

Chemical Effects of the Nuclear Isomeric Transition ^{95m}Tc - ^{95}Tc in Some Solid Pertechnetates

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Summary

The chemical effects of isomeric transition of ^{95m}Tc have been investigated in solid lithium, potassium and ammonium pertechnetate matrices. The retention of ^{95g}Tc in $\text{NH}_4^{99(95m)}\text{TcO}_4$ was about 60% and in $\text{Li}^{99(95m)}\text{TcO}_4$ and $\text{K}^{99(95m)}\text{TcO}_4$ higher than 70%. The unretained ^{95g}Tc was found preponderantly as a cationic and an uncharged species. Under corresponding storage conditions the retentions for Li TcO_4 were higher than for KTcO_4 . The influence of temperature and ambient atmosphere was studied. The samples stored in vacuum showed a higher retention than those kept in air. Thermal annealing leads to an increase in retention.

1. Introduction

Some chemical effects of the isomeric transition ^{95m}Tc (61 d) \rightarrow ^{95g}Tc (20 h) have been reported [1–2]. But no data have appeared concerning the pertechnetates. Such a study will permit a comparison with the chemical effects of I.T. in other oxyanions as well as with data for the (n, γ) reaction.

It is relevant to remember that the (n, γ) reaction in the alkali perrhenates gives virtually complete retention if the salts are dissolved in water for analysis [3–5] but angular correlation studies suggest the active rhenium is not present in normal lattice sites [6]. Further, ammonium perrhenate gives retentions ranging from 88 to 50% dependent on the temperature during irradiation and mode of analysis [7]. Finally ^{99}Tc formed by β^- decay in MoO_3 only appears as Tc(VII) [8].

2. Experimental

2.1. Preparation of $^{95m}\text{TcO}_4^-$

^{95m}Tc was obtained by irradiation of natural molybdenum powder with 20 MeV protons. Two months after the irradiation the matrix was dissolved in 3% H_2O_2 , heating gently to effect solution. To prevent loss of TcO_4^- a reflux system was used. The clear yellow solution was divided into three parts and the pH was adjusted to about 8 with LiOH , KOH and NH_4OH solutions. After the extraction of the $^{95m}\text{TcO}_4^-$ ion pair by methyl ethyl ketone the solvent was evaporated. The extraction was repeated two or three times from neutral or fairly basic solution to eliminate traces of molybdenum.

2.2. Preparation of labelled pertechnetates

Labelled samples of $\text{Li}^{99(95m)}\text{TcO}_4$, $\text{K}^{99(95m)}\text{TcO}_4$ and $\text{NH}_4^{99(95m)}\text{TcO}_4$ were used.

The starting material for preparation of $\text{Li}^{99}\text{TcO}_4$ and $\text{K}^{99}\text{TcO}_4$ was hydrated TcO_2 . This was obtained by the hydrolysis of solid $(\text{NH}_4)_2^{99}\text{TcCl}_6$ with 0.1 M NaOH solution. The black precipitate was filtered and washed three times with distilled water.

The resulted $\text{TcO}_2 \times \text{H}_2\text{O}$ was dissolved in 3% H_2O_2 and the solution boiled under reflux to destroy excess peroxide. An aliquot of HTcO_4 was titrated by 0.1 M LiOH and the pH was followed by potentiometry in order to determine the equivalence point. Excess base was back-titrated to equivalence with HTcO_4 . The same procedure was repeated with HTcO_4 and KOH . Solid $\text{Li}^{99}\text{TcO}_4$ and $\text{K}^{99}\text{TcO}_4$ were obtained by evaporation.

To solutions of $\text{Li}^{99}\text{TcO}_4$ and $\text{K}^{99}\text{TcO}_4$ carrier the aqueous solution of $^{95m}\text{TcO}_4^-$, prepared as above, was added. The two mixed solution were divided into a number of glass tubes, evaporated under reduced pressure and kept under different storage conditions.

For the preparation of $\text{NH}_4^{99(95m)}\text{TcO}_4$ the original Amersham ammoniacal solution was used. To the $\text{NH}_4^{99}\text{TcO}_4$ solution some drops of H_2O_2 were added and then the solution was evaporated to dryness. To an aqueous solution of this $\text{NH}_4^{99}\text{TcO}_4$ carrier the ^{95m}Tc was added and after evaporation solid samples were left to reach transient equilibrium.

2.3. Preparation of Tc(IV) carrier

The solid $(\text{NH}_4)_2^{99}\text{TcCl}_6$ was hydrolysed with a 0.1 M NaOH solution and the precipitate of hydrated TcO_2 , separated by centrifugation, was washed three times with distilled water. The $\text{TcO}_2 \times \text{H}_2\text{O}$ was suspended in 1 M H_2SO_4 and nitrogen gas was bubbled through for at least 6 hours so as to obtain a concentrated enough solution of Tc(IV) . The Tc(IV) carrier was separated by centrifugation from the insoluble precipitate. In some experiments a Tc(IV) carrier was prepared simply by dissolution of $(\text{NH}_4)_2^{99}\text{TcCl}_6$ in 0.5 M sulfuric solution. The concentration of $(\text{NH}_4)_2\text{TcCl}_6$ was 10^{-3} to 10^{-4} M. On electrophoresis of the carrier Tc(IV) solution only an uncharged species was observed.

2.4. Separation procedure and activity measurements

Electrophoresis and extraction procedures were used for analysis. The solid pertechnetate was dissolved in 1 M H_2SO_4 either in air or under nitrogen, in the presence or absence of the Tc(IV) carrier. The electrophoretic experiments have been performed with a Camag low voltage apparatus. The paper strips were Schleicher-Schüll No 2043 B and the supporting electrolyte was 1 M H_2SO_4 or 0.1 M H_2SO_4 . A voltage of 400 V was applied for about 2 hours. The paper strips were cut into small pieces for measurement of the activity.

The concentration of $\text{M}^{99(95\text{m})}\text{TcO}_4$ used depended on the $^{95\text{m}}\text{Tc}$ activity. Generally about 1 mg ($\sim 5\mu\text{Ci}$ in $^{95\text{m}}\text{Tc}$) was dissolved in 100 μl carrier solution. An aliquot ($\sim 10\mu\text{l}$) was applied to the paper strip and the rest of solution was used for the extraction procedure. The solution was adjusted to 3 M in sulfuric acid and the $^{95\text{g}}\text{TcO}_4^-$ was extracted with isoamyl alcohol.

The $^{95\text{m}}\text{Tc}$ and $^{95\text{g}}\text{Tc}$ activities were measured with a high resolution Ge/Li detector connected to an Ortec multi-channel analyser. The activities of $^{95\text{m}}\text{Tc}$ and $^{95\text{g}}\text{Tc}$ were obtained using the γ -rays of 835 keV and 766 keV, respectively. For the retention calculation [1] corrections were made because the extraction leads to some $^{95\text{m}}\text{Tc}$ (2–5%) appearing in the aqueous phase and thus to an equivalent fraction of $^{95\text{g}}\text{Tc}$. The electrophoretic data were treated similarly to allow for the tiny amounts of $^{95\text{m}}\text{Tc}$ found in the unretained fractions.

3. Results

The chemical distribution of $^{95\text{g}}\text{Tc}$ in KTcO_4 found after the dissolution in 1 M H_2SO_4 is shown in Table 1. The data show the retention value is higher than 60%. The unretained $^{95\text{g}}\text{Tc}$ is largely present as an uncharged and cationic species. In most of the experiments a small proportion of $^{95\text{g}}\text{Tc}$ is found on the anionic side of the starting point. As can be seen for samples kept in vacuum and at liquid nitrogen temperature dissolution in the presence or absence of carrier gives the same retention value. This suggests that no oxidation of the unretained $^{95\text{g}}\text{Tc}$ species occurs during dissolution. Storage of the samples in air appears to give a significantly lower retention than storage in vacuum. The storage temperature has very little effect on the retention value. But annealing at 473 K for 2 hours leads to an increase in the retention both with samples in which the $^{95\text{g}}\text{Tc}$ population was grown in at 80 K and at 276 K. There is also some change in the distribution of the unretained $^{95\text{g}}\text{Tc}$. Heating for 3 hours at 573 K leads to complete retention, but the sample showed some evidence of superficial decomposition.

In Table 2 are shown the results obtained for LiTcO_4 stored under different conditions and dissolved in 1 M H_2SO_4 before analysis. The retention in LiTcO_4 is higher

than 70%. As for KTcO_4 the storage temperature has very little effect on the retention. Nor does the ambient atmosphere seem important, excepting when the analysis is conducted in the absence of Tc IV carrier. In latter conditions reproducibility of the analysis is very poor. This probably reflects processes taking place during or after solution for analysis.

Electrophoretic analyses in which $^{95\text{m}}\text{Tc}$, $^{95\text{g}}\text{Tc}$ and ^{99}Tc were all measured, showed that the same trivial amounts ($\sim 1\%$) of $^{95\text{m}}\text{Tc}$ and ^{99}Tc were to be found in the cationic, uncharged and non-pertechnetate anionic fractions. This shows that no appreciable radiolytic or other decomposition processes obscure the behaviour of the $^{95\text{g}}\text{Tc}$.

A comparison of the electrophoretic and solvent extraction methods of analysis, using $\text{NH}_4^{99(95\text{m})}\text{TcO}_4$ stored in vacuum at 80 K, showed that two methods gave the same value for the retention, $63.4 \pm 2.0\%$. The proportions of $^{95\text{g}}\text{Tc}$ in the uncharged, cationic and anionic fractions, found by electrophoresis, were 11.2 ± 2.8 ; 18.2 ± 2.8 , and $6.9 \pm 4.5\%$, respectively.

A comparison of results obtained for Li, K and NH_4 pertechnetate shows that for the same conditions of storage and dissolution the retention decreases as follow: $\text{LiTcO}_4 > \text{KTcO}_4 > \text{NH}_4\text{TcO}_4$. The difference between the R values for KTcO_4 and LiTcO_4 is small.

Discussion

Following the pattern of the oxyanions of tellurium [9–13], bromine [14–17] and selenium [18] a substantial proportion of the $^{95\text{g}}\text{Tc}$ appears in products of lower oxidation state than the technetium in the matrix. The uncharged species seems likely to be a hydrated TcO_2 . Cationic species of technetium are not well characterised although there is some evidence for a $\text{TcO}(\text{OH})^+$ in acid solutions [19, 20]. The cationic product reported above may well be the same species. The anionic product is also unknown, but may be an oxyanion of technetium in lower oxidation state than seven.

It is difficult to make a realistic comparison with the behaviour of neutron irradiated NH_4ReO_4 , but the product distributions may well be quite similar. The difficulty lies mostly with paucity of information on the aqueous chemistry of the lower oxidation states of the two elements. FACETTI *et al.* [21] found two separable species, which they supposed were Re III and Re IV fractions. DE KIMPE *et al.* [5] did not explore the nature of the separable species. For the moment we prefer to regard all our separable products as Tc IV species, since there is evidence, quoted above, for such species. But more work of a purely inorganic nature is necessary before one can be confident of the oxidation state of the Tc, or Re, in each of the separable fractions.

The similarity of the distribution of the active rhenium in the neutron irradiated ammonium perrhenate to the $^{95\text{g}}\text{Tc}$

Table 1. Chemical distribution of ^{95g}Tc in the solid $\text{K}^{99(95m)}\text{TcO}_4$ using electrophoresis

Storage conditions		Annealing	Dissolution conditions	R	Unretained ^{95g}Tc		
T, K	ambient atm.				uncharged species %	cation %	anion %
80	air	none	Tc(IV) carrier under N_2	61.6 ± 1.0	11.0 ± 4.3	13.8 ± 1.6	14.3 ± 1.1
80	vacuum	none	Tc(IV) carrier under N_2	72.0 ± 2.1	7.9 ± 2.0	15.7 ± 1.8	4.4 ± 2.2
80	vacuum	2h at 473 K	Tc(IV) carrier under N_2	75.7 ± 1.3	12.2 ± 1.5	9.9 ± 0.4	2.2 ± 0.9
80	vacuum	none	without carrier in air	70.6 ± 0.6	12.4 ± 2.9	13.6 ± 3.1	2.9 ± 0.3
293	vacuum	none	Tc(IV) carrier under N_2	73.6 ± 1.7	11.8 ± 2.1	11.3 ± 2.5	3.2 ± 1.5
276	air	none	Tc(IV) carrier under N_2	65.9 ± 5.5	10.4 ± 2.4	19.4 ± 4.4	4.2 ± 1.0
276	vacuum	none	Tc(IV) carrier under N_2	72.0 ± 4.5	7.6 ± 0.9	15.1 ± 0.9	5.3 ± 4.4
276	vacuum	2h at 473 K	Tc(IV) carrier under N_2	79.9 ± 1.8	10.9 ± 3.5	7.6 ± 3.3	2.0 ± 0.8

All data mean of at least 4 determinations.

Table 2. Chemical distribution of ^{95g}Tc in solid $\text{Li}^{99(95m)}\text{TcO}_4$ using electrophoresis

Storage conditions		Annealing	Dissolution conditions	R	Unretained ^{95g}Tc		
T, K	ambient atm.				uncharged species %	cation %	anion %
80	vacuum	none	Tc(IV) carrier under N_2	74.8 ± 1.8	8.7 ± 1.1	12.1 ± 0.7	4.4 ± 2.5
80	vacuum	none	Tc(IV) carrier in air	76.2 ± 0.8	6.9 ± 2.9	16.1 ± 6.7	1.3 ± 0.2
80	vacuum	2h at 493 K	Tc(IV) carrier under N_2	82.6 ± 3.8	10.6 ± 5.1	4.0 ± 2.1	2.7 ± 2.9
293	vacuum	none	Tc(IV) carrier under N_2	75.4 ± 1.5	9.3 ± 2.7	13.9 ± 5.1	2.7 ± 1.2
276	air	none	Tc(IV) carrier under N_2	73.5 ± 5.2	9.6 ± 4.1	13.9 ± 5.9	3.0 ± 0.4
276	vacuum	none	Tc(IV) carrier under N_2	75.0 ± 2.7	8.5 ± 2.3	12.4 ± 4.3	4.1 ± 2.4

distribution in the analogous pertechnetate certainly does not extend to the potassium salts [3, 22].

But the most interesting result is the large proportion of isomeric transitions that lead to no change in the state of the technetium when investigated by chemical analysis; that is to say, the relatively high retention of ^{95g}Tc .

This isomeric transition is highly converted [23] and practically every decay event must lead to an Auger cascade, so that, at least momentarily, the ^{95g}Tc will acquire a substantial positive charge.

The same dilemma is presented as was described in a previous paper on the hexahalo-technetates arises [2]. Failure to neutralize most of the charging consequent on the Auger cascade should lead to frequent rupture of the TcO_4^- by Coulombic repulsion as the charging distributes itself over the molecule. On the other hand rapid neutralisation will lead to substantial local energy deposition, which might also be expected to lead to TcO_4^- decomposition. However, in both the hexachloro-technetate IV salts and the per-

technetates very substantial retentions are found. In both series of salts the pattern of products is what might be expected if the molecular rupture took place through recoil. There is at present no evidence demanding an oxidative role for the isomeric transition.

Between 80 K and ambient temperature little annealing is observed, but practically complete reformation of pertechnetate takes place before thermal decomposition, very possibly by a solid state exchange mechanism. There are indications that an ambient atmosphere containing oxygen reduces annealing [24]. The annealing of rhenium shows similar effects [25].

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