

# THERMAL STABILITIES OF METAL OXALATO COMPLEXES IN SOLID STATE

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The thermal decomposition reactions of a number of metal oxalato complexes in solid state were studied by the methods of TG and EGA. It was found that the thermal stabilities of the anhydrous complexes decrease approximately with the increase of electron-accepting abilities of the central metal ions.

The thermal decomposition reactions of a number of metal oxalato complexes were studied by the methods of TG (thermogravimetry) and EGA (evolved gas analysis). In Fig. 1, the plots of the decomposition temperatures of the anhydrous complexes in a nitrogen atmosphere versus the oxidation-reduction potentials<sup>1)</sup> of the central metal ions in aqueous solution are given. The redox potentials of aquo ions are considered to show electron-accepting abilities of central metal ions forming oxalato complexes, since  $Dq$  value of  $H_2O$  is near to that of  $C_2O_4^{2-}$ . Then, the result in Fig. 1 indicates

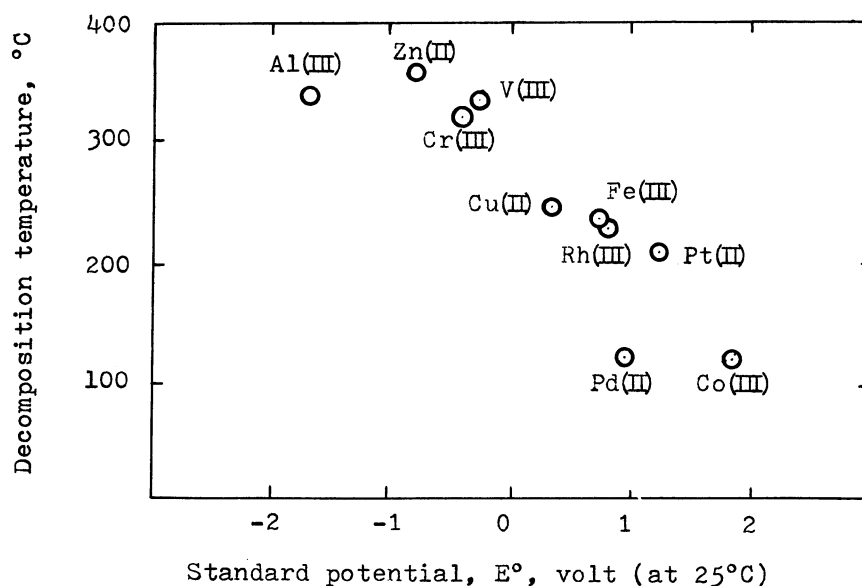


Fig. 1. Correlation of decomposition temperatures of metal oxalato complexes with oxidation-reduction potentials of central metal ions. The redox potentials adopted correspond to the couples  $M(II)/M(III)$  for V, Cr, Fe and Co,  $M(0)/M(III)$  for Al and Rh, and  $M(0)/M(II)$  for Cu, Zn, Pd and Pt, respectively.

that the thermal stabilities of the oxalato complexes decrease approximately with the increase of electron-accepting abilities of the central metal ions.

The temperature ranges of the thermal decomposition and the analyses of gaseous products which were obtained from TG and EGA curves respectively are summarized in Table 1. The complexes of Fe(III), Co(III), Rh(III), Cu(II), Pd(II) and Pt(II)

Table 1. Temperature ranges and analyses of gaseous products.

Complex	Temperature range	Gaseous product (%)
$K_3[Al(ox)_3]$	335 - 426	CO (50), $CO_2$ (50)
$K_3[V(ox)_3]$	331 - 414	CO (27), $CO_2$ (73)
$K_3[Cr(ox)_3]$	325 - 450	CO (32), $CO_2$ (68)
$K_3[Fe(ox)_3]$	230 - 265	$CO_2$
$K_3[Co(ox)_3]$	115 - 231	$CO_2$
$K_3[Rh(ox)_3]$	225 - 260	$CO_2$
$K_2[Cu(ox)_2]$	247 - 285	$CO_2$
$K_2[Zn(ox)_2]$	360 - 430	CO (44), $CO_2$ (56)
$K_2[Pd(ox)_2]$	116 - 190	$CO_2$
$K_2[Pt(ox)_2]$	207 - 223	$CO_2$

evolved only  $CO_2$ , indicating that in these complexes, the central metal ion was reduced by the coordinated oxalate.

Tanaka and Nanjo have suggested that the thermal decomposition of  $K_3[Fe(ox)_3]$  and  $K_3[Co(ox)_3]$  is initiated by the electron transfer from the coordinated oxalate to the central metal ion.<sup>2)</sup> The results obtained in this work support their suggestion.

On the other hand, the complexes of Al(III), V(III), Cr(III) and Zn(II) evolved CO and  $CO_2$ , suggesting that the decomposition of these complexes is initiated by C-O bond breaking to form a metal oxide without changing the oxidation state of the central metal. In fact, the decomposition temperatures of these complexes, as shown in Fig. 1, are almost constant independently of their redox potentials. The CO/ $CO_2$  ratios of the complexes of Al(III) and Zn(II) are about 1, but those of the complexes of V(III) and Cr(III) are considerably smaller than 1. The latter complexes may decompose through both the processes, electron transfer and C-O bond breaking.

#### References:

- 1) W. M. Latimer, "The Oxidation State of the Elements and Their Potentials in Aqueous Solutions", Prentice-Hall, New York (1952).
- 2) N. Tanaka and M. Nanjo, Bull. Chem. Soc. Japan, 40, 330 (1967).

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