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SPECTROPHOTOMETRIC STUDIES OF BERYLLIUM THENOYL TRIFLUOROACETONE [$Be(TTA)_2$]

RENE A. BOLOMEY

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Report Number: ORNL-135
Health and Biology
This document consists of 21 pages.
Copy 8 of 112 Series A.

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Work done by:

Rene A. Bolomey
Leon Wish
Jo. E. Gardner
Cyrus Feldman
M. Murray

Report written by:

Rene A. Bolomey
Leon Wish

DECLASSIFIED Per Letter Instructions Of TID-1086
MS for N. T. Bray 3-18-55 SUPERVISOR LABORATORY RECORDS ORNL

DATE ISSUED
JAN 12 1949

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ABSTRACT

SPECTROPHOTOMETRIC STUDIES OF BERYLLIUM THENOYL TRIFLUOROACETONE [$Be(TTA)_2$]

by

Rene A. Bolomey and Leon Wish[1]

Beryllium thenoyl trifluoroacetonate appears to exist in two forms of different spectral curves. The A form reported by Zebroski has an absorption band located at 349 mμ. The B form has either a maximum at 365 mμ or two maxima, one located at 349 and one at 365 mμ. The A form may be easily transformed into the B form with either a weak alkali wash or by sublimation at 60 to 80° and 12 to 18 mm. Hg. So far it has not been possible to convert the B form into the A form nor has it been possible to fractionate the double banded spectrum of the B form into two components.

[1]We wish to thank Drs. P. C. Tompkins and Henri Levy and Mr. A. Broido for helpful criticisms.

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SPECTROPHOTOMETRIC STUDIES OF BERYLLIUM THENOYL TRIFLUOROACETONE [$Be(TTA)_2$]

by

Rene A. Bolomey and Leon Wish[1]

In an earlier report (1) it was stated that removing excess thenoyl trifluoroacetone (TTA) from a benzene solution of $Be(TTA)_2$ should accelerate the extraction of Be ion by means of concentrated hydrochloric acid. It should be possible to attain this end by washing the benzene phase with alkali or by subliming off the excess TTA at controlled temperature and pressure. Treatment of a benzene phase of $Be(TTA)_2$ containing an excess of chelating reagent with sodium hydroxide gave erratic results in the subsequent rate of extraction of Be 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 Be chelate was changed from one characteristic of the Be chelate to one characteristic for the Al chelate, yet our sample contained no Al.

This observation was not expected on the basis of Zebroski's work (4). Zebroski reported that the chelates of the highly electropositive ions such as Be, Al, La, Pr, Zr and Th have absorption bands that are very similar to that of the TTA enol and that the shift in λ maximum due

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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 Al chelate. No data showing the resolution of this shoulder into a separate band in the case of the Be chelate was presented. This paper reports the results of additional studies on the phenomenon.

Experimental

Beryllium thenoyl trifluoroacetone was prepared by the method of Fernelius (3) by adding an ethanol solution of TTA 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 (4).

A spectrographic analysis of the starting beryllium chloride (Table I) revealed faint traces of Ca and of Mg. The Al content of the sample was less than 1 ppm. and could not account for the findings presented below.

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-acetyl thiophene (4). A $Be(TTA)_2$ sample containing Be^7 isolated as described earlier (2) was dissolved in benzene to which was added an excess of the β-diketone. Shaking this solution with .1 N sodium hydroxide revealed that the optical density of the benzene layer at 325 mμ decreased rapidly while Be^7 activity remained in the organic phase. Prolonged shaking of these phases finally resulted in Be^7 extraction into the aqueous phase.

[redacted]

Table I

Spectrographic Analysis of the Original Beryllium Sample

Element	Spectrographic Findings
Ag	-
Al	-
As	-
Au	-
B	-
Ba	-
Be	VS
Bi	-
Ca	FT
Cd	-
Co	-
Cr	-
Cu	-
Fe	-
Li	-
Mg	FT
Mn	-
Mo	-
Na	-
Ni	-
Pb	-
Rb	-

[redacted]

(Table I Continued)

Element	Spectrographic Findings
Sb	-
Si	-
Sm	-
Sn	-
Sr	-
Ta	-
Ti	-
V	-
Zn	-

VS = Very strong, FT = Faint trace, - = Sought, not found

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. The simultaneous appearance of a band absorbing maximally below 300 mμ indicates that a considerable amount of degradation has taken place and that this degradation product remains appreciably soluble in benzene kept in contact with either 0.1 N sodium hydroxide (curve 4) or 1 N hydrochloric acid (curve 3) during a shaking period of fifteen minutes. 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.

A similar experiment was performed on $Be(TTA)_2$ containing no excess reagent with similar results (Fig. 2). In this case the optical density at 350 mμ decreased considerably and the shoulder resolved itself into a distinct maximum (curve 2) after shaking with 0.1 N sodium hydroxide. Washing the resulting benzene phase with concentrated hydrochloric acid did not alter the 350 and 365 mμ maxima but resulted in the production of a third maximum located at about 318 mμ (curve 3). The component responsible for this maximum was found to be partially dissolved in the acid phase and could be re-extracted into benzene after adjusting the pH to a value of 6 - 7 (curve 4).

Removal of excess TTA by sublimation. - Zebroski (4) sublimed excess TTA from metal TTA chelates at 60° and 10^{-5} mm. Hg 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

[redacted]

Figure 1

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) alone.

[redacted]

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Drawing # 6523

FIG. I

EFFECT OF ALKALI TREATMENT ON THE ABSORPTION CURVE OF $Be(TTA)_2$ IN THE PRESENCE OF EXCESS TTA

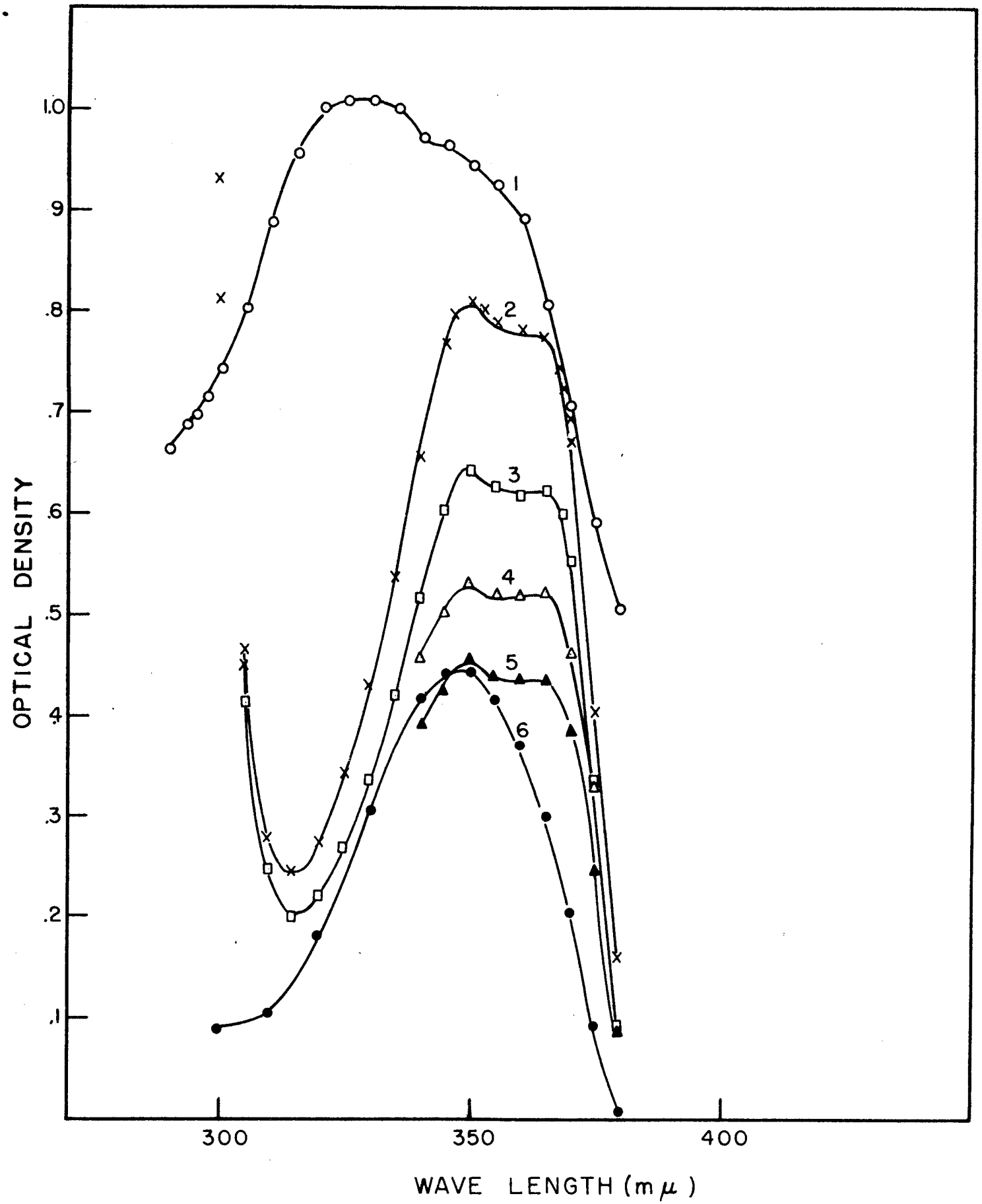


Figure 2

1 - $Be(TTA)_2$

2 - Sample 1 washed with 0.1 N sodium hydroxide.

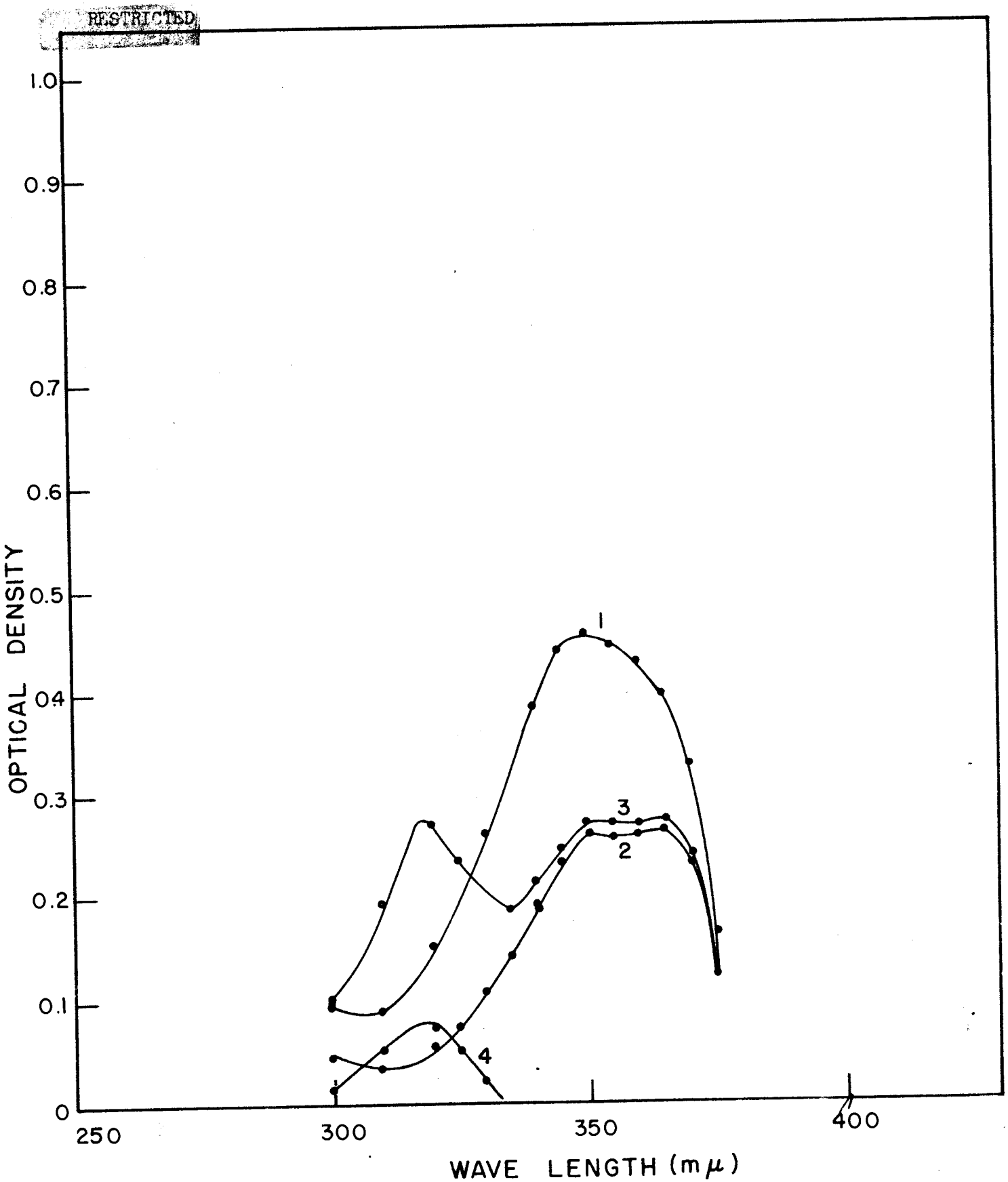
3 - Sample 2 washed with concentrated hydrochloric acid.

4 - Acid phase from sample 3 adjusted to pH 6-7 and extracted with benzene.

FIG. 2

Drawing # 6524

EFFECT OF ALKALI AND OF ACID
ON THE ABSORPTION CURVE OF $Be(TTA)_2$



to 80° and 12 to 18 mm. Hg for varying lengths of time. The samples after sublimation were dissolved in hot benzene, cooled and made to volume. The percentage TTA removed by this treatment was determined from spectrophotometric measurements of 325 mμ on aliquots of the resulting solution. Results obtained on Be-free TTA samples are shown in Table II. The results presented in Table III were obtained on a TTA-free Be chelate and indicate no significant change in the optical density at 349 mμ as a result of sublimation at 80° and 12 mm. Hg in thirty-five minutes. Similar results are shown in Table IV. These indicate that excess TTA is removed from the Be chelate by sublimation with no significant decrease in the optical density at 349 mμ.

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. 3, curve 1. The sample represented by curve 2, Fig. 3 was sublimed at room temperature and shows the typical Be chelate curve of Zebroski.

The average ratio E_{365}/E_{349} for the product resulting from the alkali treatment is about 0.97 with a range of 0.96 to 0.98 for five 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 a 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 Al chelate is striking. As our Be sample contained no Al or other impurity that could account for the results we are forced to conclude that the Be chelate exists in two forms.

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Removal of TTA by Sublimation

Conc. of TTA in benzene x 10^2 M	Temp. °C	Pressure mm. Hg	Time Min.	Density at 325 mμ Initial	Density at 325 mμ Final	Percentage TTA Removed
1.85	70	15	5	224	8.00	97.
1.85	70	17	5	224	1.70	99.2
1.85	70	14	10	224	.057	99.9
1.85	60	15	10	224	2.50	98.4
1.85	80	15	15	224	.100	99.9
1.85	80	14	15	224	.048	99.9
1.85	80	15	10	224	1.09	99.5
1.85	80	14	15	224	.057	99.9
1.85	80	14	20	224	.043	99.9
1.85	70	17	20	224	2.05	99.1
1.85	80	14	25	224	.040	99.9
.185	80	18	5	22.4	.016	99.9
.185	80	16	10	22.4	.008	99.9
.185	80	16	15	22.4	.010	99.9
.185	70	18	15	22.4	.014	99.9

[redacted]

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Table III

Resistance of $Be(TTA)_2$ to Sublimation at 80° and 12 mm. Hg

Conc. of $Be(TTA)_2$ in Benzene x 10^5 M	Time Min.	Optical Density at 349 mμ Initial	Final	Percentage recovery
1.34	15	.565	.558	99
1.34	15	.565	.568	109
1.34	20	.565	.578	102
1.34	20	.565	.580	103
1.34	15	.565	.567	102
1.34	15	.565	.552	98
1.34	15	.565	.565	100
1.34	35	.565	.573	101
1.34	15	.565	.556	99

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Table IV

Recovery of $Be(TTA)_2$ from Excess TTA by Sublimation

Be added	Excess TTA	µg Be found	Percentage recovery
36.65 µg	10.85 µg	38.02	104
"	"	33.65	92
"	"	37.20	101
"	"	34.88	95
"	"	34.42	94
"	"	36.31	99
"	"	35.55	97
3.67	"	3.26	89
"	"	3.58	97

[redacted]

Figure 3

Effect of Temperature on the Absorption Spectrum of $Be(TTA)_2$

Curve 1 sublimed at 80°

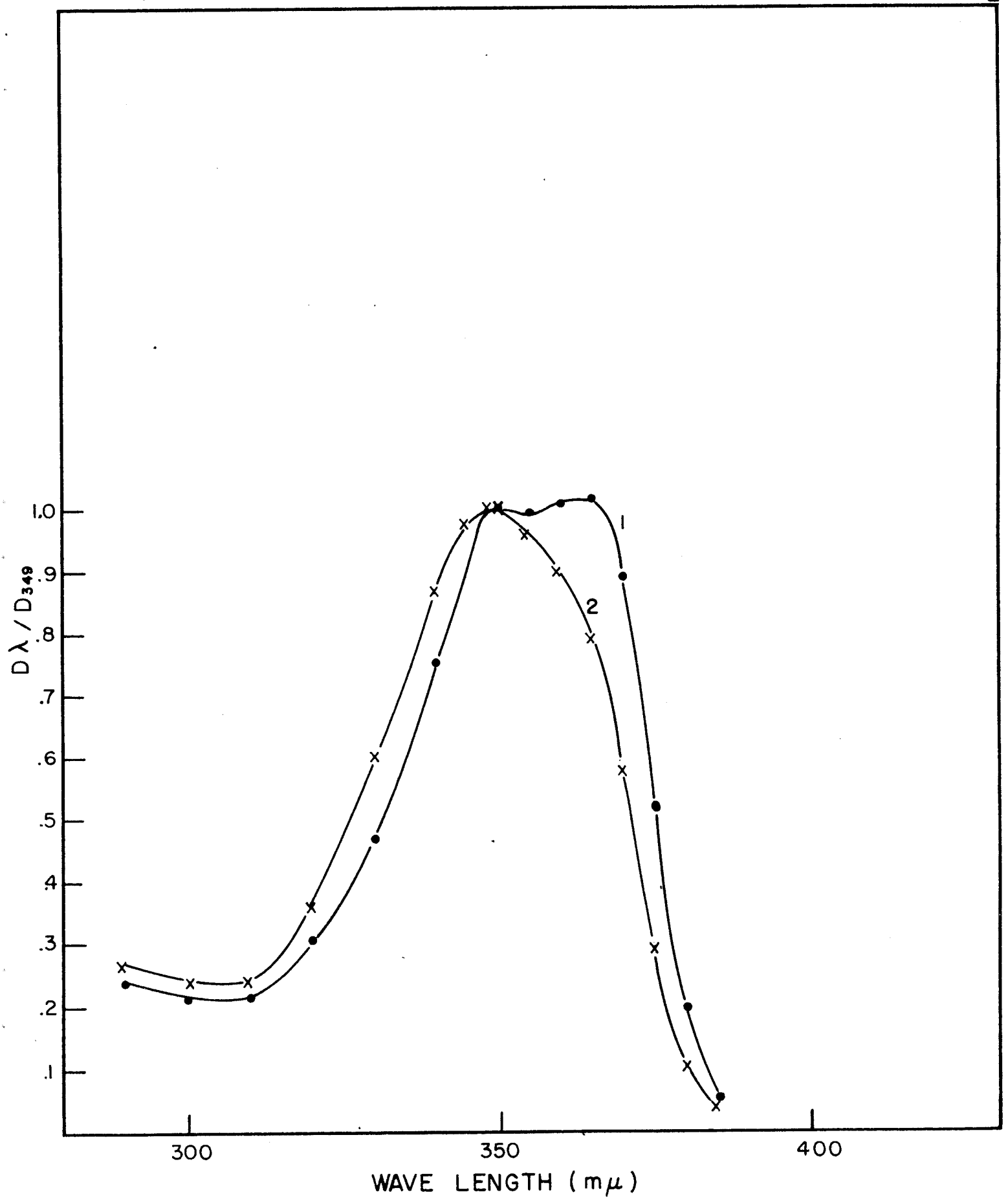
Curve 2 sublimed at room temperature.

[redacted]

FIG. 3

Drawing # 6525

EFFECT OF TEMPERATURE ON THE ABSORPTION SPECTRUM OF BE $(TTA)_2$



An analysis of the Be chelate (containing Be^7) purified by sublimation revealed a Be 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 molecular weight of 451 and a calculated Be content of 1.99%.

Our samples were sublimed at a higher pressure and temperature than were those of Zebroski (4). This may be the cause for the resolution of the shoulder into a distinct maximum in the case of our Be 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 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 Zr, La, and Cu were unsuccessful by either the alkali or the sublimation experiments. It would appear, therefore, that the Be chelate may have an absorption spectrum that resembles that of the Al complex. The Be chelate, however, differs from that of Al in that it may also have an absorption spectrum characterized by a single maximum. This would suggest that chelates of Be and of Al may exist in two forms; the A form characterized by a single absorption band located at about 350 mμ, and the B form characterized either by a single absorption band located at 365 mμ or by two bands located at about 350 and 365 mμ. In the case of

the Al chelate, the A form would be very unstable or would exist in a rapid state of equilibrium with the B form with an extinction ratio in the two maxima of 1. With Be, however, the A form would be fairly stable under ordinary circumstances so that either alkali or heat would be required to catalyze its transformation into the B form or into an equilibrium mixture with an extinction ratio in the two maxima of 1.

At present we do not have enough data to characterize fully the structure of these chelates; however, we feel that the observations presented are of sufficient importance to merit publication. Without this knowledge a Be sample may be misnamed Al should the investigator attempt to classify it on the basis of the absorption spectrum of its thenoyl trifluoroacetonate. This point is emphasized by the fact that once our Be sample gave directly the double banded Be chelate with no apparent A form stage. It may be that our TTA solution was slightly alkaline or that the temperature of the laboratory was high enough to catalyze the transformation of the A to the B form.

Summary

Beryllium thenoyl trifluoroacetonate appears to exist in two forms of different spectral curves. The A form reported by Zebroski has an absorption band located at 349 mμ; the B form has either a maximum at 365 mμ or two maxima, one located at 349 and one at 365 mμ. The A form may be easily transformed into the B form with either a weak alkali wash or by sublimation at 60 to 80° and 12 to 18 mm. Hg. So far it has not been possible to convert the B form into the A form nor has it been possible to fractionate the double banded spectrum of the B form into two components.

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