

Chemical Effects of I.T. of ^{95m}Tc in a M_2TcF_6 Solid Matrix and in Solutions

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Hexafluorotechnetate(IV)/ $^{95m}\text{Tc}/^{95g}\text{Tc}/\text{Isomeric transition}$

Summary

The chemical effects of the I.T. of ^{95m}Tc have been studied in M_2TcF_6 in the solid matrix and in solutions. The retention of ^{95g}Tc for the solid matrix was found to be about 90%. The unretained ^{95g}Tc appears as $\text{TcF}_5(\text{H}_2\text{O})^-$, neutral and TcO_4^- species. At low concentration (10^{-3} – 10^{-2} M) of K_2TcF_6 in HF , H_2SO_4 and H_2O solutions the retention was found to be about 1%. The unretained ^{95g}Tc was found preponderately as $\text{TcF}_5(\text{H}_2\text{O})^-$: 90% in HF , 80% in H_2O and 50% in H_2SO_4 . An effect of temperature on the unretained ^{95g}Tc distribution in sulfuric acid was observed. At higher concentration of K_2TcF_6 in solution, the retention increases at the expense of $\text{TcF}_5(\text{H}_2\text{O})^-$ and uncharged species. A comparison with previously obtained results on the K_2TcCl_6 is made.

Introduction

The chemical effects of I.T. of ^{95m}Tc in ammonium and potassium hexachlorotechnetate have been studied both in solutions and solid matrices [1, 2]. The retention of ^{95g}Tc in solution was found to be close to zero. The unretained ^{95g}Tc appeared preponderantly as hydrated TcO_4^- and cationic species, as $\text{TcCl}_5(\text{H}_2\text{O})^-$ and as TcO_4^- . In solid matrices the retention was found to be higher than 70%.

It is possible that the ligand halogen has an effect on the chemical behaviour of the ^{95g}Tc , so the study of the ^{95m}Tc decay has been extended to K_2TcF_6 , both in solution and solid form. The use of solutions of Ag_2TcF_6 enables one to explore the effect of scavenging some of the Auger cascade electrons. It must be noted that the I.T. in ammonium and potassium-halotellurates(IV) does not lead to any change in the chemical state of the Tc-ground state [3].

Experimental

Preparation of labelled compounds

The ^{95m}Tc was obtained by the irradiation of molybdenum powder with 25 MeV protons in the SIN cyclotron at Villigen, Switzerland. The Mo powder was dissolved in 30% H_2O_2 using a reflux system and ^{95m}Tc was separated as TcO_4^- as previously described [1, 4].

The $\text{K}_2^{99(95m)}\text{TcF}_6$ was prepared by the fusion of $\text{K}_2^{99(95m)}\text{TcCl}_6$ with KHF_2 following the method of

SCHWOCHAU and HERR [5, 6]. After 20 minutes fusion in a platinum crucible the cooled melt was dissolved in water and the much less soluble K_2TcF_6 separated from the more soluble potassium halides. The solution containing K_2TcF_6 was evaporated at room temperature. The identity of the pale pink crystals was confirmed by their X ray powder diffraction pattern [7]. The UV/visible spectrum of the solution of the K_2TcF_6 agreed with published data [8].

The solutions of $\text{Ag}_2^{99(95m)}\text{TcF}_6$ used were prepared by mixing appropriate amounts of solutions of $\text{K}_2^{99(95m)}\text{TcF}_6$ and AgNO_3 . The solutions therefore also contain K^+ and NO_3^- ions. The resulting solution was filtered and the Tc content determined spectrophotometrically after oxidation of the TcF_6^- to TcO_4^- .

Separation procedure

For the separation of the different technetium species low voltage electrophoresis was used. The paper strips used were Schleicher-Schuell No 2043 B. A voltage of 400 V was applied for 110 min. The supporting electrolyte was H_2SO_4 1 M and HF 0.1 M. The paper was cut into small pieces before the activity was measured.

Results

Like K_2ReF_6 the K_2TcF_6 is much more resistant to hydrolysis than the corresponding chloro compound. Electrophoretic measurements on our materials showed tiny amounts of $\text{TcF}_5(\text{H}_2\text{O})^-$, an uncharged species and TcO_4^- ($\leq 2.5\%$). These amounts do not change with the age of the solution after 30 minutes and up to 10 days. This may be due to small amounts of impurities in the initial K_2TcF_6 or, perhaps more likely, a limited amount of hydrolysis upon solution.

The mobility ratio of the new anionic species to the TcF_6^{2-} (0.41 ± 0.05) is very similar to the mobility ratio of $\text{TcCl}_5(\text{H}_2\text{O})^-$ and TcCl_6^{2-} . By analogy with TcCl_6^{2-} it can be assumed that the first step in TcF_6^{2-} hydrolysis produces the $\text{TcF}_5(\text{H}_2\text{O})^-$ species. Further aquation will lead to $\text{TcF}_4(\text{H}_2\text{O})_2$ or/and $\text{TcO}_2 \times \text{H}_2\text{O}$ and $\text{TcF}_3(\text{H}_2\text{O})_3^+$. The $\sim 1\%$ of TcO_4^- probably results from the oxidation of one or more of these species.

The extent of hydrolysis for the same concentration of TcF_6^{2-} (10^{-2} M) is much less important in 0.05 M HF than in water or in 1 M H_2SO_4 .

Table 1. *Distribution of ^{95}Tc in solid K_2TcF_6*

A. Samples dissolved in 1 M H_2SO_4				
	R %	$\text{TcF}_5(\text{H}_2\text{O})^-$	Unretained ^{95}Tc % neutral species	TcO_4^-
Storage in vacuum	89.4 ± 3.4	4.8 ± 1.0	2.6 ± 1.3	3.2 ± 0.8
Storage in air	89.9 ± 1.6	3.3 ± 0.7	1.9 ± 0.3	4.9 ± 1.3
B. Samples dissolved in 0.05 M HF				
	R %	$\text{TcF}_5(\text{H}_2\text{O})^-$	Unretained ^{95}Tc % neutral species	TcO_4^-
Storage in vacuum	89.8 ± 0.4	4.8 ± 0.3	2.3 ± 0.2	3.1 ± 0.1
Storage in air	88.8 ± 2.8	4.1 ± 1.2	2.2 ± 0.7	4.9 ± 1.8

Table 2. *Chemical distribution of ^{95}Tc for solutions of hexafluorotechnetates**

Salt used	Conc. (M)	Storage conditions		⁹⁵ Tc distribution				
		Ambient atmosph.	T, K	TcF ₆ ²⁻ (R)	TcF ₅ (H ₂ O) ⁻	Cationic	Uncharged	TcO ₄ ⁻
				%	%	%	%	%
A. Solutions in sulphuric acid								
K ₂ TcF ₆	10 ⁻³	N ₂	276	1.2 ± 1.0	80.9 ± 0.5	12.0 ± 1.5		5.9 ± 1.4
K ₂ TcF ₆	10 ⁻²	N ₂	276	2.3 ± 2.8	81.1 ± 1.7	10.1 ± 2.6		6.5 ± 2.4
K ₂ TcF ₆	10 ⁻²	N ₂	283	1.3 ± 0.5	54.7 ± 3.6	16.7 ± 2.1	24.2 ± 1.0	3.1 ± 0.9
K ₂ TcF ₆	10 ⁻¹	N ₂	283	34.6 ± 4.1	27.1 ± 2.5	2.5 ± 3.7	30.7 ± 4.5	5.1 ± 0.8
K ₂ TcF ₆	10 ⁻²	air	276	1.2 ± 0.6	81.3 ± 0.6	14.1 ± 1.1		3.4 ± 1.2
Ag ₂ TcF ₆	10 ⁻³	N ₂	276	1.7 ± 1.6	85.5 ± 3.1	2.4 ± 2.1	8.8 ± 3.3	1.6 ± 1.9
B. Solutions in hydrofluoric acid								
K ₂ TcF ₆	10 ⁻²	N ₂	283	0.3 ± 0.4	93.1 ± 1.6	4.2 ± 2.1		2.4 ± 0.9
K ₂ TcF ₆	5 · 10 ⁻²	N ₂	283	36.6 ± 2.6	52.4 ± 3.3	3.1 ± 1.0	4.8 ± 0.9	3.1 ± 0.8

* All data are mean values of at least 4 determinations.

Table 3. *Chemical distribution of ^{95}Tc in K_2TcF_6 , water solution. Storage temp.: 283 K.*

Conditions		^{95}Tc distribution				
Ambient atmosph.	Salt conc. (M)	TcF_6^{2-} (R) %	$\text{TcF}_5(\text{H}_2\text{O})^-$ %	Cationic %	Uncharged %	TcO_4^- %
N_2	10^{-3}	1.6 ± 1.0	76.4 ± 0.8	3.9 ± 1.1	12.8 ± 2.4	5.3 ± 1.6
N_2	10^{-2}	2.4 ± 1.0	78.2 ± 2.8	2.2 ± 1.0	12.4 ± 1.6	4.8 ± 1.2
N_2	$2 \cdot 10^{-2}$	1.7 ± 1.9	80.0 ± 2.0		12.9 ± 2.2	5.4 ± 1.1
N_2	$2 \cdot 10^{-2}$ *	2.7 ± 0.6	76.0 ± 0.5	4.3 ± 0.2	12.1 ± 1.0	4.9 ± 1.0
N_2O	10^{-2}	2.7 ± 2.3	79.6 ± 2.5		13.5 ± 1.3	4.2 ± 1.1

* Storage temperature: 293 K.

In Table 1 are presented the results for a K_2TcF_6 matrix for different storage and dissolution conditions. There is no dependence of retained ^{95g}Tc on either the ambient atmosphere (vacuum or air) or on the temperature. The R value is about 90% independently of how the sample dissolution was done, in the presence or absence of Tc(IV) carrier.

The unretained ^{95g}Tc appears largely as $\text{TcF}_5(\text{H}_2\text{O})^-$ and TcO_4^- . There is some suggestion that the presence of air leads to more $^{95g}\text{TcO}_4^-$ and less $^{95g}\text{TcF}_5(\text{H}_2\text{O})^-$. Although the amounts of each product species are small they are always a factor or two greater than the amounts of ^{95m}Tc found as the same species due to hydrolysis, or perhaps impurities in the initial K_2TcF_6 . In addition, solution in 0.05 M HF gives very much the same proportions of separable ^{95g}Tc products but the amount of ^{95m}Tc in these species is substantially reduced. The near identity of the results following solution in 1 M H_2SO_4 and 0.05 M HF indicate that no appreciable reversal of the aequation of the ^{95g}Tc products takes place.

It is interesting to compare the results obtained for solid K_2TcF_6 with those for the solution.

Table 2 shows the distribution of ^{95g}Tc in 1 M H_2SO_4 and 0.05 M HF solutions which were 10^{-3} and 10^{-2} M in K_2TcF_6 and Ag_2TcF_6 . They were kept at 276 K under nitrogen or air. The retention of ^{95g}Tc is about 1%. In sulphuric solution, the unretained ^{95g}Tc is found preponder-

antly (80%) as $\text{TcF}_5(\text{H}_2\text{O})^-$, about 12% as uncharged, including only traces of cationic, species and about 6% as TcO_4^- . The corresponding fraction for Ag_2TcF_6 represents only 1%. In hydrofluoric acid at a low concentration of K_2TcF_6 the retention is very small, the $\text{TcF}_5(\text{H}_2\text{O})^-$ fraction increases to 93% and uncharged species and TcO_4^- are much less important than in sulphuric acid, 4% and 2% respectively.

At 283 K for 10^{-2} M K_2TcF_6 in sulphuric solution the retention remains at about 1% but the distribution of unretained ^{95g}Tc is changed compared to 276 K. The cationic and uncharged species increase to 16% and 24% respectively. The $\text{TcF}_5(\text{H}_2\text{O})^-$ decreases to 54% and the TcO_4^- represents about 3%. It is clear that the further hydrolysis of $\text{TcF}_5(\text{H}_2\text{O})^-$ is favoured by the increase of temperature. Measurements at 293 K confirm this trend. In simple aqueous solution, however, the distribution of the ^{95g}Tc is substantially the same at 283–293 K for $2 \cdot 10^{-2}$ and $5 \cdot 10^{-2}$ M solutions.

Above about 10^{-2} M the distribution changes with the concentration of hexahalotchnetate. This effect is more important in hydrofluoric acid. In sulphuric acid the retention increases at the expense of the $\text{TcF}_5(\text{H}_2\text{O})^-$ and cationic species. In hydrofluoric acid the increase occurs only at the expense of $\text{TcF}_5(\text{H}_2\text{O})^-$. There are no significant changes in the proportions of the neutral species and TcO_4^- .

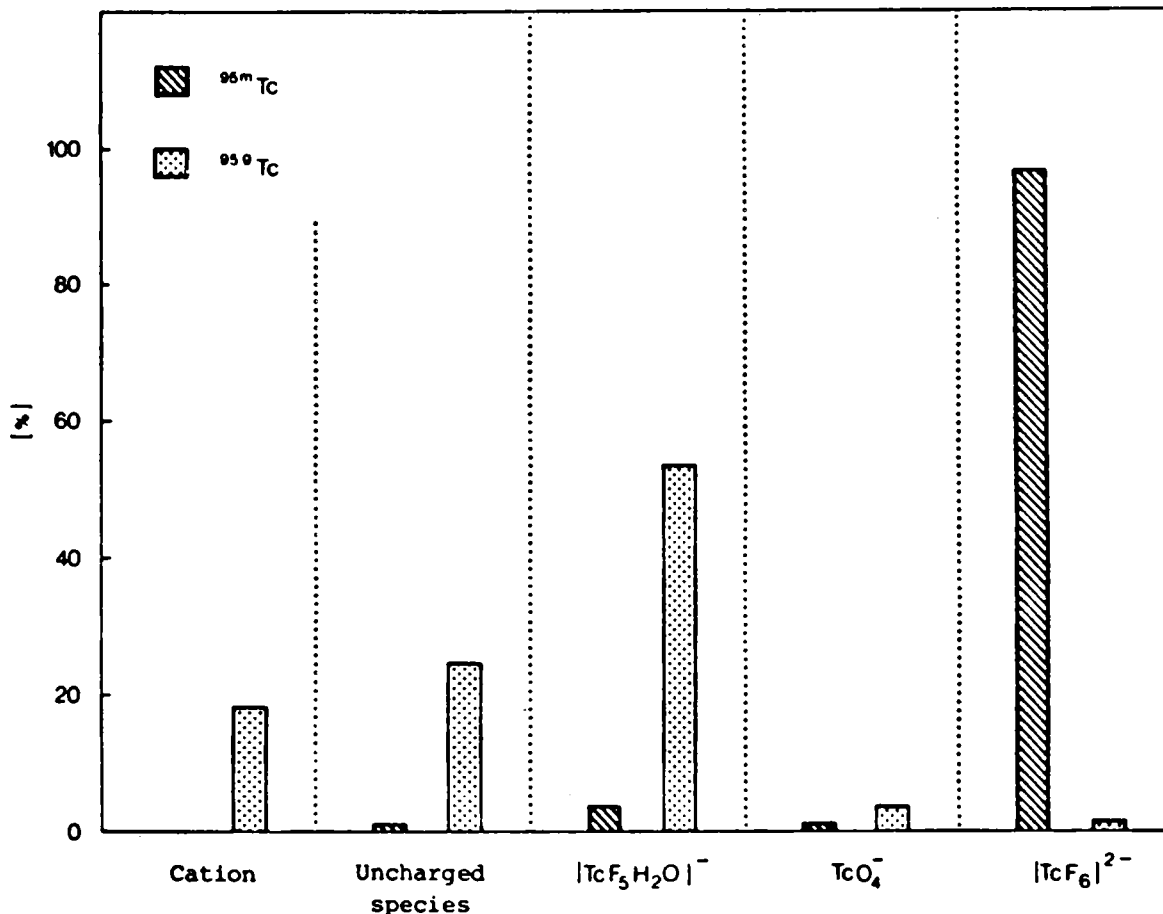


Fig. 1. Distribution of Tc in different chemical species for 10^{-2} M K_2TcF_6 in 1 M H_2SO_4 solution. Storage conditions: 283 K, N_2

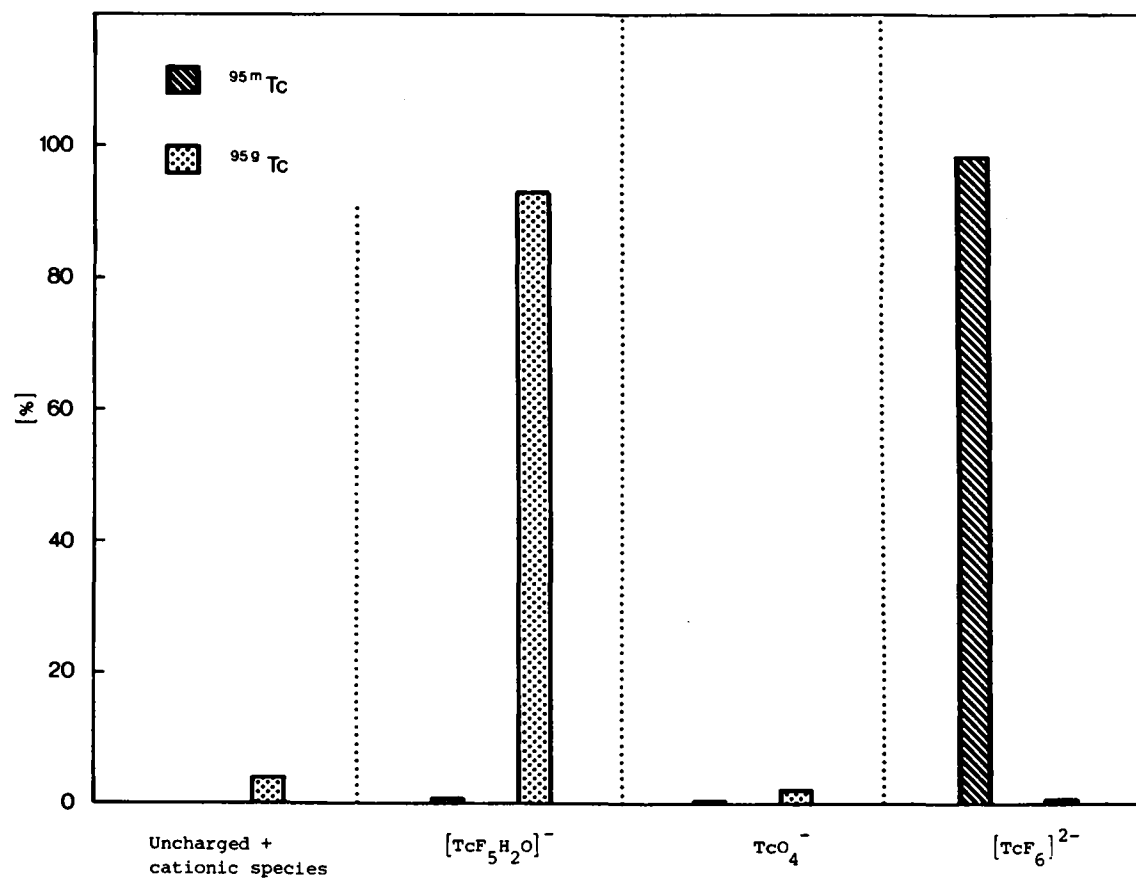


Fig. 2. Distribution of Tc in different chemical species for $10^{-2} \text{ M K}_4\text{TcF}_6$ in 0.05 M HF solution. Storage conditions: 283 K , N_2

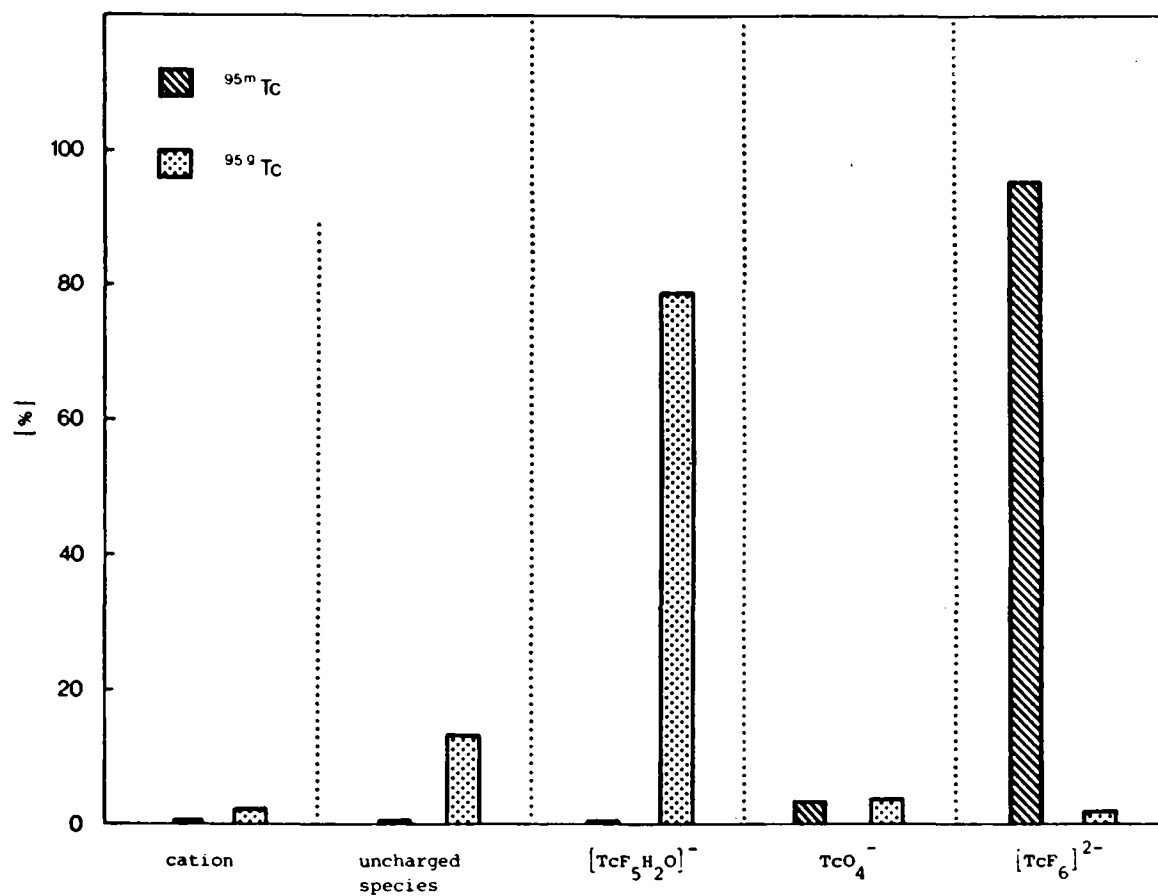


Fig. 3. Distribution of Tc in different chemical species for $10^{-2} \text{ M K}_4\text{TcF}_6$ in water. Storage conditions: 283 K , N_2

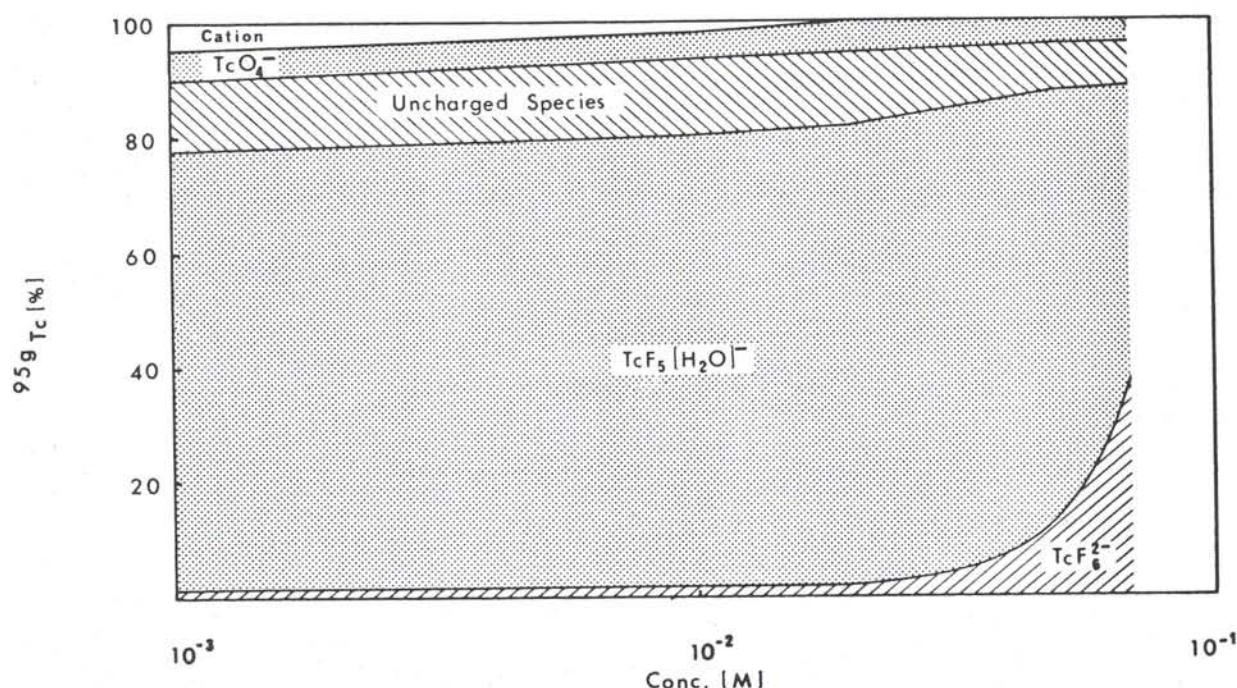


Fig. 4. ^{95g}Tc distribution for K_2TcF_6 in water as a function of potassium hexafluorotechnetate concentration. Storage conditions: 283 K, N_2

In Figs. 1 and 2 are shown the distribution of ^{95m}Tc and ^{95g}Tc in each separated species for 10^{-2} M K_2TcF_6 sulphuric and hydrofluoric acids. About 4% of ^{95m}Tc was found as $\text{TcF}_5(\text{H}_2\text{O})^-$ in sulphuric acid and only 0.5% in hydrofluoric acid. ^{95g}Tc appears exclusively as $\text{TcF}_5(\text{H}_2\text{O})^-$ in HF solution and as $\text{TcF}_5(\text{H}_2\text{O})^-$, uncharged and cationic species in H_2SO_4 solution. 2–3% of $^{95g}\text{TcO}_4^-$ is found in both acids.

The relative high stability of the TcF_6^{2-} ion allowed experiments on the ^{95m}Tc decay in water. Results are presented in Table 3. In solutions at concentrations of 10^{-3} and 10^{-2} M the retention of ^{95g}Tc is about 1%. The distribution of unretained ^{95g}Tc as neutral and cationic species, $\text{TcF}_5(\text{H}_2\text{O})^-$ and TcO_4^- is not very different from that found in sulphuric solution at 276 K (Table 2). No changes occur in solutions saturated with N_2O . In aqueous solution the cationic fraction decreases with increasing concentration; at $2 \cdot 10^{-2} \text{ M}$ this fraction practically disappears, while an increase in the yield of $\text{TcF}_5(\text{H}_2\text{O})^-$ is observed. A comparison of results in water and sulphuric acid at 283 K in the concentration range producing low retentions ($\sim 1\%$) shows that the proportion of $^{95g}\text{TcF}_5(\text{H}_2\text{O})^-$ is larger in water. These results show a higher stability of this complex in water than in sulphuric acid solution.

In Fig. 3 is shown the distribution of ^{95m}Tc and ^{95g}Tc in each separated species for 10^{-2} M K_2TcF_6 in water. A higher proportion of ^{95m}Tc as TcO_4^- in water than in HF and H_2SO_4 solutions is found (Figs. 1, 2, 3). As in HF solution, less than 0.5% of $^{95m}\text{TcF}_5(\text{H}_2\text{O})^-$ is found.

An increase of hexafluorotechnetate concentration in water produces an increase of retention (Fig. 4). In solutions of concentration higher than $2 \cdot 10^{-2} \text{ M}$ the increase of retention occurs at the expense of the uncharged and $\text{TcF}_5(\text{H}_2\text{O})^-$ species, the proportion of TcO_4^- remaining

practically constant. At the concentration $5 \cdot 10^{-2} \text{ M}$, the increase of retention is lower than in hydrofluoric acid, 13% and about 35% respectively. In aqueous solution at concentrations higher than $7 \cdot 10^{-2} \text{ M}$ the increase of retention is unexpectedly high. The solubility of K_2TcF_6 prevents the experiments being extended to higher concentrations.

Discussion

1. The solid K_2TcF_6

The much greater resistance of TcF_6^{2-} to hydrolysis facilitates the study and the interpretation of the effects of the isomeric transition. A rather clearer picture is obtained than with the TcCl_6^{2-} salts. But the results can still be explained in terms of the formation of TcX_5^- and smaller amounts of TcX_4 and TcX_3^+ in the lattice.

In this, and in the previous study on solid TcCl_6^{2-} salts, it appears that the Auger cascade seldom, if ever, leads to a long-lived oxidation of the technetium. The small amount of $^{95g}\text{TcO}_4^-$ found may well arise from the oxidation known to accompany aquation-hydrolysis.

The retention in K_2TcF_6 is greater than in K_2TcCl_6 . Both the more compact lattice of the former salt and/or the stronger $\text{Tc}-\text{F}$ (3.06 eV) than $\text{Tc}-\text{Cl}$ (1.51 eV) bond energy may be concerned.

2. Behaviour of solutions

As in TcCl_6^{2-} solutions practically every I.T. event fragments the TcF_6^{2-} . Most of the events appear to produce a TcF_5^- , a smaller, but still substantial, proportion yields

TcF_4 and possibly a little gives TcF_3^+ . These fragments undergo aquation, or in the presence of other ligands, such as F^- , some anation. As previous studies have shown these processes may be accompanied by a small amount of oxidation, by air or water, to give TcO_4^- .

Perhaps the most interesting result is the large effect of the concentration of TcF_6^- on the distribution of the ^{95}Tc . This could arise from a reaction such as



However, in its simplest form this would suggest a dependence on the first power of the TcF_6^- concentration and the data suggests more nearly a dependence on the cube. This may be explained* if the above reaction only occurs if the TcF_6^- is within a certain distance of the nascent $^{95}\text{TcF}_5^-$. A more detailed study of the concentration dependence will be required before one can commit oneself on this point.

Scavenging of Auger and secondary electrons by dissolved nitrous oxide had little effect on the distribution and the only difference in the Ag_2TcF_6 solution seemed to be a reduction in the amount of $^{95}\text{TcO}_4^-$ formed.

* We thank a referee for drawing our attention to this interpretation.

3. General conclusions

The combined results seem to suggest that the energy available for bond rupture following the isomeric transition is not extremely large compared to bond energies. This would indicate the process is not one of "Coulombic explosion" but is associated with the energy released in the numerous electron capture events that rapidly follow the Auger charging due to internally converted isomeric transition in the condensed phase.

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