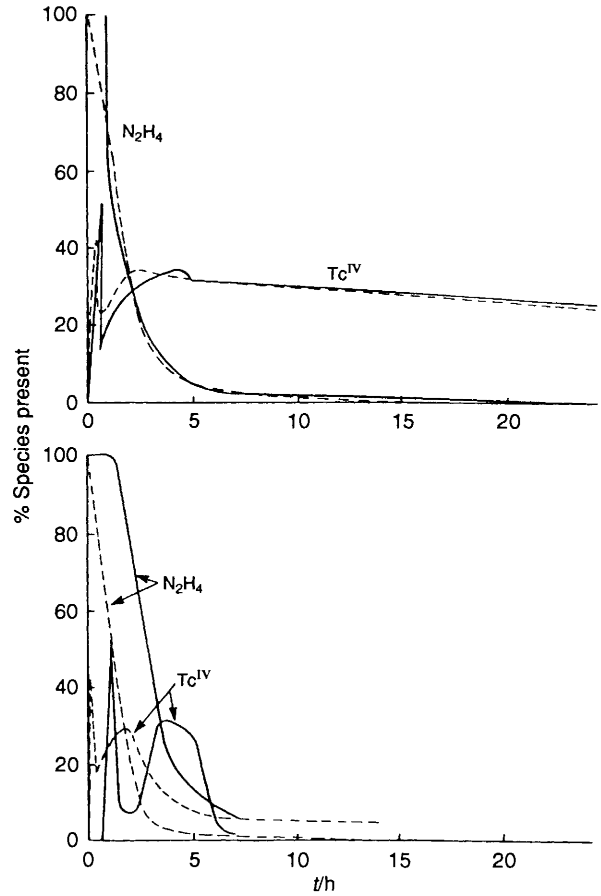


**Fig. 11** Computer simulations of the time profiles of the concentrations of $Tc^{IV}$ and $N_2H_4$ in the reaction system $TcO_4^-$–$N_2H_4$–$ClO_4^-$ at (upper) 3.0 and (lower) 1.0 mol dm$^{-3}$ acidity. Initial conditions: $[TcO_4^-] = 1.6 \times 10^{-3}$, $[N_2H_4] = 0.1$ mol dm$^{-3}$, $T$ = 308 K: (upper) $[HClO_4] = 3.0$, $[NaClO_4] = 3.9$ mol dm$^{-3}$; (lower) $[HClO_4] = 1.0$, $[NaClO_4] = 5.9$ mol dm$^{-3}$. (——) Experimental profile, (– – – –) simulated profile

## Acknowledgements

A. M. T. thanks SERC and British Nuclear Fuels for financial support through a CASE Studentship. We thank Dr. J. B. Raynor of the University of Leicester and Dr. D. Rehorek for assistance with the ESR measurements.

## References

1 T. J. Kemp, A. M. Thyer and P. Wilson, preceding paper.

2 V. I. Spitsyn, S. V. Kruychkov and A. F. Kuzina, *Sov. Radiochem.*, 1983, **25**, 471.
3 J. Garraway and P. D. Wilson, *J. Less Common Met.*, 1984, **97**, 191.
4 R. Kirmse, J. Stach and U. Abram, *Polyhedron*, 1985, **4**, 1403.
5 J. Baldas, J. F. Boas, J. Bonnyman and S. F. Colmanet, *J. Nucl. Medicine Appl. Sci.*, 1989, **33**, 272.
6 J. B. Raynor, T. J. Kemp and A. M. Thyer, *Inorg. Chim. Acta*, 1992, **193**, 191.
7 A. Zelverte, Ph.D. Thesis, University of Rennes I, FR 8862537, 1988.

*Received* 20*th April* 1993; *Paper* 3/02272B