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219. Koji Yamakawa, Keiichi Tanikawa, and Kiichi Arakawa : Organometallic Compounds. II.[*1] Gas Chromatography of Metal Acetylacetonates.

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Quasi-aromatic behavior of β-dicarbonyl-metal chelates has very recently been investigated through physical and chemical confirmations.[1] Larger number of volatile β-diketone-metal chelates has attracted the attention by having an organic character. They are soluble in most common organic solvents and insoluble in water, and some of them can be sublimed, boiled, and melted without decomposition.

Application of gas chromatography has recently been developed not only for the analysis of solid organic compounds, such as steroids, alkaloids, etc.,[2~4] but also for metal analysis by the use of volatile inorganic salts.[5~7] High-temperature technique[8] has been developed now, but there are not much informations about these fields.

Recent communications have reported gas chromatographic separation of some metal acetylacetonates. Duswalt[9] prepared and tested the acetylacetonates of aluminum, beryllium, cadmium, mercury, scandium, and zinc in which peaks are obtained for beryllium, scandium, and zinc on Silicone oil and propyleneglycol-adipate polymer supported by Celite at 225°. Biermann and Gesser[10] succeeded in separating both acetylacetonates of beryllium and aluminum, and also of aluminum and chromium by Apiezon-L on glass beads. Sievers, *et al.*[11] also separated some metal acetylacetonates by 0.5% Silicone grease on glass microbeads, but did not publish their detailed result yet.

In order to obtain the correlation between the character of acetylacetonates and the retention volume, and to subsequently utilize these results for analysis of metal chelates, the following experiments were carried out. The combination of solvent extration[12] and chelate formation should make this method of analysis very useful.

Experimental

Sample——The samples used in these studies were acetylacetonates of twelve kinds of bicoordinate (Ba, Be, Ca, Cd, Co, Cu, Mg, Mn, Ni, MoO_2, VO, and Zn), six kinds of tricoordinate (Al, Co, Cr, Fe,

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Mn, and Ti), and two kinds of tetracoordinate (Th and Zr) metals, which are shown in Table I. Acetylacetonates of Al, Be, Co (II), Co (III), Cr, Fe, Ni, VO and Zn were prepared in this laboratory, and the other chelates were Dotite reagents.

Table I. Retention Volume of Metal Acetylacetonates

Chelate	Ref.	m.p. (°C)	Column Temp. (°C)	Retention Volume (ml.)
$\mathrm{MoO_2(acac)_2}$[a]	d)	—	100	60
$\mathrm{Mg(acac)_2}$	d)	—	100	80
$\mathrm{Cd(acac)_2}$	d)	—	100	90
$\mathrm{Zr(acac)_4}$	d)	—	100	170
$\mathrm{Be(acac)_2}$	e)	108.5	150	110
$\mathrm{Mn(acac)_2}$	d)	—	150	110
$\mathrm{Zn(acac)_2}$	d)	—	150	215
$\mathrm{Co(acac)_2}$	d)	214	150	275
$\mathrm{Al(acac)_3}$	f)	195	150	415
$\mathrm{Fe(acac)_3}$	d)	182	172	208[c]
$\mathrm{Ba(acac)_2}$	d)	—	180	182
$\mathrm{Ca(acac)_2}$	d)	—	180	182
$\mathrm{Cu(acac)_2}$	g)	230	180	187
〃		230	180	429[b]
$\mathrm{VO(acac)_2}$	f)	—	180	192.5
〃		—	180	467.5[b]
$\mathrm{Cr(acac)_3}$	i)	216	180	192.5
〃		216	180	484[b]
$\mathrm{Th(acac)_4}$	d)	—	190	175.5
$\mathrm{Ti(acac)_3}$	d)	—	190	487.5
$\mathrm{Ni(acac)_2}$	d)	—	—	—
$\mathrm{Co(acac)_3}$	j)	214	—	—

a) (acac): acetylacetonate. Condition: 0.5% SE-30 on glass microbeads, 60∼80 mesh, unless otherwise noted, and He was used as carrier gas.
b) 0.5% SE-52 (General Electric Co., Phenylsilicone polymer) on glass microbeads 60∼80 mesh.
c) 0.5% SE-30+QF-1-0065 (Anal. Eng. Lab. Inc., Fluorosilicone) (6:4) on glass microbeads, 60∼80 mesh.
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j) B.E. Bryant, W.C. Fernelius: *Ibid.*, **5**, 188 (1957).

Apparatus and Method——A Shimadzu Gas Chromatograph Model GC-1B (dual column) equipped with thermal conductivity cell detector was used in this study. It was run on the range of 2.0 mV. and filament current of 220 mA. A stainless-steel column of 140 cm. (70 cm. U-shape × 2) × 4 mm. i.d. was packed with 0.5% silicon polymers on glass microbeads as shown in Table I.

Glass microbeads*3 were treated with acid and washed with distilled H_2O. After drying and siliconization with dimethyldichlorosilane in toluene solution, the solvent was evaporated. Silicon polymers were dissolved in toluene and added to the siliconized glass microbeads, the solvent was evaporated, and dried under a reduced pressure.

Column temperature was kept at 100∼200° as shown in Table I. Sample-heater temperature was kept at 25° and detector temperature at 40° higher than the column temperature. Carrier gas was He, having a flow-rate of 40∼60 ml./min.

Typical samples were 2∼3 μl. of 2∼4% solution of a metal chelate in $CHCl_3$, except $\mathrm{Be(acac)_2}$ which was 2 μl. of a 0.2% solution in $CHCl_3$.

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*3 Shibata Chemicals, 60∼80 mesh.

Results and Discussion

Although Duswalt,[9] and Biermann and Gesser[10] had limited success with chelate of acetylacetonates by silicon polymer on Celite or Apiezon-L on glass beads, its chelates of Be(II), Al(III), and Cr(III) were separated successfully although most of the metal acetylacetonates was decomposed. We reinvestigated the use of column of 0.5% Apiezon-L on glass microbeads but did not obtain satisfactory results, and felt this column was not suitable.

In the case of a column using 0.5% Apiezon-L on Shimalite-Q,[*4] acetylacetonates of Cu(II), Co(III), Ni(II), and Al(III) gave almost the same retention time (0.8, 1.0, 1.2, and 1.3 min., respectively).[*5]

Examination of optimum conditions for the determination of various metal acetylacetonates was made by using a column of 0.5% silicon polymer on glass microbeads,[*6] and results obtained are summarized in Table I.

Acetylacetonates of Be(II), Al(III), Cr(III), and VO(IV) easily gave a sharp peak, and their chromatograms were not influenced by varying temperatures of column and flow-rate of carrier gas. On the other hand, it was difficult to select conditions to obtain a stable chromatogram from acetylacetonates of Co(III), Mg(II), and Mn(II). This fact might be influenced by varying tempertures of column and flow-rate of carrier gas.

An attempt to obtain a stable chromatogram of acetylacetonate of Fe(III) by the use of 0.5% SE-30 on glass microbeads was unsuccessful. However, a peak was obtained by the use of a column with a mixture of 0.5% SE-30 and QF-1 (6:4) on glass microbeads.

Acetylacetonates of Ba(II), Ca(II), Cd(II), MoO$_2$(VI), Ti(III), Th(IV), Zn(II), and Zr(IV) were slightly soluble in organic solvents, and respectively gave a broad peak by the use of Silicone grease on glass microbeads. The cause might be their less solubility, but a good result could not be obtained by the use of larger amount of the sample, due to tailing by solvents. Better results were obtained by using crystals directly than by using its solution in CHCl$_3$.

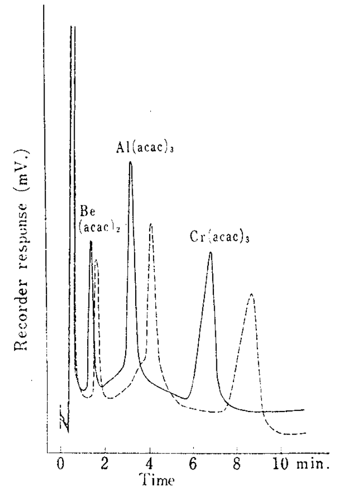

Fig. 1. Separation of a Mixture of Be (acac)$_2$, Al (acac)$_3$, and Cr (acac)$_3$ in CHCl$_3$

Broken line by using a column of 0.5% SE-30 on glass beads.
Retention time : 1.65, 4.11 and 8.70.
Solid line by using a column of 0.5% SE-30+ QF-1 (6:4) on glass beads.
Retention time : 1.28, 3.16 and 6.78.
Condition : column p. 177°, sample heater temp. 200°, detector temp. 230°, carrier gas He 40 ml./min.

[*4] Apiezon-L : Shell Co., polyhydrocarbon. Shimalite-Q : Shimadzu Seisakusyo, quartz, 100~120 mesh.

[*5] Condition : Column temp. 150°, column 2.8 m. × 6 mm., carrier gas He 50 ml./min.

[*6] Other column were also examined but satisfactory results could not be obtained. (a) 0.5% SE-30 (General Electric Co., Methylsilicon polymer) on Diasolid (Nippon Chromato Co.,) Celite, 60~80 mesh. (b) 0.5% Apiezon-L on Diasolid, 60~80 mesh. (c) 0.5% SE-30 on Chromosorb-W. (d) 0.5% SE-30 on Shimalite-Q.

Acetylacetonates of Cr(III), Cu(II), and VO(IV) gave almost the same retention volume (ca. 190 ml.) by the use of 0.5% SE-30 on glass microbeads, although they gave slightly different retention volume (429, 467.5, 484 ml. respectively) by the use of 0.5% SE-52 on glass microbeads.

Acetylacetonates of Co (II), Mn (III), and Ni (II) did not show a peak by the use of silicon polymer on glass microbeads.

From above results, a mixture of acetylacetonates of Be(II), Al(III), and Cr(III) should easily be separated. Attempted separation of a mixture of these metal chelates using a column of 0.5% SE-30 on glass microbeads gave peaks shown in Fig. 1. A more satisfactory result was obtained by the use of a mixture of 0.5% SE-30 and QF-1 on glass microbeads.

This work is now being extended toward the programmed temperature chromatography equipped with an ionization detector.

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Summary

Gas chromatography of twenty kinds of metal acetylacetonates [Al(III), Ba(II), Be(II), Ca(II), Cd(II), Co(II), Co(III), Cr(III), Cu(II), Fe(III), Mg(II), Mn(II), Mn(III), MoO_2(VI), Ni(II), Th(IV), Ti(III), VO(IV), Zn(II), and Zr(IV)] was investigated, using various liquid-phase column. Analysis of the metal chelates was effected by the use of a column of 0.5% silicon polymers (SE-30, SE-52, and QF-1) on glass microbeads.

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〔Added in Proof〕 Recently, we received a detailed paper [R. E. Sievers, B. W. Ponder, M. L. Morris, R. W. Moshier : Inorg. Chem., **2**, 693 (1963)] in which they described metal chelates of trifluoroacetylacetone and hexafluoroacetylacetone, which is more volatile and could be eluted at much lower column temperatures than corresponding complexes of acetylacetone.