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.

Removal of Excess TTA with Alkali.—Preliminary experiments showed that excess TTA may be removed from a benzene phase with alkali. The reactions for the process are of two main types: (1) simple extraction of the enolate ion into the aqueous phase and (2) hydrolysis of the β-diketone to lower components such as trifluoroacetic acid and 2-acetylthiophene. A Be(TTA)₂ sample containing radioactive beryllium isolated as described earlier[5] was dissolved in benzene to which was added an excess of the β-diketone. Shaking this solution with 0.1 N sodium hydroxide revealed that the optical density of the benzene layer at 325 mμ decreased rapidly while the beryllium activity remained in the organic phase. Prolonged shaking of these phases finally resulted in beryllium extraction into the aqueous phase. In order to be in a better position to follow the reaction, aliquots of the original Be(TTA)₂ solution were successively shaken for fifteen minutes at room temperature with 0.01, 0.1 and 1.0 M sodium hydroxide. The absorption curves of the benzene solution were determined after each successive treatment. An analysis of the resulting curves (Fig. 1) reveals that the excess reagent has been removed within fifteen minutes with the weaker alkaline solution. The simultaneous appearance of a band absorbing maximally below 300 mμ indicates that a considerable amount of degradation has taken place. Accompanying the disappearance of the 325 mμ band a second maximum appears at about 365 mμ. Successive alkali washings decrease the optical density of the 350 and 365 mμ bands at the same rate.
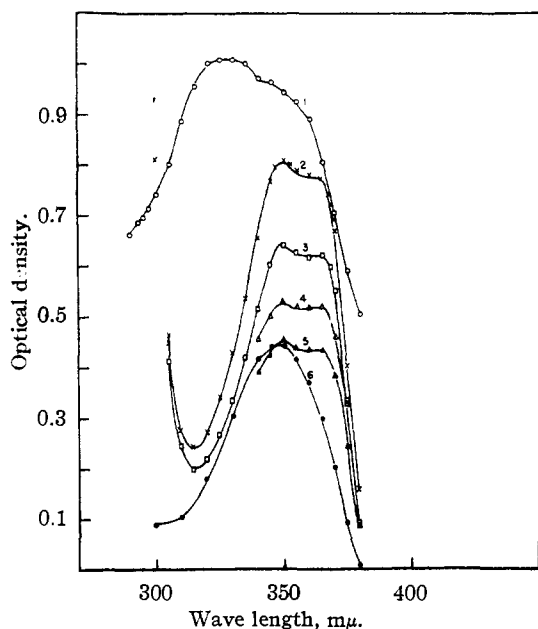

Fig. 1.—Effect of alkali treatment on the absorption curve of Be(TTA)₂ in the presence of excess TTA: 1, Be(TTA)₂ plus excess TTA; 2, Sample 1 washed with 0.01 N sodium hydroxide; 3, Sample 1 washed with 0.1 N sodium hydroxide; 4, Sample 1 washed with 1.0 N sodium hydroxide; 5, Sample 5 washed with 1.0 N sodium hydroxide; 6, Be(TTA)₂ alone.

A similar experiment was performed on Be(TTA)₂ containing no excess reagent with similar results. In this case the optical density of 350 mμ decreased considerably and the shoulder resolved itself into a distinct maximum after shaking with 0.1 N sodium hydroxide.

Removal of Excess TTA by Sublimation.—Zebroski[3] sublimed excess TTA from metal TTA chelates at 60° and

10⁻⁵ mm. after recrystallizing the metal chelates several times from dry benzene or benzene–heptane solutions. In our experiment TTA was dissolved in benzene and sublimed at 60 to 80° and 12 to 18 mm. for varying lengths of time. The residues after subliming off the excess TTA were dissolved in hot benzene, cooled and made to volume. The results[6] showed that the excess TTA could be sublimed quantitatively from the beryllium chelate and that no loss of the chelate could be detected by this treatment in thirty-five minutes.

Absorption spectra of the chelate obtained after heating a mixture of the chelate and excess TTA are quite similar to those obtained by the alkali treatment mentioned above. A typical curve obtained on a heat sublimed sample is shown in Fig. 2, curve 1. The sample represented by curve 2, Fig. 2 was sublimed at room temperature and shows the typical beryllium chelate curve of Zebroski. For comparison the absorption curve of the aluminum chelate (curve 3) is included in this figure.
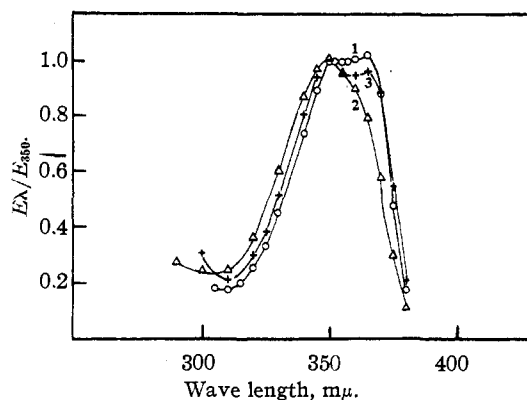

Fig. 2.—Absorption spectra: 1, O, BeTTA heat sublimed; 2, △, BeTTA sublimed at room temperature 3; +, AlTTA.

The average ratio E_{365}/E_{349} for the product resulting from the alkali treatment is 0.97 with a range of 0.96 to 0.98 for 5 samples. The same ratio obtained on the heat sublimed sample is 1.03 with a range of 1.01 to 1.09. This difference is apparently due to lack of contamination in the heat sublimed samples with the substance absorbing maximally below 300 mμ obtained by the alkali wash.

The similarity of these absorption curves to those of the aluminum chelate is striking. As our beryllium sample contained no aluminum or other impurity that could account for the results we are forced to conclude that the beryllium chelate can exist in two forms.

An analysis of the beryllium chelate (containing radioberyllium) purified by sublimation revealed a beryllium content of 1.95%. The lowering of the freezing point of benzene containing the chelate indicated a molecular weight of 455. These results are in agreement with the formula Be(TTA)₂ which has a calculated beryllium content of 1.99% and a calculated molecular weight of 451.

Our samples were sublimed at a higher pressure and temperature than were those of Zebroski. This may be the cause of the resolution of the shoulder into a distinct maximum in the case of our beryllium chelate. Also the presence of an excess of reagent may accelerate the resolution of the shoulder into a distinct maximum.

Attempts to resolve the products obtained by either the alkali or the sublimation experiments into two components of different absorption characteristics by recrystallization from petroleum ether or from benzene were unsuccessful. Nor was it possible to alter the ratio E_{365}/E_{349} by prolonged treatment with either alkali or by sublimation. Such treatments resulted only in a decreased extinction

(5) René A. Bolomey and Leon Wish, This Journal, 72, 4483 (1950).

(6) R. A. Bolomey and L. Wish, Atomic Energy Commission Report ORNL-135 (1949).

value due to a loss of the complex by solution into the aqueous phase or by sublimation, the ratio E_{365}/E_{349} remaining constant within the limits of the measurements.

Attempts to produce similar changes in the absorption spectra of the chelates of zirconium, lanthanum and copper were unsuccessful by either the alkali or the sublimation experiments. It would appear, therefore, that the beryllium chelate may have an absorption spectrum that resembles that of the aluminum complex. The beryllium chelate, however, differs from that of aluminum in that it may also have an absorption spectrum characterized by a single maximum.

At present we do not have enough data to fully characterize the structure of these chelates; however, we feel that the observations presented are of sufficient importance to merit publication. Without this knowledge a beryllium sample may be misnamed aluminum should the in-

vestigator attempt to classify it on the basis of the absorption spectrum of its thenoyltrifluoroacetonate. This point is emphasized by the fact that once our beryllium sample gave directly the double-banded beryllium chelate. It may be that our solutions were not acid enough or that the temperature of the laboratory was too high.

Summary

Beryllium thenoyltrifluoroacetonate can exhibit two different spectra in solution, one of which resembles the TTA enol and absorbs maximally at about 350 mμ. The other resembles the aluminum chelate and absorbs maximally at about 350 mμ and 365 mμ.

Spectrophotometric Methods of Establishing Empirical Formulas of Colored Complexes in Solution[1]

BY AUBREY E. HARVEY, JR.,[2] AND DELMER L. MANNING[2]

Various methods have been applied to the investigation of the empirical formulas of colored complexes in solution.[3-8] This paper presents an experimental comparison of the present methods of formula proof. A new method for determining formulas and a modification of the molar ratio method[8] are proposed. The applicability of these methods to the three complexes of ferric ions and disodium 1,2-dihydroxybenzene-3,5-disulfonate, trade name Tiron, and to the complex of ferric and thiocyanate ions was studied.

New Methods Proposed

Slope Ratio Method.—In the reaction

$$mA + nB \rightleftharpoons A_mB_n$$

if the concentration of B is constant and in sufficient excess to make dissociation negligible, the equilibrium concentration of the complex A_mB_n will be essentially proportional to the analytical concentration of A added in the reaction; so

$$[A_mB_n] = C_A/m \qquad (1)$$

where the brackets refer to equilibrium concentration and C to the analytical or total concentration.

From Beer's law there is the relation

$$E = \epsilon d[A_mB_n] \qquad (2)$$

where E is the measured extinction, ϵ the molecular extinction coefficient and d the thickness of the cell in cm. Substituting the value of $[A_mB_n]$ from (1) into (2)

$$E = \epsilon d C_A/m \qquad (3)$$

E is plotted against different analytical concentrations of A, keeping the concentration of B constant and in excess. Over the straight line portion of the curve, equation (3) is valid and this straight line will have a slope given by

$$Slope_1 = \epsilon d/m \qquad (4)$$

Similarly if A is the component in constant excess and the concentration of B is varied

$$[A_mB_n] = C_B/n \qquad (5)$$

and if E is plotted against C_B, the slope of the straight line portion of the curve will be

$$Slope_2 = \epsilon d/n \qquad (6)$$

The ratio of n to m in the complex may be determined by taking the ratio of the two slopes

$$Slope_1/Slope_2 = n/m \qquad (7)$$

This method, in common with other spectrophotometric methods, serves only to establish the ratio of color forming radicals to the metal ion.

Modification of Molar Ratio Method.—Yoe and Jones[8] found that for a very stable complex a plot of optical density against molar ratio of component B to component A, with A constant, rose from the origin as a straight line and broke sharply to constant density at the molar ratio of the components in the complex.

However, a complex that undergoes appreciable dissociation in solution gave a continuous curve which became approximately parallel to the molar ratio axis only when an excess of the variable component was added. Results obtained by extrapolation of this curve are uncertain. It was found in the present investigation that in some cases such a curve may be made to break sharply at the correct molar ratio, if the ionic strength of the solutions is adjusted by the addition of an unreacting electrolyte. Thus the application of the molar ratio method may be extended by carefully controlling the ionic strength of the solutions.

(1) Abstracted from the Master's Thesis of Delmer L. Manning, University of Louisville.

(2) Chemistry Department, University of Arkansas, Fayetteville, Ark.

(3) Job, Ann. chim., [10] 9, 113 (1928).

(4) Vosburgh and Cooper, THIS JOURNAL, 63, 437 (1941).

(5) Bent and French, ibid., 63, 568 (1941).

(6) Molland, ibid., 62, 541 (1940).

(7) Edmonds and Birnbaum, ibid., 63, 1471 (1941).

(8) Yoe and Jones, Ind. Eng. Chem., Anal. Ed., 16, 111 (1944).