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Study of Reduction of TcO_4^- in 6 M HBr

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Abstract

The reduction of pertechnetate by 6 M HBr takes place in two steps: (i) Tc(VII) → Tc(V) and (ii) Tc(V) → Tc(IV). The kinetics of both reactions were studied. The first step corresponds to a pseudo first order reaction. The second step of the reduction appears to be a combination of a first order with a zero order process. The same Tc(V) species was formed when the TcO_4^- was reduced with either 8.7 M or 6 M HBr. The spectrophotometric characteristics of this species were comparable to those of Rb^+ and Cs^+ salts of $[TcOBr_5]^{2-}$.

Introduction

Recently, a kinetic study of the reduction of $[TcOBr_5]^{2-}$ to $[TcBr_6]^{2-}$ by concentrated (8.7 M) HBr has been reported [1]. The effect of Tc(V) concentration on the reaction rate has been investigated. Below 10^{-3} M, the reaction proceeded more rapidly as the [Tc(V)] decreased. It has been found that the reduction reaction was a combination of a first order with a zero order process. In concentrated HBr the reduction of TcO_4^- to Tc(V) is a fast reaction, therefore the kinetics of the reaction could not be studied.

In the present work, the reaction of TcO_4^- with 6 M HBr is investigated. Under these conditions, both steps of the reduction reaction Tc(VII) → Tc(V) → Tc(IV) can be studied. The electrochemical reduction of $[TcOCl_5]^{2-}$ in 4 M HCl is also reported [2].

Experimental

Materials

^{99}Tc was obtained from the Radiochemical Center, Amersham as an ammonium pertechnetate solution. Hydrobromic acid (47%, 8.7 M) of p.a. quality was used.

Kinetic Run

Solutions 10^{-2} M and 10^{-3} M in 6 M HBr, were prepared from the original ammonium pertechnetate (34 mg/ml); the final volume was kept at 1 ml. 10^{-5} and 10^{-4} M NH_4TcO_4 in 6 M HBr were prepared from 10^{-3} M NH_4TcO_4 aqueous solution. The Tc concentrations were determined by measuring the ^{99}Tc radioactivity using a Packard Tri-Carb 460 CD liquid scintillation system. The kinetic studies were carried out at 16 °C. The method used was ascending paper chromatography described previously [1]. At appropriate time intervals, a 5 μl aliquot from the reaction solution was put on the paper strips (Schleicher-Schull No 2040 B). The ^{99}Tc was measured with a TLC Linear Analyser LB 282 consisting of a position sensitive proportional counter tube connected to a multichannel analyser. The time for chromatographic development in 1 M HBr was 30 min at a temperature of 16 °C. The R_f values of Tc(V) species, $[TcBr_6]^{2-}$ and TcO_4^- were 0.26–0.28, 0.78–0.80 and 0.80–0.82 respectively.

Results and Discussion

Chemical Species of Tc(V) and Tc(IV)

From the reaction of TcO_4^- with conc. HBr, salts of $[TcOBr_5]^{2-}$ ions with Cs^+ and Rb^+ were isolated [3, 4]. The infrared absorption bands at 950 cm^{-1} (Cs^+ salt) and 973 cm^{-1} (Rb^+ salt) were assigned to the stretching of the Tc=O bond. For $Cs_2[TcOBr_5]$, a cubic structure was found [3]. The UV–Vis spectrum in 4 M HBr shows absorption maxima at 238, 275, 354 and 616 nm ($\epsilon = 10300$, 9400, 3100 and 15 l M^{-1} cm^{-1} respectively) [4]. The spectrophotometric characteristics of the Rb^+ salt are similar. Our attempt to isolate $(NH_4)_2[TcOBr_5]$ was unsuccessful because of its high solubility. Only at a low temperature (−50 °C) was a green precipitate formed, but it dissolved rapidly as the temperature increased. Alternatively, the $[TcOBr_4]^-$ ion was isolated with $(n\text{-}Bu)_4N^+$ from the solution of TcO_4^- reduced by 8.7 M HBr. The UV–Vis spectrum in dichloromethane exhibits absorption maxima at 248, 353, 478 and 615 nm ($\epsilon = 10400$, 3750, 113 and 22 l M^{-1} cm^{-1} respectively) and the Tc=O stretching frequency occurs at 1011 cm^{-1} [5]. It has been reported [6] that the addition of $(CH_3CH_2)_4N^+$ to the solution resulting from TcO_4^-

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reduction with concentrated HX (X = Cl, Br) led to a salt of $TcOBr_5^{2-}$. However, the product which we have isolated from the reaction solution (TcO_4^-/ conc. HBr) was $(CH_3CH_2)_4N[TcOBr_4H_2O]$. The crystal structure of the latter has been determined by single crystal X-ray diffraction methods [7]. The UV–Vis spectrum of this complex in CH_2Cl_2 is similar to that of $(n\text{-}Bu)_4N[TcOBr_4]$ [5]. It must be noted that the equilibrium between $TcOCl_4^-$/$TcOCl_5^{2-}$ has been investigated in CH_2Cl_2 and 12 M HCl solutions by Raman spectroscopy. In both media, $TcOCl_4^-$ was found to be the predominant species. However, the studies of Chang-su Kim and Murmann [8] indicate that the major species in concentrated HCl and HBr is $[MoOX_5]^{2-}$. To our knowledge, there are no data on the $TcOBr_4^-$/$TcOBr_5^{2-}$ system in HBr solutions.

In the present work, we tried to characterise spectrophotometrically the Tc(V) species formed in the reaction of TcO_4^- with 8.7 M and with 6 M HBr. The UV–Vis spectrum of the reacting solution ($[Tc(V)] = 10^{-3}$ M) in 8.7 M HBr showed an absorption maximum at 616 nm ($\epsilon = 18\ 1\ M^{-1}\ cm^{-1}$) and a shoulder at about 482 nm. When an aliquot from the above solution was added into a cooled cell containing 8.7 M HBr ($[Tc(V)] = 2.6 \times 10^{-5}$ M), the spectrum changed continuously and soon the absorption maxima of $[TcBr_6]^{2-}$ appeared. These results were in agreement with the statements previously made that the reduction rate of Tc(V) to Tc(IV) in 8.7 M HBr increases with a decrease in the Tc(V) concentration [1]. As, at low concentrations, Tc(V) is more stable with respect to further reduction in dilute acid, the spectrophotometric measurements were performed in 4 M HBr. An aliquot from a 10^{-3} M solution in 8.7 M HBr was transferred into a cooled cell containing 4 M HBr and immediately measured. The absorption spectra (Fig. 1 a, b) show maxima at 273 and 360 nm (ϵ = 13969 and 4100 respectively) and a shoulder at 482 nm.

The absorption spectrum of the Tc(V) species formed in the reaction of NH_4TcO_4 ($c = 1.3 \times 10^{-3}$ M) with 6 M HBr showed a maximum at 616 nm and a shoulder at 482 nm. For a diluted solution ($c = 1 \times 10^{-4}$–3×10^{-5} M) in 4 M HBr, the spectrum exhibited absorption maxima at 274 and 360 nm and a shoulder at 482 nm. These results indicate that the same Tc(V) species is formed by the reduction of NH_4TcO_4 with either 8.7 M or 6 M HBr. The similarity of its absorption spectrum, except the inflection at 482 nm, with those of Rb^+ and Cs^+ salts suggest the formation of $[TcOBr_5]^{2-}$ species in >6 M HBr solutions. The variation observed in ϵ values arises from some differences in the composition of the solutions used in the spectrophotometric measurements. In the solution resulting from TcO_4^- reduction to Tc(V), the errors in the measurements are introduced from the Br_2 and Br^- absorptions. These errors are eliminated when Rb^+ and Cs^+ salts are directly dissolved in 4 M HBr.

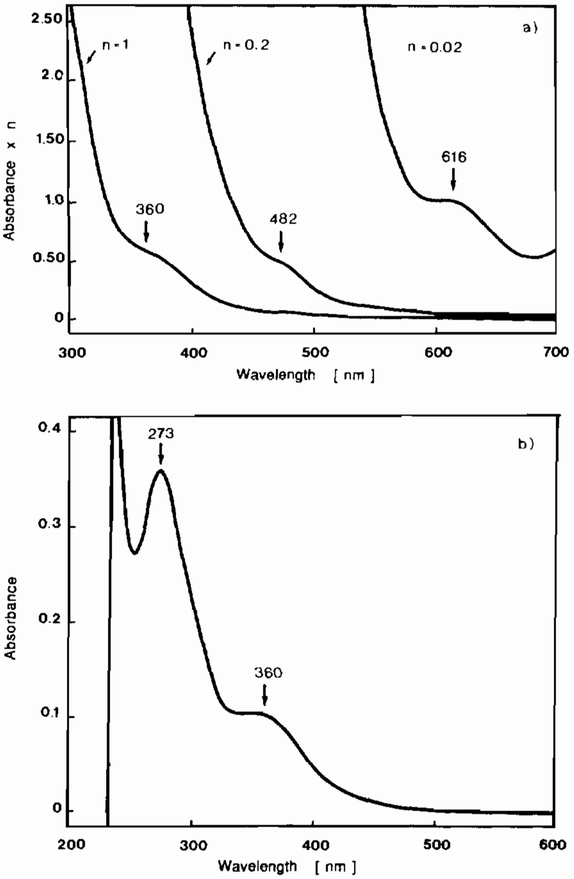

Fig. 1. Absorption spectrum of Tc(V) species in 4 M HBr. (a) $[Tc(V)] = 1.17 \times 10^{-4}$ M, (b) $[Tc(V)] = 2.57 \times 10^{-5}$ M.

The spectrophotometric characteristics of $(n\text{-}Bu)_4N[TcOBr_4]$ in dichloromethane [5] are rather similar to those of $[TcOBr_5]^{2-}$ in bromhydric acid. However it should be noted that:

(a) The absorption spectra are different in the region of 230–300 nm.

(b) When $(n\text{-}Bu)_4N[TcOBr_4]$ is dissolved in 4 M HBr, its absorption spectrum is the same as those of Rb^+ and Cs^+ salts. The spectrum is different compared to the spectra of known hydrolysed Tc(IV) species [9]. This fact permits the assumption that the disproportionation to Tc(IV) and TcO_4^- does not occur during the measurements. The absorption spectra of $M_2[TcOBr_5]$, M = Cs^+, Rb^+ and $M[TcOBr_4]$, M = $(n\text{-}Bu)_4N^+$, $(CH_3CH_2)_4N^+$ in dimethyl sulfoxide are different. However, as the spectra change continuously, it indicates that both anions are not stable in this solvent. These results suggest that, in HBr solution, $TcOBr_5^{2-}$ can be formed by a Br^- coordination in *trans* position to the oxo group in $[TcOBr_4]^-$ ion.

(c) The electrochemical reduction of $[TcOCl_5]^{2-}$ in 4 M HCl has been studied by coulometry and spectrophotometry [2]. The above Tc(V) species was obtained by the reduction of NH_4TcO_4 with 11.8 M HCl. The reduction of $[TcOCl_5]^{2-}$ to $[TcCl_6]^{2-}$ took place in two steps. In the first step, the electrochemical reduction of $[TcOCl_5]^{2-}$ led to $[Tc(H_2O)Cl_5]^-$ formation and in the second one, an aquo-anation reaction produced $[TcCl_6]^{2-}$. Direct formation of hexachlorotechnetate from oxopentachlorocomplex by an electrode process was not excluded. This study confirms the results of the present work, *i.e.* the existence of the $[TcOX_5]^{2-}$ ion in 4 M HX solutions. In 6 M HBr the transient species $[Tc(H_2O)Br_5]^-$ ($\lambda = 405$, 456 nm) [9, 10] was not observed.

As the reduction of TcO_4^- takes place in 6 M hydrobromic acid, the $[Br^-]$ is still high enough to convert $[TcOBr_4]^-$ mostly into $[TcOBr_5]^{2-}$.

The end product of the reaction Tc(VII) → Tc(V) → Tc(IV) in 6 M HBr was $[TcBr_6]^{2-}$. The spectrum shows absorption maxima at 444, 383, 325 and 261 nm ($\epsilon = 6053$, 7115, 10 831 and 15 876 l M^{-1} cm^{-1}, respectively). These measurements are in agreement with earlier published data [11].

Reduction of TcO_4^- *by 6 M HBr*

This reaction takes place in two steps

$$\text{(i)}\quad TcO_4^- + 6H^+ + 7Br^- \longrightarrow TcOBr_5^{2-} + Br_2 + 3H_2O$$

$$\text{(ii)}\quad 2TcOBr_5^{2-} + 4H^+ + 4Br^- \longrightarrow 2TcBr_6^{2-} + Br_2 + 2H_2O$$

It has been shown that in conc. HBr, the first step was too fast to be kinetically studied. In 6 M HBr the reduction rate is slower, therefore the kinetics of both reactions could be studied.

(i) $Tc(VII) \xrightarrow{k_1} Tc(V)$

The concentration of TcO_4^- ranged from 0.97×10^{-2} M to 5.68×10^{-4} M in 6 M HBr and the temperature was kept constant at 16 °C.

As the concentration of HBr was in large excess with respect to $[TcO_4^-]$, the rate constant was determined assuming a pseudo first order process

$$\frac{-\,d[TcO_4^-]}{dt} = k_1[TcO_4^-] \qquad (1)$$

The plots of $\ln[Tc(VII)]_0/[Tc(VII)]$ as a function of time, where $[Tc(VII)]_0$ is the initial concentration of TcO_4^- and $[Tc(VII)]$ the unreacted TcO_4^-, are straight lines; their slopes give the rate constant k_1.

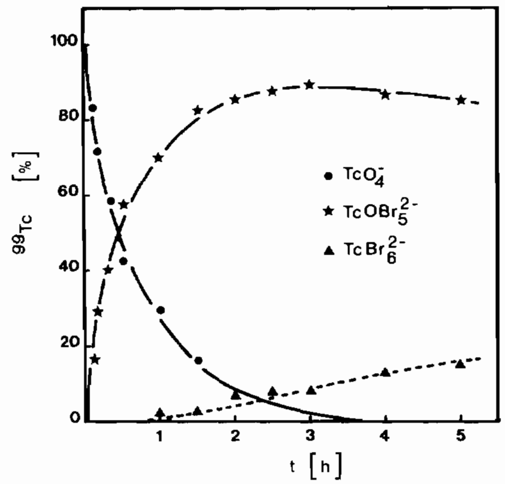

Fig. 2. ^{99}Tc chemical distribution *vs.* time in 6 M HBr, [Tc] = 0.97×10^{-2} M, $T = 16$ °C.

TABLE I. Rate Constants for TcO_4^- Reduction in 6 M HBr, $T = 16$ °C

$[TcO_4^-]$ (M)	$k_1{}^a$ (h^{-1})
0.97×10^{-2}	1.07
4.57×10^{-3}	1.29
1.19×10^{-3}	1.22
5.68×10^{-4}	1.10

^{a}Correlation coefficient = 0.99.

As two consecutive reactions take place, three species coexist in the solution: TcO_4^-, $[TcOBr_5]^{2-}$ and $[TcBr_6]^{2-}$ (Fig. 2). The chromatographic separation of TcO_4^- and $[TcBr_6]^{2-}$ being unsatisfactory, the rate of the first step was followed until the $[TcO_4^-]$ had fallen to *ca.* 20% of its initial value. In these conditions, $[TcBr_6]^{2-}$ was formed in negligible amount. The k_1 values for different TcO_4^- concentrations are presented in Table I. The mean value of the rate constant is $k_1 = 1.17 \pm 0.10$ h^{-1}.

An accurate k_1 value could not be determined for $[TcO_4^-] < 5.7 \times 10^{-4}$ M. As the reduction rate of the second step (Tc(V) → Tc(IV)) increases with the decrease in the Tc(V) concentration (see step (ii)), the $[TcBr_6]^{2-}$ produced in this way will disturb the chromatographic measurements. As this method did not allow an accurate separation of TcO_4^- and $[TcBr_6]^{2-}$, it was not possible to verify if the rate law assumed so far is valid for $[TcO_4^-] < 5.7 \times 10^{-4}$ M. For the TcO_4^- concentrations studied, the first order kinetic is respected.

(ii) $Tc(V) \xrightarrow{k_2} Tc(IV)$

The first step of the reduction being much faster than the second, at a time $t = t_1$, the TcO_4^- will be completely reduced and consequently only $[TcOBr_5]^{2-}$ and $[TcBr_6]^{2-}$ will be present in solution.

TABLE II. Rate Constants for Tc(V) Reduction in 6 M HBr, T = 16 °C

[Tc] (M) $t = 0$	[Tc(V)] (M) $t = t_1$	$k_2{}^a$ (h^{-1})	k_2 (h^{-1})
0.97×10^{-2}	7.76×10^{-3}	1.03×10^{-2}	$(1.13 \pm 0.09) \times 10^{-2}$
4.57×10^{-3}	3.58×10^{-3}	1.10×10^{-2}	$(1.27 \pm 0.08) \times 10^{-2}$
1.19×10^{-3}	9.34×10^{-4}	1.01×10^{-2}	$(1.02 \pm 0.06) \times 10^{-2}$

[a] Calculated by linear regression, correlation coefficient = 0.99.

Under these conditions, the kinetics of this reaction can be studied. To eliminate any contributions from the first step, the reaction was followed from the starting point $t_1 \simeq 8$ h; the [Tc(V)] was about 80% from the initial technetium concentration.

As in the reduction of Tc(V) to Tc(IV) in conc. HBr [1], the effect of the Tc concentration on the reaction rate was also observed. Below 10^{-3} M, the reduction reaction proceeds more rapidly as the [Tc(V)] decreases. Consequently, we have assumed that the kinetics of this process are the same as those found for the reduction in 8.7 M HBr. Indeed, assuming that the reaction is a combination of a first order with a zero order process, it was possible to find a rate law fitting all experimental results. The reaction rate can be written as

$$-\frac{\mathrm{d}[\mathrm{Tc(V)}]}{\mathrm{d}t} = k_2[\mathrm{Tc(V)}] + k'_2 \qquad (2)$$

The general solution of this differential equation is

$$\frac{[\mathrm{Tc(V)}]_t}{[\mathrm{Tc(V)}]_{t_1}} = \mathrm{e}^{-k_2(t-t_1)}\left\{1 + \frac{k'_2}{k_2[\mathrm{Tc(V)}]_{t_1}}\right\} - \frac{k'_2}{k_2[\mathrm{Tc(V)}]_{t_1}} \qquad (3)$$

where the constants k_2 and k'_2 have to be determined. This expression gives no possibility for determining them using the experimental data, but approximative solutions can be found in the limiting cases.

If $k'_2 \ll k_2[\mathrm{Tc(V)}]$, *i.e.* in the case of high Tc(V) concentrations ($>10^{-3}$ M), k'_2 can be neglected and eqn. (3) becomes

$$\frac{[\mathrm{Tc(V)}]_t}{[\mathrm{Tc(V)}]_{t_1}} = \mathrm{e}^{-k_2(t-t_1)} \qquad (4)$$

A plot of $\ln[\mathrm{Tc(V)}]_{t-t_1}/[\mathrm{Tc(V)}]_{t_1}$ *versus* time allows the determination of k_2 using a linear regression for a set of experiments (Table II).

The rate constant k_2 for each experimental point was also calculated using eqn. (5)

$$k_2 = \frac{1}{t-t_1}\ln\frac{[\mathrm{Tc(V)}]_{t_1}}{[\mathrm{Tc(V)}]_{t-t_1}} \qquad (5)$$

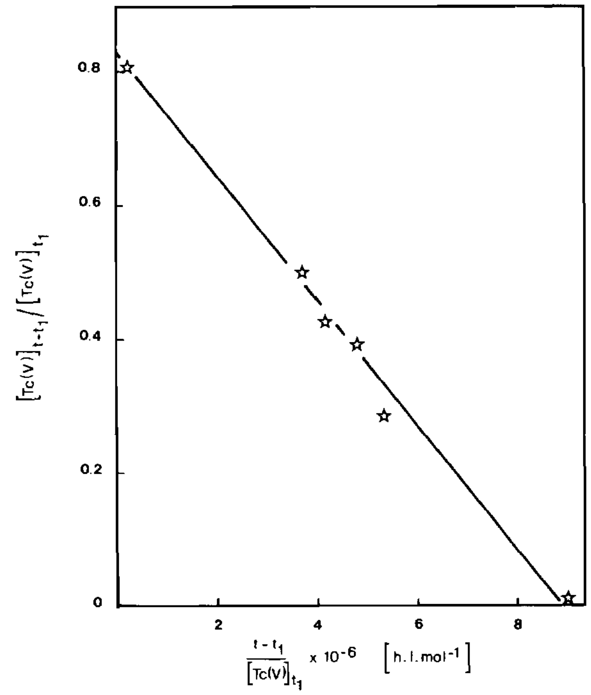

Fig. 3. $[\mathrm{Tc(V)}]_{t-t_1}/[\mathrm{Tc(V)}]_{t_1}$ *vs.* $t - t_1/[\mathrm{Tc(V)}]_{t_1}$ for 4.5×10^{-6} M Tc(V) concentration.

The mean values of k_2 at different Tc(V) concentrations are shown in Table II. The mean value of the rate constant determined by both methods was found equal to $k_2 = (1.09 \pm 0.1) \times 10^{-2}$ h^{-1}.

At low Tc(V) concentrations (4.5×10^{-6} M), $k_2[\mathrm{Tc(V)}] \ll k'_2$ and the approximate solution is given by

$$\frac{[\mathrm{Tc(V)}]_t}{[\mathrm{Tc(V)}]_{t_1}} = 1 - k'_2\frac{t-t_1}{[\mathrm{Tc(V)}]_{t_1}} \qquad (6)$$

By plotting $[\mathrm{Tc(V)}]_{t-t_1}/[\mathrm{Tc(V)}]_{t_1}$ as a function of $t - t_1/[\mathrm{Tc(V)}]_{t_1}$, a linear dependence was found with a slope equal to $k'_2 = 1.1 \times 10^{-7}$ mol l^{-1} h^{-1} (Fig. 3).

The types of processes describing the reaction rate at different Tc(V) concentrations are given in Table III. Using the k_2 and k'_2 values as well as the general solution (3), a set of curves $[\mathrm{Tc(V)}]_{t-t_1}/[\mathrm{Tc(V)}]_{t_1}$ as a function of time were plotted (Fig. 4). A good fit with experimental data is obtained.

TABLE III. The Types of Processes Describing Reaction Rates at Different Tc(V) Concentrations

[Tc(V)] (M)	k_2 (h^{-1})	k'_2 ($mol\ l^{-1}\ h^{-1}$)	Order	Equation
$7.76 \times 10^{-3} \rightarrow 9.34 \times 10^{-4}$	1.10×10^{-2}		1	(4)
$7.8 \times 10^{-5} \rightarrow 9.2 \times 10^{-6}$			1 and 0	(3)
4.5×10^{-6}		1.1×10^{-7}	0	(6)

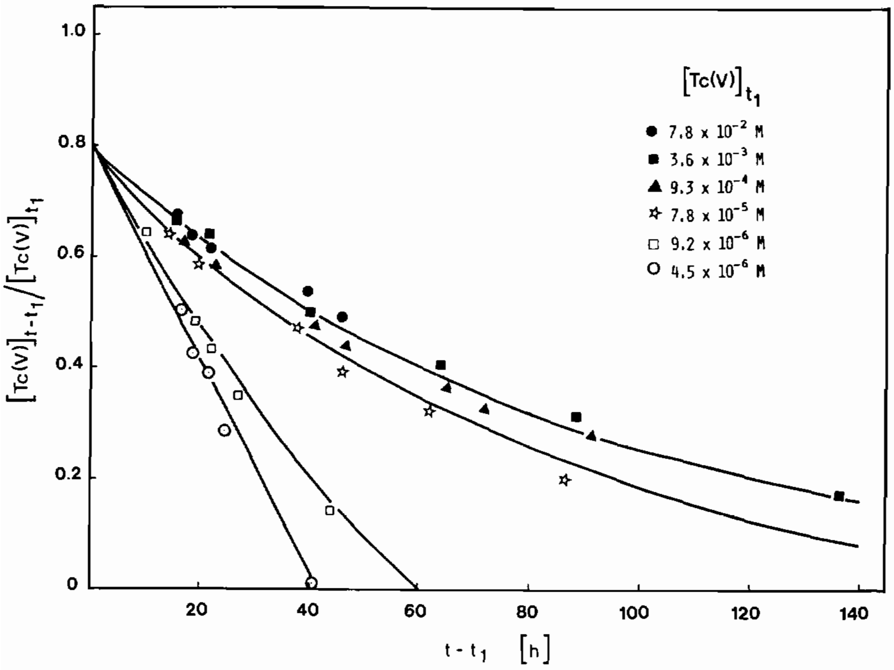

Fig. 4. $[Tc(V)]_{t-t_1}/[Tc(V)]_{t_1}$ *vs.* time for different Tc(V) concentrations: full line, theoretical curves (eqn. (3)); symbols, experimental data.

Comparison with the results given for the reduction of Tc(V) in 8.7 M HBr [1] shows that the reduction of Tc(V) in conc. HBr is faster than in 6 M HBr. These results indicate that below 6 M HBr the reduction reactions Tc(VII) → Tc(V) → Tc(IV) should proceed more slowly when the HBr concentration lowers. Indeed, the reaction of 1.12×10^{-2} M NH_4TcO_4 in 4 M HBr at 16 °C showed only a 35% reduction after 25 days. On the other hand, as the Tc(V) → Tc(IV) reduction is a very slow reaction, it is reasonable to assume that the aquation and/or the hydrolysis of Tc(V) and Tc(IV) complexes could play an important role. Indeed, the absorption spectrum of the solution after 150 days at 16 °C shows a mixture of $[TcBr_6]^{2-}$ and $[TcBr_5(H_2O)]^-$. The absorption maxima at 395 and 452 nm are attributed to the latter complex [9, 10]. Thus, the kinetic study of Tc(VII) → Tc(V) → Tc(IV) reduction reactions in 4 M HBr is limited by the complexity of reactions occurring in this system.

References

1 S. Caron, E. Ianovici, P. Lerch and A. G. Maddock, *Inorg. Chim. Acta, 109,* 209 (1985).
2 P. Rajec and F. Macasek, *J. Inorg. Nucl. Chem., 43,* 1607 (1981).
3 J. E. Fergusson, A. M. Greenaway and B. R. Penfold, *Inorg. Chim. Acta, 17,* 29 (1983).
4 E. Ianovici, D. Mantegazzi and P. Lerch, *J. Lab. Comp. Radiopharm., 23,* 1160 (1986).
5 R. Thomas, A. Davison, H. Trop and E. Deutsch, *Inorg. Chem., 19,* 2840 (1980).
6 R. W. Thomas, M. J. Heeg, R. C. Elder and E. Deutsch, *Inorg. Chem., 24,* 1472 (1985).
7 E. Ianoz, D. Mantegazzi, P. Lerch and K. Tatsumi, manuscript in preparation.
8 Chang-su Kim and R. K. Murmann, *Inorg. Chem., 23,* 263 (1984).
9 M. Colin, E. Ianovici, P. Lerch, A. G. Maddock, *J. Radioanal. Nucl. Chem., 92/2,* 283 (1985).
10 M. Kawashima, M. Koyama, T. Fuginaga, *J. Inorg. Nucl. Chem., 38,* 819 (1976).
11 C. K. Jorgensen and K. Schwochau, *Z. Naturforsch., Teil A, 20,* 65 (1965).