

Chemical Effects of the Isomeric Transition of ^{95m}Tc in a $(\text{NH}_4)_2^{99}\text{TcCl}_6$ Matrix

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Summary

The chemical effects of the isomeric transition of ^{95m}Tc in a $(\text{NH}_4)_2^{99(95m)}\text{TcCl}_6$ solid matrix have been studied by solvent extraction and electrophoretic separation methods. A suitable method of calculation of the retention from the measured photo-peak intensity of the ground and metastable states has been developed. The retention value found by the extraction method was close to 100% in contrast with that found by electrophoretic separation which was about 77%.

1. Introduction

There are comparatively few isomeric pairs in which the lifetime of the parent, which decays predominantly by a highly converted isomeric transition, permits growth to transient equilibrium of a shorter-lived ground state species. Tellurium is an exceptional element in that it provides three such isomeric pairs and these have been used to explore the effects of the storage conditions (such as temperature and dose rate of ionizing radiation) on the chemical effects following the isomeric decay process. A highly converted isomeric transition might be expected to lead to the ground state species appearing in an oxidised form. But experiments with a few tellurium IV compounds labelled with the excited tellurium isomers show little evidence for such oxidation, while telluric VI acid gave considerable yields of ground state species in the tetravalent state [1–6]. Work with the ^{80m}Br transition has also given only lower oxidation state products [7–9].

The isomeric pair $^{95m}\text{Tc} - ^{95g}\text{Tc}$ is another pair that is suitable for such studies. The parent ^{95m}Tc has a half-life of 61 d, while the ground state, ^{95g}Tc has a half-life of 20 h [10]. The transition is highly converted, $\alpha = 7.63 \times 10^4$ [11] and the ^{95m}Tc may be measured using the 786 or 835 keV γ radiation, while the ^{95g}Tc can be determined from the 766 keV emission. Technetium with its numerous oxidation states, is well-suited to the detection and measurement of such oxidation or reduction effects.

BOYD and LARSON [12] have indeed reported that the transition leads to $^{95g}\text{TcO}_4^-$ production if decay takes place in $^{99(95m)}\text{TcCl}_6^-$ adsorbed on an anion exchange resin.

The aim of this work is to study the chemical effects of I. T. in the $(\text{NH}_4)_2^{99(95m)}\text{TcCl}_6$ solid matrix.

2. Experimental

2.1. Preparation of ^{95m}Tc

The ^{95m}Tc was obtained by the irradiation of natural molybdenum powder with 20 MeV protons in the S. I. N. cyclotron at Villigen, Switzerland. Two months after irradiation the target was dissolved in nitric acid, diluted 1 : 1 with water, and the solution evaporated to dryness (some volatilization of HTcO_4 may take place during this step). The residue was dissolved in 0.1 M sodium hydroxide and the $^{95m}\text{TcO}_4^-$ extracted with methyl ethyl ketone (MEK) in the presence of lithium sulphate [13]. The solvent was removed under reduced pressure. A better procedure was to dissolve the irradiated powder in H_2O_2 [13] heating gently the solution. The $^{95m}\text{TcO}_4^-$ was extracted from a neutral or fairly basic solution by MEK. Recovery was about 95% for both methods of dissolution.

2.2. Synthesis of $(\text{NH}_4)_2\text{TcCl}_6$

The $(\text{NH}_4)_2^{99}\text{TcCl}_6$ carrier was prepared by the reduction of the original (Amersham) ammoniacal solution of $\text{NH}_4^{99}\text{TcO}_4$, by heating with concentrated hydrochloric acid at 95°C for 26 hours [14]. The solution was then evaporated to reduce the volume and yellow crystals of the product separated. Their identity was confirmed by their powder X-ray diffraction pattern and by their behaviour on electrophoresis. The labelled $(\text{NH}_4)_2^{99(95m)}\text{TcCl}_6$ crystals were prepared by a similar reduction with the extracted $\text{H}^{95m}\text{TcO}_4$ dissolved in concentrated HCl. To this solution was added the carrier $(\text{NH}_4)_2^{99}\text{TcCl}_6$ and the solution was then evaporated to a small volume and the crystals separating were divided for different storage conditions. The samples were left for at least 10 days to reach transient equilibrium.

2.3. Separation procedure

For the separation of the different technetium species solvent extraction and electrophoresis were used. The extraction method allows the separation of TcO_4^- from the previously hydrolysed TcCl_6^- [15]. The solid $(\text{NH}_4)_2^{99(95m)}\text{TcCl}_6$ was dissolved in an acetate buffer solution at pH 6. The solution was adjusted to 3 M in sulphuric acid and the TcO_4^- extracted with isoamyl alcohol. In some cases extraction by MEK from a neutral solution was used.

In this procedure the TcCl_6^- is hydrolysed to yield TcO_2 , while the TcO_4^- extracts as an ion-pair species. Unless the TcCl_6^- is hydrolysed it is also partly extracted by the alcohol [15].

The electrophoretic experiments have been performed with a Camag high voltage electrophoresis apparatus. The paper strips were Schleicher-Schuell No 2043 B. The supporting electrolyte was 1 M H_2SO_4 . A voltage of 400 V was applied for two hours. The sample was dissolved in 1 M H_2SO_4 and immediately applied to the paper strip. The paper was cut into small pieces when the activity was measured.

2.4. Measurement of the activity

Measurements were made with a standardised geometry using a high resolution Ge/Li detector. The ^{95g}Tc was measured using

the photopeak from the 766 keV emission. The ^{95m}Tc was measured by means of the 786 or 835 keV photopeaks [16–18]. Measurements of the peak intensity for the two isomers on a sample stored till transient equilibrium gave the ratio of counting efficiencies for the two isomers. The ratio proved to be the same for both the aqueous and organic phases.

3. Retention calculation

Two kinds of retention calculations were used. In one case the measurement of the activity of the ground state 766 keV photopeak has been followed by repeated measurements over two days. The calculation was made using the function $a_g = f(t)$, where a_g is the intensity of the 766 keV photopeak and t is the time elapsed between the separation of the fractions and the measurements of their activity. Such measurements were performed on the fractions separated by the solvent extraction method. In the case of electrophoretic separation the paper strip was cut in about 10 pieces and each was measured only once, as soon as possible after separation.

(a) Solvent extraction separation

Considering the activity of an aqueous phase separated at zero time from a system in transient equilibrium

$$A_g = \frac{\lambda_g}{\lambda_g - \lambda_m} A_m^0 (e^{-\lambda_m t} - e^{-\lambda_g t}) + A_g^0 e^{-\lambda_g t} \quad (1)$$

Where A denotes the disintegration rate, or true activity at time t , λ denotes a decay constant, and t the time elapsed since the separation. The subscripts m and g distinguish quantities relating to the isomers and ground state species, respectively and the index 0 a value at the time of separation.

This expression assumes all isomeric state disintegrations take place by isomeric transition. To allow for a fraction f so doing, requires the first term of the right hand side of equation (1) to be multiplied by f .

Transforming to measured activities, a , requires allowance for the emission probabilities and detection efficiencies of the photon emissions used in the measurements, ϵ .

Thus

$$a_g = \frac{\lambda_g}{\lambda_g - \lambda_m} \frac{\epsilon_g}{\epsilon_m} f a_m^0 (e^{-\lambda_m t} - e^{-\lambda_g t}) + a_g^0 e^{-\lambda_g t}$$

or

$$a_g e^{\lambda_g t} = \left(\frac{\lambda_g}{\lambda_g - \lambda_m} \frac{\epsilon_g}{\epsilon_m} f \right) a_m^0 (e^{-(\lambda_m - \lambda_g)t} - 1) + a_g^0 \quad (2)$$

Hence for a given separation if a_g is measured as a function of t , this equation takes the form $y = mx + c$, where

$$x = (e^{-(\lambda_m - \lambda_g)t} - 1) \text{ and } m = \frac{\lambda_g}{\lambda_g - \lambda_m} \frac{\epsilon_g}{\epsilon_m} f a_m^0$$

All these equations are true irrespective of the efficiency of the solvent extraction.

Representing the retention by R , let us suppose that only retained activity is left in the aqueous phase, but that the extraction leads to some ^{95m}Tc appearing in the organic phase. It is reasonable to suppose that the same fraction of the retained ^{95g}Tc will also be transferred to the organic phase.

Now the retained activity is $R(a_g^0 + \bar{a}_g^0)$ where the bar refers to the organic phase. So the retained activity transferred to the organic phase is

$$\frac{\bar{a}_m^0}{a_m^0 + \bar{a}_m^0} R(a_g^0 + \bar{a}_g^0)$$

Thus,

$$\begin{aligned} a_g^0 &= R(a_g^0 + \bar{a}_g^0) - \frac{\bar{a}_m^0}{a_m^0 + \bar{a}_m^0} R(a_g^0 + \bar{a}_g^0) \\ &= R \frac{(a_g^0 + \bar{a}_g^0)}{(a_m^0 + \bar{a}_m^0)} a_m^0 \\ R &= \frac{(a_m^0 + \bar{a}_m^0)}{(a_g^0 + \bar{a}_g^0)} \frac{a_g^0}{a_m^0} \end{aligned} \quad (3)$$

$$\text{But } \frac{(a_m^0 + \bar{a}_m^0)}{(a_g^0 + \bar{a}_g^0)} = \frac{(\lambda_g - \lambda_m)\epsilon_m}{\lambda_g \epsilon_g f}$$

$R = c/m$ and can be calculated from the $a_g(t)$ data.

The ratio $\frac{(\lambda_g - \lambda_m)\epsilon_m}{\lambda_g \epsilon_g f}$ can also be measured by a com-

parison of the ratio of activities a_m and a_g of a system in transient equilibrium. It was verified that this ratio was the same whether the species were in the aqueous or organic phase.

(b) Electrophoretic data

The values of a_m^0 and a_g^0 can be obtained from the measured values a_m and a_g by the relations

$$\begin{aligned} a_m^0 &= a_m e^{\lambda_m t} \\ \text{and } a_g^0 &= a_g e^{\lambda_g t} + \left\{ \frac{\lambda_g}{\lambda_g - \lambda_m} \frac{\epsilon_g}{\epsilon_m} f \right\} a_m (e^{\lambda_m t} - e^{\lambda_g t}) \end{aligned}$$

The quantity in parentheses are measured as indicated above.

Now consider the activity of the i^{th} species on the paper strip at the moment of separation. Because of some hydrolysis of the TcCl_6^- some ^{95m}Tc activity will be found, so that a portion of the observed ^{95g}Tc activity will not be due to the isomeric transition. This portion will be

$$R \frac{a_m^0(i)}{\sum_i a_m^0(i)} \sum_i a_g^0(i)$$

Suppose the TcCl_6^- peak is the j^{th} species. Then

$$a_g^0(j) = R \sum_i a_g^0(i) - R \left\{ \frac{\sum_i a_g^0(i)}{\sum_i a_m^0(i)} \right\} \sum_i a_m^0(i) + \\ + R \left\{ \frac{\sum_i a_g^0(i)}{\sum_i a_m^0(i)} \right\} a_m^0(j).$$

So that

$$R = \frac{a_g^0(j)}{a_m^0(j)} \left\{ \frac{\sum_i a_m^0(i)}{\sum_i a_g^0(i)} \right\}$$

The term in parentheses is the same as the one appearing above.

For any other species (i)

$$a_g^0(i) = Y_i \sum_i a_g^0(i) + R \left\{ \frac{\sum_i a_g^0(i)}{\sum_i a_m^0(i)} \right\} a_m^0(i) \\ Y_i = \left[\frac{a_g^0(i)}{\sum_i a_g^0(i)} - R \frac{a_m^0(i)}{\sum_i a_m^0(i)} \right]$$

Thus the Y_i can be calculated knowing all the $a_g^0(i)$ and $a_m^0(i)$.

It was verified that the effect of the change in counting rate during the period of the measurement was negligible.

4. Results and discussion

The separation by extraction gave the same results irrespective of whether iso-amyl alcohol or methyl ethyl ketone were used. The time allowed in the hydrolysis step was unimportant over the interval of 2–10 minutes.

The results obtained by this method are presented in Table 1. The retention values are close to 100% and only a very small yield of pertechnetate is found. The storage conditions, temperature and ambient atmosphere seem to have no appreciable effect on the small amount of oxidised

Table 1. Retention values obtained by solvent extraction

Storage conditions		$R \pm \sigma_{\bar{R}}$ %
$T^\circ\text{C}$	Ambient atmosphere	
20	air	99.3 ± 0.82
20	vacuum	98.6 ± 0.85
–195	air	99.2 ± 0.52
–195	vacuum	97.3 ± 0.99

^{95g}Tc . The results are not influenced by the storage time even over a period of 3 months.

With the extraction method one may doubt whether the ^{95g}Tc found in the aqueous fraction corresponds only to TcCl_6^- ion. A priori the presence in the sample of some intermediate species which at pH = 6 may also hydrolyse to $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ cannot be excluded.

Using a sample of high specific activity, it was possible to perform electrophoretic analyses. The results are presented in Table 2. The samples were divided in two parts. One was separated by solvent extraction (see Table 1) and the other analysed by electrophoresis. As can be seen, the retention found by the latter technique is smaller than that obtained by the extraction procedure. From Table 2 it seems that the retention at -195° is slightly higher than at 20°C .

The unretained ^{95g}Tc amounts to only a few percents of TcO_4^- , about one third or less is present as another anionic species and about two thirds or more as neutral and cationic species, these last two being incompletely separated are taken together. This fact and the weak activity of the fractions limit the precision of our data for ^{95g}Tc distribution.

A comparison of the electrophoretic and extraction results shows that the cationic and the anionic species hydrolyse, together with the TcCl_6^- , to TcO_2 when the sample is dissolved at pH = 6. Thus in the extraction procedure some hydrolysed ^{95g}Tc remains in the aqueous phase, leading to apparently high retentions. The extraction method in this case only gives information on the ^{95g}Tc in the highest oxidation state, e. g., TcO_4^- . The proportion found in this form by either method is very low. But the retention values are different. These observa-

Table 2. Retention values and the non-retained ^{95g}Tc distribution obtained by electrophoresis

No	Storage conditions			R %	$\bar{R} \pm \sigma_{\bar{R}}$ %	Non-retained ^{95g}Tc		
	$T^\circ\text{C}$	ambient atmosphere	time days			TcO_4^- %	anion %	neutral and cation %
1	20	air	37	71.3 ± 2.4	73.6 ± 1.3	0.8	11.2	17.5
2	20	"	43	77.2 ± 3.2		0.4	6.8	15.7
3	20	"	45	73.8 ± 2.5		2.2	8.1	16.7
4	20	"	16	72.2 ± 5.8		1.7	8.8	17.1
5	–195	"	9	80.5 ± 3.6	80.9 ± 0.91	1.4	6.1	11.7
6	–195	"	10	82.0 ± 4.3		1.5	4.9	13.0
7	–195	"	11	82.6 ± 3.8		1.1	5.7	10.8
8	–195	"	11	78.5 ± 5.2		1.3	6.4	13.4

tions emphasize the usefulness of widely different methods for the analysis.

The electrophoretic data show that the ground state species appear at the same positions as the technetium compounds formed by the partial hydrolysis of $^{99}\text{TcCl}_6^-$. Each of the peaks in the activity plots of the electrophoretic strips shows the same proportions of ^{99}Tc and $^{95\text{m}}\text{Tc}$ but an enhanced amount of $^{95\text{g}}\text{Tc}$. This excess activity permits us to calculate the proportions of the different crystal precursors, produced by the isomeric transition in $(\text{NH}_4)_2^{95\text{m}}\text{TcCl}_6$, yielding the hydrolysed species on solution. To this extent the effects of the isomeric transition closely resemble those of the (n, γ) reaction on the hexachloroiridates(IV) [19].

These hydrolytic products have been investigated by KANCHIKU [20] using, amongst other techniques, electrophoresis. The distances travelled by our different products, expressed as a fraction of that travelled by the $^{99}\text{TcCl}_6^-$, agree with those reported by KANCHIKU and with control experiments on solutions of $(\text{NH}_4)_2^{99}\text{TcCl}_6$.

The extent of this hydrolysis of the matrix material, taking place after the dissolution of the aged crystals, depends on the illumination and on the time elapsing before electrophoresis. It varied from 10 to 40% of the total technetium, but in the faster separations chosen for measurement it always permitted reasonable accuracy in the calculation of the yields of the different forms of the $^{95\text{g}}\text{Tc}$. (Probable errors $\pm 2\%$) (see also Retention Calculation).

It appears, therefore, that the isomeric transition leads to $^{95\text{g}}\text{Tc}$ crystal precursors that immediately form the normal TcCl_6^- hydrolysis products upon solution. It has been established that these are $\text{TcCl}_5\text{H}_2\text{O}^-$, $\text{TcCl}_4(\text{H}_2\text{O})_2$ or perhaps more likely TcO_2 , and some cationic species, perhaps $\text{TcCl}_3(\text{H}_2\text{O})_3^+$. These last two are poorly resolved because of tailing effects and have generally been combined in our data [20].

The precise mode of formation and even the identity of the crystal precursors of the unretained $^{95\text{g}}\text{Tc}$ are still a matter of some difficulty. It is clearly quite easy to see how such hydrolytic species could result from the dissolution of ligand deficient $^{95\text{g}}\text{Tc}$ species such as $^{95}\text{TcCl}_5$, TcCl_4 and TcCl_3^+ . But this implies that the isomeric transition can lead to bond rupture, albeit not very efficiently since the minimum retention is about 70%.

However, it is also possible to envisage the hydrolytic $^{95\text{g}}\text{Tc}$ products finding their origin in oxidized $^{95\text{g}}\text{Tc}$ species formed in the crystals, such as TcCl_6 , TcCl_6 and TcCl_6^+ . These would probably suffer a rapid reductive hydrolysis. It is possible that experiments in solution will answer this question.

The very substantial retention calls for some comments. The reattachment of the emitted Auger electrons presumably takes place sufficiently rapidly to exclude the coulombic explosion, such as seems to occur in the gas phase [21, 22]. Reformation of $^{95}\text{TcCl}_6^-$ by an ejected $^{95\text{g}}\text{Tc}$ can occur, but it would be surprising to find it so efficient even at the temperature of liquid nitrogen. The

same qualification applies to reformation by a replacement reaction in TcCl_6^- .

The majority ($> 70\%$) of the isomeric transition events take place without permanent rupture of the TcCl_6^- unit. The transition is known to be highly internally converted ($> 99.9\%$) and it is difficult to see how an Auger cascade can be avoided. But the Auger electrons are very soft indeed and one is driven to the conclusion that, after most of the events, they return to the positive holes they have vacated, without causing molecular rupture.

The substantial retention implies rarity of electron trapping and indicates that NH_4^+ is not a very effective trap in this salt. It should be noticed that isomeric transition in tellurium, in salts of the halo-tellurates, leads also to very high retentions [6].

To some extent this result might be considered at variance with the results of the (n, γ) reaction on ammonium salts, where very low retentions are frequently found and this has been attributed to electron trapping with production of reducing radicals, such as NH_2 . However, it would still be possible to attribute the separable $^{95\text{g}}\text{Tc}$ to the reactivity of the ammonium cation. But this interpretation is not tenable. Experiments have also been made on the potassium salt, $\text{K}_2^{99(95\text{m})}\text{TcCl}_6$. Although final results for this matrix are not yet available, replicate electrophoretic analyses on two independent samples of $^{95\text{m}}\text{Tc}$ labelled potassium salt, stored at liquid nitrogen temperature, give a mean retention of 69%. About 1% of the $^{95\text{g}}\text{Tc}$ appears as TcO_4^- and the remainder in the same anionic and neutral plus cationic species as are found with the ammonium salt. Thus the potassium salt gives the same distribution of species and a rather higher retention of $^{95\text{g}}\text{Tc}$ than the ammonium salt. It does not appear reasonable to attribute the separable products to any peculiarity of the ammonium salts.

By contrast with the solid compound, the retention values of $^{95}\text{TcCl}_6^-$ in aqueous solution, is significantly lower. Our preliminary results on $^{99(95\text{m})}\text{TcCl}_6$ in 1 M H_2SO_4 kept at 20°C until transient equilibrium show a retention value of about $\leq 3\%$. The non-retained $^{95\text{g}}\text{Tc}$ is found predominantly as a cationic fraction, but the percent of TcO_4^- seems to be higher than that found for the solid. In the case of I. T. occurring in solution it can be supposed that the Auger electrons are trapped by the water and produce radiolytic products.

Conclusion

The I. T. in $^{95\text{m}}\text{Tc}$ in $(\text{NH}_4)_2\text{TcCl}_6$ leads in less than one third of the events to chemically separable $^{95\text{g}}\text{Tc}$. Although oxidative processes cannot be logically excluded, the data are most easily interpreted in terms of the production of ligand deficient species such as $^{95}\text{TcCl}_5^-$. Thus our results agree with those obtained on the compounds of tellurium and bromine.

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