Response of Electron Capture Detector to Metal Trifluoroacetylacetonates

Taitiro FUJINAGA and Yoshinori OGINO

Chemistry Institute, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto

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Gas chromatography of metal β-diketonates has recently been developed.[1] Ross *et al.*[2-4] has described the use of the electron capture detector for fluorine containing β-diketone metal chelates. They have shown that the electron capture detector is capable of detecting trace quantities of trifluoroacetylacetonates and hexafluoroacetylacetonates. They also have shown that the influence of the metallic ion of the chelate on the response of the electron capture detector is significant and the chelates of chromium and rhodium exhibit greater electron affinity than the corresponding chelates of aluminum.

The present authors have found that there exists a regularity between the response of the detector and the wavelength at the maximum absorption of the ultraviolet spectra of metal trifluoroacetylacetonates.

Experimental

Preparation of the Samples. The trifluoroacetylacetonates of beryllium, aluminum, scandium, copper, iron, chromium and thorium were synthesized and purified by the same methods reported in the previous paper.[5]

Ultraviolet Measurements. All spectra were measured with a Shimadzu Model SV-50A recording spectrophotometer using 1-cm quartz cells. All the sample solutions measured were 5×10^{-5}—5×10^{-6} M in chelates dissolved in *n*-hexane.

Gas Chromatographic Measurements. Shimadzu Model GC-IB equipped with electron capture detector was used for the investigation. The operating conditions were as follows.

Column, 4 mm×0.75 m stainless steel packed with 1 % by weight of Apieson L on 80—100 mesh glassy carbon; Column temp., 85°C; Flash heater temp., 200°C; Detector temp., 170°C; Cell voltage, 32 Vd.c., Carrier gas, N_2 50 ml/min; Sample size, 3 μl of 10^{-4} M benzen solution.

The relative electron capture coefficients K for differerent metal chelates were obtained by caluculating the ratios of peak areas of chromatograms of those metal chelates to that of scandium trifluoroacetylacetonate.

Results and Discussion

As shown in the Fig. 1, the logarithm of the relative electron capture coefficients is linear to the wavelength at the maximum absorption of the ultraviolet spectra. This may be explained as follows: The trifluoroacetylacetone shows strong single band at 282 mμ which seems to be due to a π-π* transition. If the cation completes the ligand, a red shift should be observed: The magnitude of a red shift may be related to the energy of the lowest vacant molecular orbital (MO).[6,7]

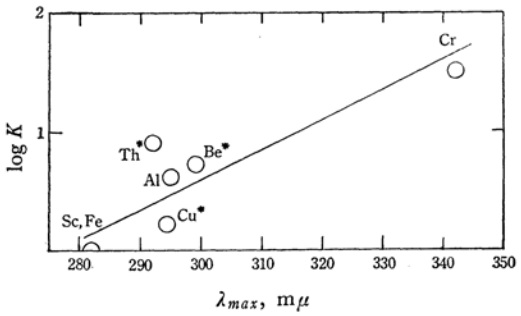

Fig. 1. The relation between the response of the electron capture detector and the wavelength at the maximum absorbtion of the ultraviolet spectra of metal trifluoroacetonates.
* The K-values for Cu and Be are multiplied by 3/2 and for Th, 3/4 in order to equalize the number of the ligand.

On the other hand, the logarithm of the relative electron capture coefficient is related to the electron affinity,[8] that is, the energy of the lowest vacant MO if the electron capture process is non-dissociative.

The detail works will be reported shortly afterwards.

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