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Mass Spectrometry of Holmium tris-Acetylacetonate Monohydrate

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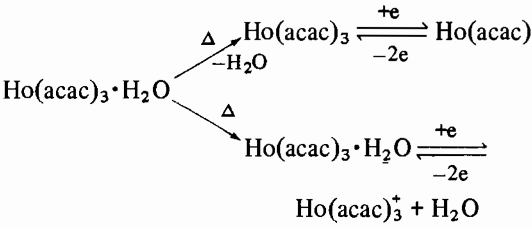
Mass spectrometry has been used for the study of acetylacetonate complexes of various metals [1–4]. However, the compounds of rare earth elements have not been studied. The only known results are those reported for lanthanum tris-acetylacetonate [1] for an adduct of neodymium tris-acetylacetonate with phenanthroline [4]. As for heavy rare earth elements, there are no mass spectral data in the literature.

We have studied the behaviour of holmium tris-acetylacetonate monohydrate under electron impact. The mass spectra were measured on an AEI MS-30 instrument at an ionizing energy of 70 eV; the temperature of the direct sample introduction system was 260–350 °C and the temperature in the ionization chamber was 300 °C.

No molecular ion corresponding to the parent monohydrate was abundant in the mass spectrum and the ion with the maximum mass turns out to be dehydrated $Ho(acac)_3$ (Table I). A similar picture appears in the spectrum of neodymium tris-acetylacetonate adduct with phenanthroline, where $Nd(acac)_3^+$ was found to be the heaviest ion [4]. Importantly, the corresponding molecular ions in the mass spectra of hydrated acetylacetonates of Co, Ni and Zn were also absent [1].

The dehydration of $Ho(acac)_3\cdot H_2O$ during mass spectrometric analysis may occur either on the vaporization stage (1) or the ionization stage (2).



$$Ho(acac)_3\cdot H_2O \xrightarrow[-H_2O]{\Delta} Ho(acac)_3 \underset{-2e}{\overset{+e}{\rightleftharpoons}} Ho(acac)_3^+ \quad (1)$$

$$Ho(acac)_3\cdot H_2O \xrightarrow{\Delta} Ho(acac)_3\cdot H_2O \underset{-2e}{\overset{+e}{\rightleftharpoons}} Ho(acac)_3^+ + H_2O \quad (2)$$

According to thermogravimetric analyses, $Ho(acac)_3\cdot H_2O$ at 125 °C undergoes only endothermic decomposition, which is not connected with the formation of anhydrous product [5], but a complete decomposition takes place at 350 °C. The mass spectrum, however, was obtained at an inlet temperature of 260 °C *i.e.*, 90 °C less than the sample decomposition temperature. Attempts to prepare anhydrous acetylacetonates of rare earth elements by sublimation in high vacuum proved unsuccessful [6]. Thus it follows that the dehydration of holmium acetylacetonate monohydrate occurs due to electron impact. The same may be concluded for the phenanthroline adduct of neodymium tris-acetylacetonate (which is stable up to 280 °C according to DTA) whereas its mass spectrum was obtained at 125 °C [4].

In the mass spectra of $Ho(acac)_3\cdot H_2O$ there are no masses higher than those of molecular ions, indicating a monomeric structure of holmium acetylacetonate in the gas phase, and the non-occurrence of gas phase ion-molecular reactions of the substance under consideration in the ionization chamber of the mass spectrometer observed earlier for a number of acetylacetonates of transition metals [1].

Comparison of the mass spectra of acetylacetonate complexes of holmium, neodymium and lanthanum (Table I) shows a common mechanism of decom-

TABLE I. Comparison of Mass Spectra of Acetylacetonates of Different Metals.[a]

Ion	$Ho(acac)_3\cdot H_2O$	$Nd(acac)_3\cdot Phen$ [4]	$La(acac)_3$ [1]	$Fe(acac)_3$ [1]	$Al(acac)_3$ [1]
$M(acac)_3^+$	462(28)	441(29)	436(38)	353(20)	324(9)
$M(acac)_2^+$	363(100)	342(100)	337(100)	254(100)	225(100)
$(acac)M(OH)^+$	281(10)	260(20)	255(9.5)	172(3)	143(4)
$M(acac)^+$	264(10)	243(8)	238(5)	155(21)	126(1)
$M(acac{-}H)^+$	263(11)	242(13)	237(5)	154(–)	125(–)

[a] The mass spectra of polyisotope elements are reduced to the single-isotope type.

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position of these compounds. In all cases the molecular unsolvated ion $P^{+} = M(acac)_3^{+}$ first eliminates an acetylacetonate group, thus transforming to the most intensive ion $M(acac)_2^{+}$. This ion transforms further into P-181^{+} of the ascribed structure (acac)–M–(OH)$^{+}$. The rearranging ion P-181^{+} eliminates a molecule of water resulting in P-199^{+} which eventually corresponds to the loss of two acetylacetonate groups and a hydrogen atom by the unsolvated parent molecular ion.

The maximum peak in the mass spectra of the discussed complexes is that of the ion $M(acac)_2^{+}$, where the atom of the metal is in its characteristic oxidation state +3. At the same time, the intensities of peaks for the $M(acac)^{+}$ ions with the metal atom in the +2 oxidation state increase in the series Al La Nd Ho Fe *i.e.*, in accordance with the concept of valency change [1]. The stability of the oxidation state + 2 for rare earth elements lies between aluminium (no stable divalent compounds) and iron (divalent compounds are well-known). Here the intensity of divalent ions $M(acac)^{+}$ tends to increase on the transition from light to heavy rare earth elements.

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