CHEMISTRY LETTERS, pp. 207-208, 1979. Published by the Chemical Society of Japan

THE ELECTRON CAPTURE REACTION OF METAL COMPLEX

Yoshio KUGE, Yukikazu HATTORI, Shingo ASADA*, and Shoichiro YAMADA**
*Environmental Pollution Control Center of Osaka Prefecture, 1-3-62, Nakamichi,
Higashinari-ku, Osaka 537
**Institute of Chemistry, College of General Education, Osaka University,
Toyonaka, Osaka 560

The temperature dependence of the electron capture process was investigated for elucidating high electron capture sensitivity of the Cr(III) complexes of the ligands acetylacetone [H(acac)], trifluoroacetylacetone [H(tfa)], and hexafluoroacetylacetone [H(hfa)]. The electron affinity or the activation energy for the electron capture reaction were calculated for individual compounds.

The electron capture detector(ECD) permits the highest sensitivity for the detection of the metal complexes of $Cr(acac)_3$, $Cr(tfa)_3$, and $Cr(hfa)_3$$^{1)}$, however the mechanisms of the electron capturing phenomena are not obvious. To clarify this problem, we intend to determine the electron capture coefficients of these compounds at various detector temperature. The close relation between these coefficients and molecular structure was reported by Kojima et al.$^{2,3)}$ and authors.$^{4,5)}$

According to Wentworth's theory,$^{6,7)}$ there are roughly two reaction modes in an electron capture reaction of metal complexes; a nondissociative reaction where an anion radical is produced from a sample molecule and a dissociative reaction where a reduced metal and a radical of ligand may be produced.

$$ML + e^- = ML^- \quad \text{(nondissociative)} \quad (1)$$

$$ML + e^- = M^- + L^\bullet \quad \text{(dissociative)} \quad (2)$$

(M; Metal L; Ligand)

Wentworth and co-workers have correlated the electron capture coefficient K to the electron affinity of a sample molecule in the nondissociative reaction or the activation energy for the dissociative reaction as expressed in the following equations;

$$\ln KT^{3/2} = Z + EA/RT \quad \text{(nondissociative)} \quad (3)$$

$$\ln K = Z - E^*/RT \quad \text{(dissociative)} \quad (4)$$

where EA and E^* are the electron affinity and the activation energy in kcal/mol, R is a gas constant, and T is the absolute temperature in the detector. Z is a pre-exponential factor.

The K value was calculated from the following equation(5) derived by Wentworth and co-workers.$^{6)}$

$$K = (F/S\cdot N) \left\{ (I_b - I_{ep})/I_{ep}\cdot W \right\} \quad (5)$$

where F is the carrier gas flow rate(l/min), S is the chart speed(cm/min), N is the amount of sample injected(mol), and I_b and I_{ep} are the detector current without and with capturing species in the corresponding to the maximum peak height. I_{ep} can be obtained by substructing $(I_b - I_{ep})$ from I_b.

The procedure used in this report is similar to our papers previously reported.$^{4,5)}$

The Arrhenius plots of lnK and $\ln KT^{3/2}$ for $Cr(acac)_3$, $Cr(tfa)_3$, and $Cr(hfa)_3$ are shown in Figures 1 and 2. Since the plots of $Cr(acac)_3$ are negative slope, it can be seen that $Cr(acac)_3$ captures free electrons dissociatively. As for $Cr(tfa)_3$ and $Cr(hfa)_3$, the plots of these compounds show positive slopes. These facts would indicate that these compounds capture free electrons nondissociatively.

In Table 1 are given the activation energy for dissociative electron capture reaction of $Cr(acac)_3$, and the electron affinities for nondissociative electron capture reaction of $Cr(tfa)_3$ and $Cr(hfa)_3$. The obtained value of the electron affinity for $Cr(tfa)_3$ is larger than that of $Cr(hfa)_3$.

Further studies on the determination of the electron capture coefficients for calculating the electron affinity and the activation energy of another metal complexes are now in progress.

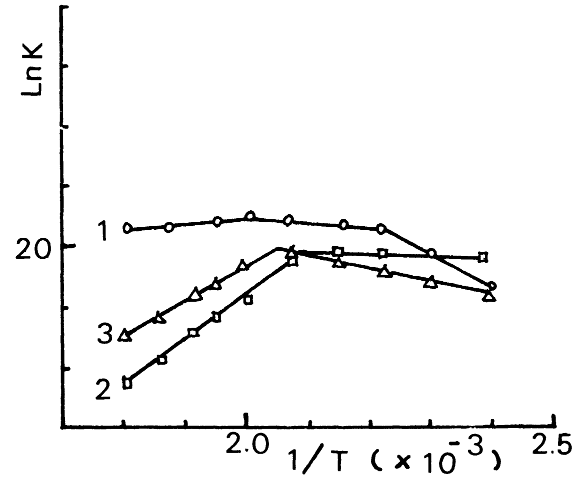

Fig. 1 Temperature dependence of electron capture coefficients(K) for metal complexes (1) $Cr(acac)_3$, (2) $Cr(tfa)_3$, (3) $Cr(hfa)_3$

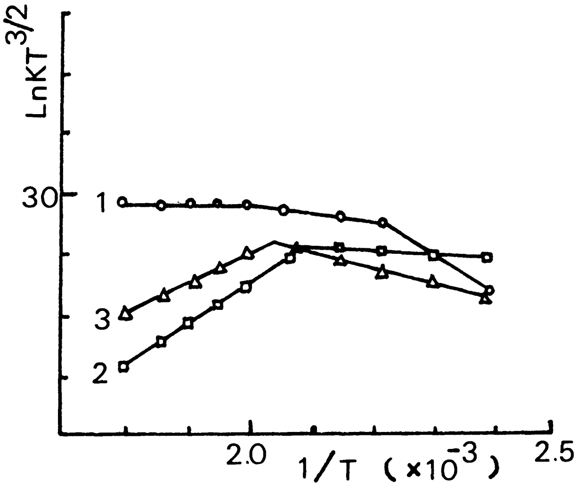

Fig. 2 Arrhenius plots of K for metal complexes (1) $Cr(acac)_3$, (2) $Cr(tfa)_3$, (3) $Cr(hfa)_3$

Table 1
Electron affinities, EA, or activation energy, E^*, for $Cr(acac)_3$, $Cr(tfa)_3$, and $Cr(hfa)_3$

Compound	EA	E^*
$Cr(acac)_3$		12.3(451~499)$^{a)}$
$Cr(tfa)_3$	13.3(483~555)$^{a)}$	
$Cr(hfa)_3$	9.5(499~555)$^{a)}$	

(in kcal/mole)

a) Determined temperature range K

References
1) P. C. Uden and D. E. Henderson, Analyst, 120, 889(1977).
2) T. Kojima and A. Satouchi, Bunseki Kagaku, 22, 1428(1973).
3) T. Kojima and Y. Tanaka, Anal. Chem., 48, 1760(1976).
4) Y. Hattori, Y. Kuge, and S. Nakagawa, Bull. Chem. Soc. Jpn., 51, 2249(1978).
5) Y. Hattori, Y. Kuge, and A. Asada, Nippon Kagaku Kaishi, 1978, 1102.
6) W. E. Wentworth and E. Chen, J. Gas Chromatogr., 5, 170(1967).
7) W. E. Wentworth, E. Chen, and J. E. Lovelock, J. Phys. Chem., 71, 1652(1967).

(Received September 16, 1978)