Thenoyltrifluoroacetone as a Complexing Agent for the Isolation and Purification of Carrier-free Radioberyllium

BY RENÉ A. BOLOMEY AND LEON WISH

The usual methods for the purification of radioberyllium require the addition of a beryllium carrier. Therefore, the common chemical methods of separation are not applicable to the isolation of trace quantities of carrier-free radioberyllium.

Beryllium ion forms a basic acetate[2,3,4,5] and chelates with a number of reagents such as the β-diketones.

Acetylacetone has been employed for the separation and purification of radioberyllium.[6] The resulting chelate is so volatile that the radioactivity of a sample may be lost completely when a benzene solution is evaporated prior to counting if a great deal of care is not taken.[6] Once the benzene has been removed the sample will show detectable losses in activity if it is allowed to stand for fifteen to thirty minutes in the open at room temperature. This high degree of volatility was not anticipated from the characteristics of macroquantities of beryllium acetylacetonate described by Arch and Young.[7]

Thenoyltrifluoroacetone (commonly referred to as TTA), a substituted β-diketone, was prepared by Reid and Calvin.[8] It has been investigated as a complexing agent for the separation and purification of various metallic ions such as aluminum, beryllium, cobalt, copper, iron, zinc, yttrium, zirconium and hafnium, etc.[9–13,16] The advantages of this reagent over acetylacetone are that it easily complexes some metallic ions; that it is particularly stable at the low pH ranges; that it is relatively insoluble in neutral and acid aqueous solutions; and that the chelates it forms are not volatile under ordinary conditions although they may be easily sublimed under a high vacuum.

(1) Operated by Carbide and Carbon Chemicals Corporation under Contract No. W-7405-Eng-26 for the Atomic Energy Commission.

(2) H. S. Booth and G. G. Torrey, *J. Phys. Chem.*, **35**, 2465 (1931).

(3) I. S. Bubes, Manhattan Project Report, CC-1663 (1944).

(4) F. Haber and G. van Oordt, *Z. anorg. Chem.*, **40**, 465 (1904).

(5) S. F. Tompkins, G. W. Grossman and L. J. Tolmach, Manhattan Project Report, CC-3524 (1946).

(6) R. A. Bolomey and A. Broido, Atomic Energy Commission Report, ORNL-196 (1948).

(7) W. C. Fernelius, Editor, "Inorganic Syntheses," Vol. II, McGraw–Hill Book Co., Inc., New York, N. Y., 1946.

(8) J. C. Reid and M. Calvin, Atomic Energy Commission Report MDDC-1405 (1947).

(9) M. Calvin and E. L. Zebroski, Atomic Energy Commission Report BC-42 (1947).

(10) W. M. Latimer, Atomic Energy Commission Report BC-46 (1947); *ibid.*, BC-61 (1947).

(11) H. A. Levy and A. Broido, *ibid.*, CNL-37 (1948).

(12) E. H. Huffman and L. J. Beaufait, THIS JOURNAL, **71**, 3179 (1949).

(13) E. L. Zebroski, Atomic Energy Commission Report BC-63 (1947).

Experimental

Preparation of Reagents.—Radioberyllium was prepared by bombarding a lithium target (mounted on brass) with deuterons for a few hundred microampere hours in the Berkeley cyclotron. The reaction is: $_3Li^7(d,2n)_4Be^7$. The lithium target existed mainly as the carbonate at the time of separation. It was purified by means of acetylacetone.[8] Spectrographic analysis of the sample indicated that silver, chromium, lithium, sodium, nickel, lead and silicon were removed beyond detection and that the impurities in the final product were calcium, iron and magnesium. These are the usual contaminants present in the reagents. The sample, when mounted on thin polystyrene films, showed 0.48-Mev. γ emission only as determined by lead and aluminum absorption curves.

Radioactive isotopes of the other metals were obtained from the Operations Division of the Oak Ridge National Laboratory. In all cases, except where specified, the salt concentrations were kept to a minimum.

The distribution of the metal between the TTA complex and ionic states was expressed in terms of the ratio of the radioactivities in the benzene phase to those in an equal volume of the aqueous phase after evaporating suitable aliquots in porcelain dishes. This gave an evaluation of the expression $(MT_n)/(M^{n+})$ in the equilibrium equation[11,14,15]

$$K_{eq} = \frac{(MT_n)_B (H^+)_A^n}{(M^{n+})_A (HT)_B^n}$$

The aluminum, copper and ferric complexes were quantitated in the benzene phase by spectrophotometric analysis at 350, 344 and 470 mμ, respectively, with a Beckman spectrophotometer.

Attempts to determine the equilibrium constant for the formation of the beryllium chelate lead to certain difficulties. For example, the average of four determinations in the pH range of 3.3 to 5.3 based on the forward reaction after twenty hours shaking was $6.3 \times 10^{-4} \pm 0.9 \times 10^{-4}$ ($\pm 14.3\%$). Similar values were obtained after only four hours shaking suggesting that equilibrium conditions had been reached. Repeating the determination of K_{eq} based on the reversed reaction after eight days of continuous shaking at a pH range of 1.1 to 2.5 gave the results shown in Table I. These values are not in agreement with

TABLE I

EQUILIBRIUM CONSTANTS (K_{eq}) FOR $Be(TTA)_2$ BASED ON DATA OBTAINED FOR THE BACKWARD REACTION

HT, moles l.$^{-1}$ × 10^{-2}	pH	Be_B/Be_A	$K_{eq}{}^a$	$K_{eq}{}^b$
1	1.10	2.78	175.1	22.1
1	1.29	4.50	118.4	23.1
1	1.63	2.88	15.9	6.8
1	1.95	5.01	6.3	5.6
1	2.32	6.54	1.5	3.1
1	2.50	7.60	0.8	2.4

^{a} $K_{eq} = ((BeT_2)_B(H^+)_A^2)/((Be^{++})_A(HT)_B^2)$. ^{b} $K_{eq} = ((BeT_2)_B(H^+)_A)/((BeT^+)_A(HT)_B)$ or $((BeT^+)_B(H^+)_A)/((Be^{++})_A(HT)_B)$.

(14) P. C. Tompkins and A. Broido, Atomic Energy Commission Report, Mon N-311 (1947).

(15) Connick and McVey presented a more inclusive formulation of the equilibrium equation in that they included the hydrolyzed zirconium complexed species. R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

those obtained for the forward reaction. At a pH above 3 the $(M^{n+})_A$ values obtained for the back extraction were too small to be relied upon. The calculated K_{eq}^b values reported in Table I are based on the assumption that a single hydrogen ion and a single TTA molecule are involved in the backward reaction.

Aluminum seems to behave similarly to beryllium. An apparent K_{eq} value, based on the forward reaction after twenty hours shaking at a pH range of 3.0 to 3.6 of $5.9 \times 10^{-6} \pm 1.1 \times 10^{-6}$ (or $\pm 18.6\%$) was obtained. Errors of this order of magnitude are to be expected on the basis of small errors in pH measurements. Equilibrium values for the complexes of other metallic elements are given in Table II.

TABLE II

K_{eq} FOR VARIOUS METAL TTA COMPLEXES

Complex	K_{eq}	Reference
Be(TTA)$_2$	6.3×10^{-4a}	16
Al(TTA)$_3$	5.9×10^{-6a}	16
Fe(TTA)$_3$	$>>1$	17
Sr(TTA)$_2$	9×10^{-15}	18
	7.5×10^{-15}	16
Y(TTA)$_3$	$\sim 1 \times 10^{-7}$	11
Ca(TTA)$_2$	1×10^{-12}	17
Cu(TTA)$_2$	4.8×10^{-20}	16

^{a} K_{eq} in these instances were determined on the basis of the forward reaction only.

At pH values above 6 the extraction of beryllium is quite rapid (Fig. 1). At a pH of about 4 the extraction is quite slow (Fig. 1). The optimum pH for the extraction
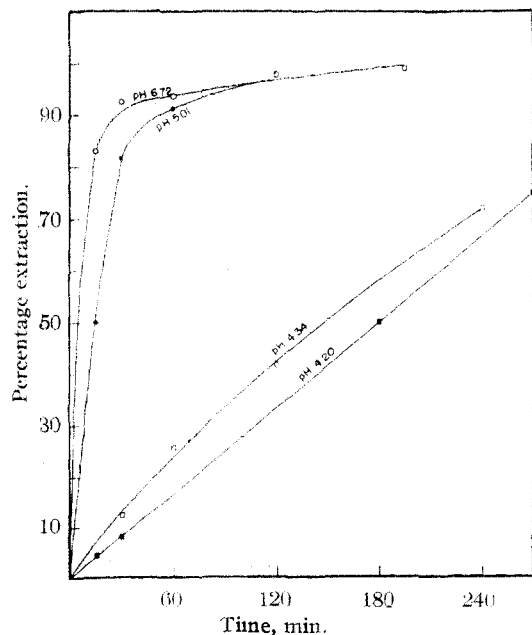

Fig. 1.—Rate of extraction of Be by 0.01 M TTA in benzene at different pH values.

of beryllium into a benzene phase of TTA seems to be about 7. Ferric ion extracts at a slow rate at pH 6.4 and more rapidly at pH 4.5 (Fig. 2). The optimum pH for the extraction of iron appears to be around 2 to 3. Alu-

(16) R. A. Bolomey and L. Wish, Atomic Energy Commission Report, ORNL–136 (1948).

(17) J. C. Reid, ibid., CN-3343 (1945).

(18) A. Broido and P. C. Tompkins, ibid., MonN-432 (1947).

minum extracts rapidly at pH 5.5 and slowly at pH 3.4 while copper extracts rapidly at the latter pH (Fig. 2).
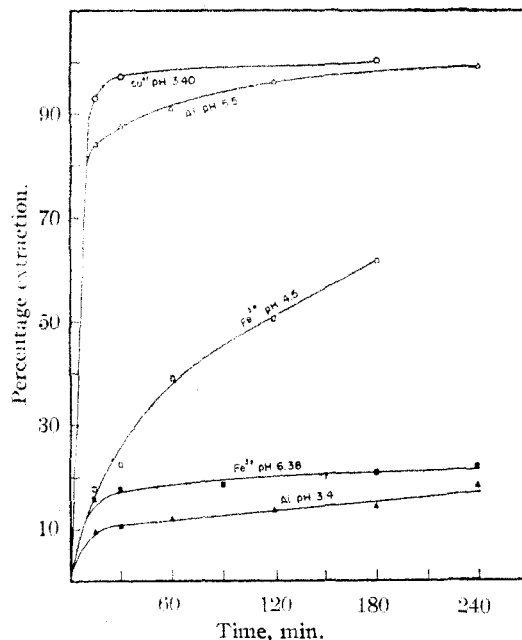

Fig. 2.—Rate of extraction of various metallic ions by 0.01 M TTA in benzene at different pH values.

Figure 3 demonstrates the rate of back extraction of various metallic ions with concentrated hydrochloric acid from a benzene solution made 0.01 M with respect to TTA. Iron, copper, strontium, yttrium, calcium and zinc were "completely" back extracted within fifteen minutes. Aluminum required six hours and beryllium at least eighty hours for "complete" back extraction. In six hours of shaking about 40% of the beryllium is extracted into the hydrochloric acid phase. It should be possible to re-
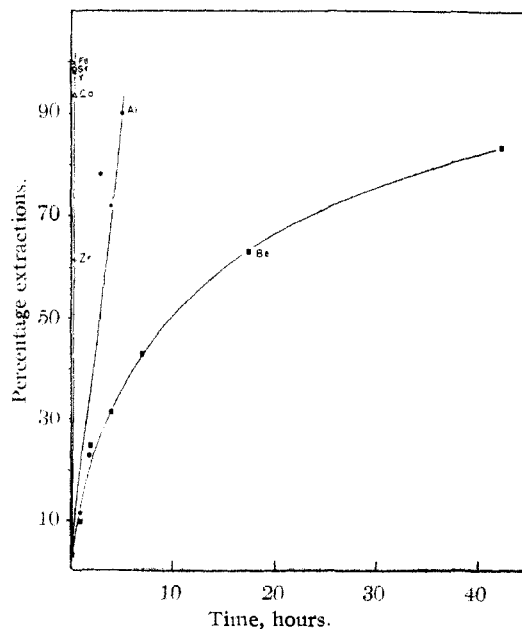

Fig. 3.—Back extractions of several metallic ions with concd. hydrochloric acid.

cover the beryllium from the aluminum–beryllium fraction obtained after six hours extraction with concentrated hydrochloric acid by recycling this fraction a few times through the process after removing the acid by evaporation to dryness.

The Separation and Purification of Radioberyllium.— The particular target employed for purification by means of TTA was delivered to our laboratory about two hundred days after irradiation. Therefore, all short-lived radioactive impurities had decayed before the target was processed. Also, the target material existed mainly as the carbonate and required more hydrochloric acid for solution than did other targets. Most of the greasy film covering the lithium face was hard and gummy.

The method employed to dissolve a target was varied slightly with each target depending on the condition of the targets at the time of processing. All operations were conducted in a well ventilated hood. The target was placed face up in a crystallizing dish which was tipped slightly for drainage. A bell jar having a half-inch opening at the top was placed over the crystallizing dish to minimize contamination of the hood with possible spray and to protect the operator from radiations. All solutions were added or removed from the evaporating dish by means of pipets equipped with syringes. The pipets were held by means of tongs. The target was flooded with benzene to dissolve the thick coating of grease which covered the lithium face. The benzene was stirred by actuating the syringe fitted to the 25-ml. pipet employed for this purpose. The target was then rinsed with two more portions of fresh benzene. The benzene was removed from the crystallizing dish and about 5 to 10 ml. of water was added dropwise to the lithium surface of the target. This wash water was recycled over the surface of the target through a pipet fitted with a syringe. Fresh targets apparently contained enough free lithium to produce a violent reaction with the water while no visible gas evolution resulted with targets that had "cooled" for some time. Once the evolution of gas ceased about 5 to 10 ml. of concentrated hydrochloric acid was added dropwise to the surface of the target and the combined water and hydrochloric acid washings were recycled over the surface of the target until all of the material supported on the brass mount was removed. Frequently the greasy film was polymerized to a bakelite-like substance and could not be entirely removed with benzene. In such cases this substance was chipped off with the end of the pipet used to add the water or hydrochloric acid. At times it was necessary to employ the sharp edge of a freshly broken glass rod to help to loosen this substance. It is best to work as fast as possible so as to minimize the amount of brass that goes into solution in the presence of the acid.

The solution was filtered and evaporated to dryness. The residue was taken up in 40 ml. of water and the pH was adjusted to 6.0 and shaken for two hours with 75 ml. of 0.1 M TTA in benzene. During this time the pH of the aqueous phase dropped to a value of about 3 and the aqueous layer became milky in appearance due to the high salt (lithium) content. The benzene phase became dark green due to the extraction of copper.

The layers were separated and the benzene phase was extracted for a few minutes with concentrated hydrochloric acid (first acid wash). The color of the benzene layer turned red (iron TTA), then yellow as the copper and iron were back extracted into the acid phase. The benzene layer and 25 ml. of a fresh 0.1 M TTA solution were recombined with the pre-extracted target solution. The pH was readjusted to 6 and the mixture was shaken for three hours. At this time very little activity remained in the aqueous layer which contained lithium and other non-extractable ions. The benzene phase was washed once with 50 ml. of concentrated hydrochloric acid for two minutes (second acid wash), then twice with water. The benzene extract was shaken with an equal volume of concentrated hydrochloric acid for seventy-two hours. The acid layer (third acid wash) was separated and evaporated to dryness on a hot-plate. The residue (about 25 mg.) was light orange in color due to a trace of iron. It was

dissolved in 25 ml. of water and shaken with two portions of equal volume of 0.01 M TTA in benzene at pH 2.5 for two hours each. This treatment extracted the iron and about 0.1 to 1.0% of the beryllium activity.

Spectrographic analysis on the original solution and on the three acid washes (Table III) showed that silver, lithium, sodium, lead, silicon and zinc were removed beyond detection. A quantitative spectrographic analysis for copper on the second and third acid washes indicated, respectively, 8,500 and 4.3 p.p.m. of copper after correcting for the volume of the solution. The concentrations of calcium and magnesium were raised considerably in the second and third acid washes as a result of contamination from the reagents. From the spectrographic results there appeared to be no great reduction in the iron content of the solutions in direct contrast with the color changes of the TTA–benzene phase which showed a marked degree of separation of this metal. Iron, like calcium and magnesium, is a common contaminant encountered in the reagents. The presence of these impurities is exaggerated as the solutions were more concentrated than the original solution as indicated by the volume (Table III).

TABLE III

SPECTROGRAPHIC ANALYSIS OF THE TARGET SOLUTION BEFORE AND AFTER PURIFICATION

Element	Target soln., 75 ml. c	First acid wash, 50 ml. c	Second acid wash,b 30 ml. c	Third acid wash,b 10 ml. c
Ag	VW^d	T	—	—
Al	T	VFT	VFT	VW
As	—	•—	—	—
Au	—	—	—	—
B	—	—	—	—
Ba	—	—	—	—
Be	—	—	⋮	—
Bi	—	—	←—	—
Ca^a	VW	T	VS	VS
Cd	—	—	—	—
Co	—	—	—	—
Cr	—	—	—	—
Cu	VS	VS	S	VFT
Fe^a	FT	FT	FT+	T—
Hg	—	—	—	—
K	—	—	—	—
Li	VS	VW	FT	—
Mg^a	VW	T	M	M—
Mn	VFT	—	FT	T—
Mo	—	—	—	—
Na	VFT	VFT	—	—
Ni	—	—	—	—
Pb	T—	—	—	—
Rb	—	—	—	—
Sb	—	—	—	—
Si	FT	—	—	—
Sn	—	—	—	—
Sr	—	—	—	—
Ta	—	—	—	—
Te	—	—	—	—
Ti	—	—	—	—
V	—	—	—	—
W	—	—	—	—
Zn	—	FT—	T	—

^{a} Present in the reagents. ^{b} Total solids 25 mg. or less. ^{c} Total volume of solution. ^{d} Not found but sought for, F = faint, M = moderate, S = strong, T = trace, V = very, W = weak.

The identity of radioactive elements was established by chemical separation procedures based on Noyes and Swift's methods.[19] Five mg. of each element was added as carrier and each fraction tested for radioactivity. The only radioelements found in the first two acid washes were zinc and cobalt. These were finally isolated as the zinc basic carbonate and the potassium cobaltinitrite. The aluminum and lead absorption curves of the radiozinc sample indicated the presence of a 0.4-Mev. β particle and two γ rays of 0.45 and 1.3 Mev. The correspondingly accepted values for Zn^{65} are 0.4, 0.45 and 1.14.[20,21] The aluminum and lead absorption curves of the radiocobalt samples indicated the presence of a 1.6-Mev. β particle, a 3.2-Mev. γ ray and a softer γ component. Co^{56} is characterized by a 1.5-Mev. β particle and by two γ rays of 0.84 and 3.25 Mev.[20,21] No other radioisotopes were found in these samples. The third acid wash containing the beryllium activity emitted a 0.48-Mev. γ ray. No other radioisotope could be detected in this sample.

Summary

1. Equilibrium and rate studies for the forma-

tion and dissociation of the thenoyltrifluoroacetone complexes (dissolved in benzene) of aluminum, beryllium, calcium, copper, iron, strontium and yttrium have been reported. Equilibrium studies on the beryllium chelate based on the reversed reaction gave results that did not agree with those obtained on the forward reaction.

2. Carrier-free radioberyllium has been successfully separated from most of the other elements studied with TTA dissolved in benzene by adjusting the pH of the extracting medium and by taking advantage of the wide differences in rates of extraction. Co^{56} and Zn^{65}, the only other radioisotopes found in a 200-day-old lithium target bombarded with deuterons in a cyclotron, were successfully separated from the Be^7. The spectrographic contaminants found were calcium, magnesium, iron, aluminum, copper and manganese. Calcium, magnesium and iron were found in the reagents employed for the separation. With especially purified reagents these elements with the exception of aluminum should not be present.

(19) A. A. Noyes and E. H. Swift, "A Course of Instruction in the Qualitative Analysis of Inorganic Substances," The Macmillan Co., New York, N. Y., 1945.

(20) U. S. Atomic Energy Commission, Radioisotopes—Catalogue and Price List No. 21 (47).

(21) Segré, Chart of Nuclear Properties, Instrument Development Laboratories, Chicago, Illinois. 1947.

Spectrophotometric Studies of Beryllium Thenoyltrifluoroacetone

BY LEON WISH AND RENÉ A. BOLOMEY

Previous work[2] performed at Oak Ridge National Laboratory indicated that removing excess thenoyltrifluoroacetone (TTA) from a benzene solution of beryllium thenoyltrifluoroacetone [Be(TTA)$_2$] should accelerate the extraction of beryllium ion by means of concentrated hydrochloric acid and that it should be possible to attain this end by washing the benzene phase with alkali or by subliming off the excess TTA at controlled temperatures and pressures. Treatment of a benzene phase of Be(TTA)$_2$ containing an excess of chelating reagent with sodium hydroxide gave erratic results in the rate of extraction of beryllium with concentrated hydrochloric acid.

In an attempt to obtain a better understanding of the phenomena involved, the removal of excess TTA from a benzene solution of Be(TTA)$_2$ was followed spectrophotometrically. These studies revealed that the absorption curve of the resulting beryllium chelate was changed from one characteristic of the beryllium chelate to one characteristic for the aluminum chelate, yet our sample contained no aluminum.

This observation was not expected on the basis

of Zebroski's work.[3] This author reported that the chelates of the highly electropositve ions such as beryllium, aluminum, lanthanum, praseodymium, zirconium and thorium have absorption spectra that are very similar to that of the TTA enol and that the shift in λ maximum due to complex formation is about the same for all of these metals. On the longer wave length side of the maximum, these chelates are characterized by a very slight shoulder which resolves itself, according to Zebroski, into a band only in the case of the aluminum chelate. This investigator presents no data showing the resolution of this shoulder into a band in the case of the beryllium chelate.

Experimental

Beryllium thenoyltrifluoroacetone was prepared according to Fernelius[4] by adding an ethanol solution of the substituted β-diketone to a slightly acid solution of beryllium chloride. The chelate was recrystallized several times from petroleum ether before use. The absorption curves for TTA and for the chelate were found to be in good agreement with those presented by Zebroski.[3]

A spectrographic analysis of the starting beryllium chloride revealed faint traces of calcium and magnesium. The aluminum content of the sample was less than 1 p. p. m. and could not account for the findings presented below.

(3) E. L. Zebroski, Atomic Energy Commission Report BC-63 (1947).

(4) W. C. Fernelius, Ed., "Inorganic Syntheses," Vol. II. McGraw-Hill Book Co., Inc., New York, N. Y., 1946.