PHYSICAL REVIEW C VOLUME 21, NUMBER 1 JANUARY 1980

Effect of chemical state on the decay constant of $^{99}Tc^m$

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(Received 4 April 1979)

The chemical effect on the decay constant λ of $^{99}Tc^m$ has been investigated by means of the differential method. Two combinations of sources, Tc_2S_7-TcO_4^- and Tc_2S_7-metallic Tc, were measured, of which the results are $\lambda(TcO_4^-) - \lambda(Tc_2S_7) = (31.8 \pm 0.7) \times 10^{-4}\lambda(Tc_2S_7)$ and $\lambda(Tc_2S_7) - \lambda(\text{metal}) = (5.6 \pm 0.3) \times 10^{-4}\lambda(\text{metal})$. The present results agree well with those presented by Bainbridge *et al.*

[RADIOACTIVITY $^{99}Tc^m$; measured $T_{1/2}$, double ionization chamber, chemical effect.]

I. INTRODUCTION

In 1947, Segrè[1] and Daudel[2] first suggested that nuclear decay rate might be changed in the case where the orbital electrons involved contribute directly to the nuclear decay, either by an orbital electron capture or by a partly converted isomeric transition of nucleus. In this case, a change in electron density at the nucleus by an external effect may result in a change in the decay constant λ.

One of the most interesting cases is $^{99}Tc^m$ ($T_{1/2} = 6.0$ h). This isomer is the second excited state decaying to the ground state ^{99}Tc ($T_{1/2} = 2.12 \times 10^5$ y) through a cascade nuclear transition, of which the transition energies are 2.17 and 140.5 keV, respectively. The isomeric transition of $^{99}Tc^m$ to the first excited state has an $E3$ character and proceeds almost completely by the internal conversion, where the conversion can take place only in the M and N shell due to its low transition energy. This indicates that the change in the conversion probability (or decay rate) may be observable when the isomer is in different environmental conditions. The earliest experiment with $^{99}Tc^m$ was by Bainbridge *et al.*[3,4] in 1951. They compared the decay constant of $^{99}Tc^m$ in three kinds of chemical states, metallic Tc, Tc_2S_7, and $KTcO_4$, by measuring the 140-keV γ rays. Since then, the measurements with the isomer in various kinds of external conditions have been performed.[5]

Because of the small change in λ, the most reliable experimental method is the differential method first introduced by Rutherford.[6] With an intention of measuring a minute difference in intensities of two γ-ray sources by means of the differential method, we constructed a double ionization chamber, which consists of two essentially identical chambers. For measurements of ion current, a conventional sampling method was adopted. Details of the chamber construction and the measuring system were previously reported.[7] With this device, the change in λ of $^{99}Tc^m$ in three different chemical states (metallic Tc, Tc_2S_7, ϕ_4AsTcO_4) was measured. Comparisons of our results with those by Bainbridge *et al.*[3,4] show essential agreement. (It is reasonably said that the chemical effect on λ as pertechnetate is similar for both $KTcO_4$ and ϕ_4AsTcO_4.)

Up to the present, only one simple theoretical estimation has been reported by Slater.[8] Introducing the concept of the atomic bond length and using the fact that the Tc-O bond length in $KTcO_4$ is smaller than the Tc-Tc distance in Tc metal, he claimed that the Tc atom is squeezed more in $KTcO_4$, and that this squeezing effect gives rise to the larger conversion probability of the 2.17-keV transition in $KTcO_4$. This explanation qualitatively supports the experimental results.

II. EXPERIMENTAL

A. Source preparation

The radioisotope $^{99}Tc^m$ was chemically extracted through a $^{99}Tc^m$ generator (^{99}Mo-$^{99}Tc^m$ milking device, initial intensity is 100 mCi) with 20 ml of the physiological salt solution, and then it was divided into two parts. These solutions were used to prepare a pair of $^{99}Tc^m$ sources in different chemical forms (see below). Radioactive contaminants in the sources were carefully examined by using a Ge(Li) detector. The ^{99}Mo contaminant involved in the source was found to be less than 10^{-10} of the initial activity of the sources, being negligible for the present measurement, and no other contaminants were found.

1. Metal

The method for preparing metallic Tc was by electrodeposition and reduction, of which the details were previously reported in our relevant works.[7,9-13] To the ^{99}Tc^{m} solution extracted from the generator were added 0.2 g of NH_4F, 1.0 ml of 12*N* HCl solution, 3.0 mg of ^{99}Tc (carrier) in the chemical form of NH_4TcO_4, and three-times-distilled water. The electrolyte thus prepared was 100 ml, pH = 1.0. In this working solution, Tc was electrolytically deposited on the cathode, a Cu plated tungsten wire (0.4 mm in diameter and 18 cm length). The electrodeposition was continued for about 2 h with a current of 20 mA at 40 ° C.

In order to achieve uniform and smooth deposition of Tc, the electrolyte was stirred by bubbling pure nitrogen gas through a capillary tube. The quantity of Tc recovered on the cathode was estimated from the activity of the residual solution. The electrodeposited Tc is expected to be in the chemical form of Tc-TcO_2 mixture. The cathode was then transferred into a reduction chamber where Tc was reduced in flowing pure hydrogen gas at 800–1000 °C, by supplying an electric current of 20 A through the sample wire. The reduction was continued until the deposited Tc became silvery metal of somewhat dull luster. The thickness of Tc thus prepared was about 10^4 Å. The sample was then cut into several pieces (3 cm each), and was mounted in a source holder made of Lucite. Cutting and mounting of the sample wire were both carried out in the reduction chamber.

To ensure the production of metallic Tc by the method mentioned above, the sample was x-ray analyzed. The diffraction pattern confirmed the hcp structure of Tc, having lattice constants of $a = 2.74$ Å and $c = 4.40$ Å. Since the metallic Tc thus prepared is considered to be bulk materials as a superconductor, another test of the samples was performed by observing the superconducting transition by means of the ac susceptibility measurement. The measurement of ac susceptibility as a function of temperature (4.2–8.0 K) showed that the superconducting transition temperature is a little bit lower than the current value, probably due to some inhomogeneity in the present sample, but the typical transition curve between the normal and the superconducting states surely confirmed the production of metallic Tc.

2. *Sulfide*

A few milligrams of long lived isotope carrier $^{99}TcO_4^-$ were added to about 10 ml of the $^{99}Tc^{m}O_4^-$ solution eluted from the ^{99}Mo parent. The dark brown sulfide of heptavalent technetium Tc_2S_7 was precipitated from the 4N H_2SO_4 solution at the temperature of boiling water by bubbling hydrogen sulfide through the solution. The sulfide was digested at this temperature for 2 h and was filtered through a Millipore 5 μ Teflon membrane. The elemental sulfur in the precipitate was removed by washing it with carbon disulfide. The sulfide was thoroughly washed with hot water, vaporized to dryness, and coated with paraffin. The reproducibility of Tc_2S_7 sources has been satisfactory.

3. *Pertechnetate*

Among the insoluble pertechnetate salts, the most popular precipitate is in the form of tetraphenylarsonium pertechnetate ϕ_4AsTcO_4. This precipitation was carried out from the neutral pertechnetate solutions containing the long lived $^{99}TcO_4^-$ with an excess of tetraphenylarsonium chloride ϕ_4AsCl. The pertechnetate precipitate was digested for 1 h at 60 °C, filtered through the Millipore membrane, washed with hot water, taken to dryness, and then coated with paraffin. The reproducibility of this pertechnetate has also been satisfactory.

B. Measurements of ion current

In Fig. 1 is shown the block diagram of the measuring system. As seen in the figure, measurements of ion current employed in this experiment are the differential method which has been extensively used in investigations of the change in λ. In this method, two radioactive sources are simultaneously measured under as nearly identical conditions as possible and only the difference current produced by two sources is measured as a function of time. Using the present system, a minute difference in intensities (1 part in 10^5) of two γ-ray sources can be observed. Since details of the chamber construction and the whole performance of the system were previously reported,[7] only the principle of measurements is crudely

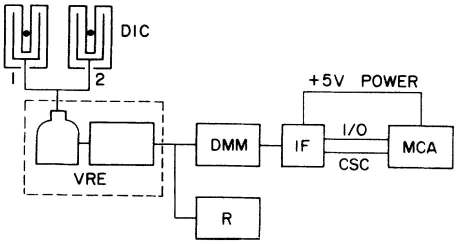

FIG. 1. Block diagram of the measuring system. Double ionization chamber (DIC); vibrating reed electrometer (VRE); digital multimeter (DMM); recorder (R); interface (IF); control signals connector (CSC); 1024-channel pulse-height analyzer (MCA). Solid circles in DIC indicate the sources.

given here.

Let $I_1(0)$ and $I_2(0)$ be the initial ion currents produced in chambers 1 and 2, respectively. The ion current at time t is expressed as $I_1(t)=I_1(0) \times \exp(-\lambda_1 t)$ and $I_2(t)=I_2(0)\exp(-\lambda_2 t)$, where λ_1 and λ_2 are respectively the decay constants of two γ-ray sources mounted in chambers 1 and 2. As the collecting voltage of two chambers are opposite in sign, the net current $I(t)$ is given by

$$I(t)=I_1(0)e^{-\lambda_1 t}-I_2(0)e^{-\lambda_2 t}. \tag{1}$$

Supposing $\lambda_2=\lambda_1+\Delta\lambda$ ($\Delta\lambda/\lambda_1 \ll 1$), $I(t)$ is approximately given by

$$I(t)e^{\lambda_1 t}=[I_1(0)-I_2(0)]+I_2(0)\Delta\lambda t. \tag{2}$$

The first term of the right-hand side in Eq. (2) is zero if perfect balancing of the chamber ion currents can be achieved, corresponding to $I_1(0) = I_2(0)$. However, since this case is idealized, a small fraction of chamber current is left as the residual. The best balancing achieved in the actual procedure was $[I_1(0)-I_2(0)]/I_2(0)=2\times10^{-4}$. The difference ion current is then measured through a vibrating reed electrometer with the aid of the conventional sampling method, i.e., for obtaining the mean value of ion current varying each moment due to the statistical nature of nuclear decay, the output ion current is recorded intermittently and the mean value in a certain time period is calculated. For ion currents of 2×10^{-10} A, $\sigma/I_1(0)=0.003\%$, where σ is the standard deviation. This is the limit of accuracy of the present device. As Eq. (2) has a linear form $y = a+bt$, the slope of the least-squares line of observed values $I(t)\exp(\lambda_1 t)$ is equal to b, i.e., $I_2(0)\Delta\lambda$, from which one can calculate the relative change in the decay constant, $\Delta\lambda/\lambda_1$.

The initial ion current $I_1(0)$ [or $I_2(0)$] was chosen as about 2×10^{-10} A or less, because for a larger ion current, the linearity of output current slightly deteriorates, probably due to the recombination of ions in the chamber. In addition, it has been found that for an initial ion current larger than 2×10^{-10} A, the present chamber system sometimes gives a sine-wave shape output current as a function of time. Some details of this phenomenon will appear elsewhere.

As in usual cases, it is expected to take time to get stabilization of the whole measuring system after setting of radioactive sources. Repeated tests have revealed that it takes about 8 h before the ion current is fully stabilized. Taking into consideration the time response of the system, all measurements were started 10 h after source setting.

The chamber and subsidiary electric instruments were set in a room without window and located in the basement. All other things which may give any electric or magnetic disturbance to the measurement were removed from the room. The temperature in the room was carefully controlled and was kept at 20.0 ±0.1 ℃ during the measurement.

III. RESULTS AND DISCUSSION

The measurements of $\Delta\lambda/\lambda$ have been performed for three combinations of sources, i.e., TcO_4^--TcO_4^- (both in solution), Tc_2S_7-ϕ_4AsTcO_4, and Tc_2S_7-metallic Tc (electrodeposited and reduced in hydrogen gas).

The whole performance of the measuring system was examined with the first pair (TcO_4^--TcO_4^-). The physiological salt solution (20 ml) used to extract $^{99}Tc^m$ (in the chemical form of TcO_4^-) from the ^{99}Mo parent was poured into two bottles (10 ml each), and then these were set in each chamber as the γ-ray sources. Since they are chemically identical, the slope of the observed values of $I(t)\exp(\lambda t)$ should be zero within experimental error. However, the observed slope of the TcO_4^--TcO_4^- pair gave a small nonzero value out of the

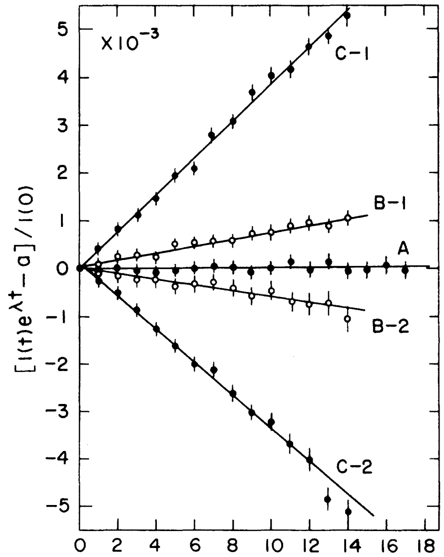

FIG. 2. Three combinations of sources are measured. Data are normalized to the initial intensity $I(0)$ after subtracting the initial difference current a. (A) TcO_4^--TcO_4^- (both in solution); (B-1, 2) Tc_2S_7-metallic Tc; (C-1, 2) Tc_2S_7-ϕ_4AsTcO_4. For B and C, chamber-source combinations are inversed in the measurements 1 and 2.

TABLE I. Relative differences in the decay constant of $^{99}Tc^m$ in different chemical environments.

Source pair	$(\Delta\lambda/\lambda)\times10^4$	References
$\dfrac{\lambda(TcO_4^-)^{a} - \lambda(Tc_2S_7)}{\lambda(Tc_2S_7)}$	27.0 ± 1.0	3, 4
$\dfrac{\lambda(Tc_2S_7) - \lambda(\text{metal})^{b}}{\lambda(Tc_2S_7)}$	3.1 ± 1.2 [c]	3, 4
$\dfrac{\lambda(TcO_4^-)^{d} - \lambda(Tc_2S_7)}{\lambda(Tc_2S_7)}$	31.8 ± 0.7	present work
$\dfrac{\lambda(Tc_2S_7) - \lambda(\text{metal})^{e}}{\lambda(\text{metal})}$	5.6 ± 0.3	present work

[a] $KTcO_4$.

[b] Electroplated on nickel and reduced in H_2 at 1000 °C.

[c] In the abstract of Ref. 4, they give $\lambda(\text{metal}) - \lambda(Tc_2S_7) = (3.1 \pm 1.2) \times 10^{-4}\lambda(Tc_2S_7)$. However, from their statements in Refs. 3 and 4, it is evident that the sign of the difference $\lambda(Tc_2S_7) - \lambda(\text{metal})$ as measured by Bainbridge *et al.* is positive as referred to in this Table.

[d] ϕ_4AsTcO_4.

[e] Electrodeposited on a Cu plated tungsten wire and reduced in H_2 at 800–1000 °C.

experimental error. Repeated tests have shown that this extremely small, but nonzero value in the slope of Eq. (2) systematically appears, even for a chemically identical source pair, indicating the existence of systematic error of the present system. The origin of this character is not clear yet, but is probably due to the indistinguishable asymmetry of the double ionization chamber.

Taking into account this small systematic error of the device, in the following experiment, each source pair (Tc_2S_7-ϕ_4AsTcO_4, Tc_2S_7-metallic Tc) was measured two times, by exchanging the source-chamber combination, and the average value of two measurements was adopted as the final result for each pair. The observed curves are shown in Fig. 2, and in Table I are listed the numerical results obtained by a computer least-squares fitting, as well as those by Bainbridge *et al.*[3,4]

In conclusion, the chemical effect on λ of $^{99}Tc^m$ has been finely observed in the present experiment. Our results support the previous observations by Bainbridge *et al.* and are also consistent with qualitative explanation by Slater.[8]

The authors wish to express their thanks to Professor S. Shimizu for stimulating suggestions.

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