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# Behavior of β-Diketone Metal Chelates in Gas Chromatography and Effect of Chelate Stability on Detection Sensitivity

A difference in detection sensitivity of β-diketone metal chelates by gas chromatography is produced by the difference in the metal present, irrespective of the difference in ligands or of detectors and the reason for it was examined by gas chromatography–mass spectrometry (GC–MS). When the chelates of copper(II) and iron(III), which show poor sensitivity in gas chromatography, were introduced directly into the ion source of a mass spectrometer, their ionic intensity was large but the ratio of molecular ion to total ion was smaller than that of the chelates of rhodium(III) and chromium(III), which show good detection sensitivity. When the sample was heated for gasification and collected in a gas reservoir for mass spectrometry, chelates of copper(II) and iron(III) showed great disintegration of the molecular ion and a large number of fragment ion species was produced. Ratio of molecular ions to total ions was greater in rhodium(III) and chromium(III) chelates, with smaller number of fragment ions. Thus the difference in detection sensitivity according to the kind of a metal present was related to the ratio of molecular ions present to total ions of the metal chelates, and the difference in the detection sensitivity of β-diketone metal chelates in gas chromatography is affected largely by thermal stability of the chelates rather than by ionization efficiency of flame ionization detector and electron caputure ionization detector or to the stability of these chelates to ionization.

Gas chromatography is being used widely in recently years for the detection of β-diketone metal chelates,[1,2] and the technique is being used for the analysis of actual samples.[3a–d] About 20 kinds of metals have been the objects of analysis of β-diketone metal chelates by gas chromatography. It has been concluded from past experiments that β-diketone chelates of beryllium(II), aluminium(III), and chromium(III), which are easily desorbed, are adapted to gas chromatographic analyses. We have also carried out gas chromatography of metal acetylacetonate [$M^{n+}(AA)_n$],[4a] metal trifluoroacetylacetonate [$M^{n+}(TFA)_n$],[4b] metal hexafluoroacetylacetonate [$M^{n+}(HFA)_n$],[4c] and metal pivaloyltrifluoroacetonate [$M^{n+}(PTA)_n$],[4d] and observed the same phenomenon. At the same time, it was found that there was a difference in the detection sensitivity according to the kind of a metal present in the chelate compounds. For example, chelates of rhodium(III) has greater sensitivity than the chelates of chromium(III) with large volatility or of beryllium(II), aluminium(III), copper(II), and iron(III), and this order is the same irrespective of the difference in the ligand or of a detector. In order to find the factor or factors responsible for this difference in the detection sensitivity according to the kind of a metal present in the chelates, examinations were made by gas chromatography-mass spectrometry (GC–MS).

The gas chromatograph used was Yanaco-G80 (with thermal conductivity detector (TCD), flame ionization detector (FID), and electron caputure ionization detector (ECD) detectors), with helium as a carrier gas, and a glass column (4 mm internal diameter) packed with SE-30/Chromosorb-W (60—80 mesh), and concentration of the stationary phase liquid was 1% coating for $M^{n+}$ $(AA)_n$ and $M^{n+}$ $(TFA)_n$, and 10% for $M^{n+}$ $(HFA)_n$. Optimal length

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2) K. Arakawa and K. Tanikawa, "Gas Chromatography of Organometallic Compounds," (in Japanese), Gihodo, Tokyo, 1969.

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and temperature of the column were selected for each ligand from the results of previous experiments.[4a–c] The β-diketone metal chelates used were $M^{n+}(AA)_n$, $M^{n+}(TFA)_n$, and $M^{n+}(HFA)_n$ prepared in this laboratory as reported previously. The metals used were beryllium(II), aluminium(III), chromium(III), iron(III), copper(II), and rhodium(III). It was thereby found that the detection sensitivity was in the order of $10^{-5}$ mole with TCD, $10^{-7}$ mole with FID, and $10^{-13}$ mole with ECD, and calibration curves suitable for quantitative analysis were obtained. Detection sensitivity of metal chelates decreased in the order of rhodium (III) chromium(III) beryllium(II), aluminium(III), copper(II), and iron(III), in which the detection sensitivity of rhodium(III) and chromium(III), chelates was about the same, and was considerably different from that of other metal chelates. Measurement of ion by an ionization detector in gas chromatography is considered to be the same as the measurement of total ions in mass spectrometry. Consequently, behavior of β-diketone metal chelates during ionization and their effect to heat were examined by GC–MS.

Gas chromatograph–mass spectrometer used was Hitachi M-52, under the same condition for GC as used in gas chromatography alone. The ionization detector used was the total ion monitor (TIM), and conditions for the measurement of mass spectra were as follows: Ionization voltage, 15 eV; acceleration voltage, 1923 V (full $m/e$ to 750) and 2900 V ($m/e$ to 500); vacuum, $1\times10^{-7}$ Torr; ion source temperature, 200°.

Beryllium(II), copper(II), aluminium(III), chromium(III), iron(III), and rhodium(III) chelates of (AA), (TFA), and (HFA) were submitted to GC–MS. Detection sensitivity by gas chromatography with TIM was in the order of $10^{-7}$ mole, and the order of this sensitivity was the same as that in the gas chromatography detectors described above. Relative molar sensitivity according to the difference in the metal was 99 for $Cr(TFA)_3$, 55.1 for $Be(TFA)_2$, 43.3 for $Al(TFA)_3$, and 29.1 for $Cu(TFA)_2$, taking $Rh(TFA)_3$ as 100. The values were approximately the same in the case of other ligands. In order to examine the reason for this difference in sensitivity due to metals, GC–MS analyses were made. Ratio (%) of molecular ions of metal chelates to total ions was calculated by the measurement of mass spectrum and, at the same time, examinations were made on fragment ion species. It was thereby found that the chelates of rhodium(III) and chromium(III), which showed high sensitivity in gas chromatography, showed high relative intensity of molecular ions and the number of fragment ion species was small, while the chelates of copper(II) and iron(III), which showed lower sensitivity in gas chromatography, had a large number of fragment ion species with small relative intensity of molecular ions. Percentage of molecular ion was 57 for $Rh(TFA)_3$, 46 for $Cr(TFA)_3$, 33 for $Be(TFA)_2$, 5.7 for $Al(TFA)_3$, 25 for $Cu(TFA)_2$, and 0.8 for $Fe(TFA)_3$. Although the molecular ion of copper(II) was greater than that of aluminium(III) chelate, sensitivity in gas chromatography was greater for the aluminium chelate and, consequently, $Cu(TFA)_2$, which produced a large number of fragment ion species in GC–MS, is considered to be more stable to heat than $Al(TFA)_3$ or has less stability to ionization. The amount of molecular ion was the largest in rhodium(III) chelate, suggesting that it has the best thermal and ionization stability. The molecular ion of iron(III) chelate is present in a small amount but the number of fragment ion species was large, indicating that this chelate has a low stability to both heat and ionization. Essentially, a large number of fragment ion species signifies a large ion intensity but, in the case of copper(II) and iron(III) chelates, sensitivity to TIM in GC–MS is extremely low. Since this phenomenon is not affected by the ligand, these metal chelates seem to be easily affected by heat or ionization. This point was examined by the following experiment.

Mass fragmentation of $M^{n+}(AA)_n$[5] was examined by direct introduction into the ion source and after heating at 200° for 5 min and the gas collected in a 300 ml gas reservoir. It was

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[5] $Be(AA)_3$ is highly volatile and is lost during the heating so that it was excluded from the sample for measurement by the mass spectrometer.

Table I. Mass Fragmentation of Metal Acetylacetonates

| Ion Species | $M^{n+}(AA)_n$ | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Cu(AA)_2$ | | | $Al(AA)_3$ | | | $Cr(AA)_3$ | | | $Fe(AA)_3$ | | | $Rh(AA)_3$ | | |
| | m/e | D (%) | G (%) | m/e | D (%) | G (%) | m/e | D (%) | G (%) | m/e | D (%) | G (%) | m/e | D (%) | G (%) |
| $[O\text{-}C(CH_3)]^+$ | 43 | | 41.4 | 43 | | 22.8 | 43 | | 4.5 | 43 | | 28.9 | | | |
| $[(AA)\text{-}CO]^+$ | 72 | | 4.8 | 72 | | 2.2 | | | | 72 | | 3.1 | | | |
| $[(AA)\text{-}CH_3]^+$ | 85 | | 29.7 | 85 | | 13.9 | | | | 85 | | 25.3 | | | |
| $[(AA)]^+$ | 100 | | 24.1 | 100 | | 10.0 | | | | 100 | | 15.7 | | | |
| $[M^{II}(AA)]^+$ | 162 | 4.0 | | | | | | | | | | | | | |
| $[M^{III}(AA)]^+$ | | | | | | | | | | 155 | 6.4 | 5.0 | | | |
| | 160<br>≀<br>231 | 26.4 | | | | | | | | | | | | | |
| | 244 | 18.5 | | | | | | | | | | | | | |
| $[M^{II}(AA)_2\text{-}CH_3]^+$ | 246 | 7.9 | | | | | | | | | | | | | |
| $[M^{III}(AA)_2\text{-}CH_3]^+$ | | | | | | | | | | 239 | 10.6 | 7.0 | | | |
| $[M^{II}(AA)_2]^+$ | 261 | 17.6 | | | | | | | | | | | | | |
| $[M^{III}(AA)_2]^+$ | | | | 225 | 39.2 | 44.4 | 250 | 64.2 | 64.6 | 254 | 58.5 | 15.0 | 301 | 46.2 | 47.3 |
| | 259 | 25.6 | | 226 | 38.8 | 4.7 | | | | 255 | 9.6 | | 302 | 7.6 | 8.3 |
| $[M^{III}(AA)_3]^+$ | | | | 324 | 22.0 | 2.0 | 349 | 35.8 | 30.9 | 354 | 14.9 | | 400 | 46.2 | 44.4 |

D = by direct introduction into ion source
G = by gasification with heating

thereby found that, by direct introduction into the ion source, the ion intensity was the greatest in $Cu(AA)_2$ and $Fe(AA)_3$, which were about the same degree, followed by $Rh(AA)_3$ and $Cr(AA)_3$ of about the same degree, and the smallest in $Al(AA)_3$. In the measurement of mass spectrum, however, as shown in Table I, a large number of molecular ions was found in $Rh(AA)_3$ and $Cr(AA)_3$ under both the above conditions, with a small number of fragment ion species, and this tendency decreased in the order of $Rh(AA)_3$, $Cr(AA)_3$, $Al(AA)_3$, $Cu(AA)_2$, and $Fe(AA)_3$. In the case of $Al(AA)_3$, amount of molecular ion was relatively large and the number of fragment ion species was small when introduced directly into the ion source, while the number of molecular ion was small and that of fragment ion species were large after heating and gasification. These facts indicate that $Al(AA)_3$ has a good stability against ionization but is less stable to heating. However, it has better heat stability than $Cu(AA)_2$ and $Fe(AA)_3$, in which the molecular ion was not detected at all and they were found to have the poorest stability to ionization.

Thus, measurement of ionic intensity by TIM in GC–MS and examination of the fragmentation pattern have shown that the difference in the detection sensitivity of $\beta$-diketone metal chelates by the ionization detector in gas chromatography is due largely to the thermal stability of the chelates, besides their ionization efficiency and stability to ionization. The difference in the detection sensitivity by the use of a thermal conductivity detector is also largely affected by the thermal stability of $\beta$-diketone metal chelates.

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