Consecutive Unimolecular Dissociations of Fluorinated β-Diketone Chelates

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Summary The apparent one-step loss of a ligand in the mass spectral decomposition of tris-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)aluminium is suggested to occur, rather, in two steps.

UNDER the assumptions of the quasi-equilibrium theory of mass spectra, the rate of a unimolecular reaction proceeding through a given transition state is a function of the energy in the parent which is in excess of the activation energy for the process. Delayed dissociations which are observed as metastable peaks result, therefore, from ions having energy only slightly above the activation energy. In the normal case, consecutive reactions occur from parents of relatively high energies, so that a sufficient portion for further dissociation is left in the primary fragment. These primary fragmentations take place very rapidly in the source region with secondary dissociation occurring in accordance with the excess of energy in the primary fragment.

Examples have recently been found,[1-3] however, where ions undergo delayed dissociation in the first field-free region of a double-focussing mass spectrometer (Region I), with the resulting primary fragment dissociating further in the second field-free region (Region II). We discuss here a class of compounds for which such delayed consecutive reactions appear to be relatively common.

Hexafluoroacetylacetonate anion (hfa) forms neutral, volatile tris-chelates with Al^{III}, Cr^{III}, and Fe^{III}. For each of these chelates, metastable peaks are observed for the reactions: (M = metal, L = hfa)

(1) $ML_3^+ \rightarrow ML_2(L - CF_3)^+ + CF_3$ (hereafter $ABC^+ \rightarrow AB^+ + C$)

(2) $ML_2(L - CF_3)^+ \rightarrow ML_2^+ + (L - CF_3)$ $(AB^+ \rightarrow A^+ + B)$

(3) $ML_3^+ \rightarrow ML_2^+ + L$ $(ABC^+ \rightarrow A^+ + BC)$

In addition, the consecutive two-region metastable,

$$(4)\quad ABC^+ \xrightarrow{(I)} AB^+ \xrightarrow{(II)} A^+,$$

is observed with surprising intensity. Relative intensities of these peaks for the aluminium chelate are summarized in Table 1.

TABLE 1

Intensities of normal ions and metastables for AlL_3

Ion or metastable	Relative abundance
AlL_3^+	28·3
$AlL_2(L{-}CF_3)^+$	8·2
AlL_2^+	100·0
$AlL_3^+ \rightarrow AlL_2(L{-}CF_3)^+$ (Region I)	1·2
$AlL_2(L{-}CF_3)^+ \rightarrow AlL_2^+$ (Region I)	1·5
$AlL_3^+ \rightarrow Al_2$ (Region I)	0·6
$AlL_3^+ \rightarrow AlL_2(L{-}CF_3)^+ \rightarrow AlL_2^+$ (Region I then II, consecutive)	0·04

The direct observation of process (4) indicates a possibility that the metastable observed in reaction (3) may be due entirely to fast consecutive dissociations within a single region and that this reaction may not occur as a primary process. Recent theoretical calculations for consecutive metastables in toluene[3] show that the consecutive process occurring with Region I (which is collected as the apparent metastable $ABC^+ \rightarrow A^+$) gives a peak about five to ten times larger than the observable two-region consecutive metastable (4). Although these chelates in no way resemble toluene, the observed factor of fifteen (Table 1) suggests strongly that reaction (3) is very likely to be the consecutive reaction (4) instead for these molecules also. The plausibility of this suggestion is strengthened by the fact that reaction (3) involves the breaking of two metal–chelate bonds. A preceeding loss of CF_3 may facilitate such a double break, since the resulting $CF_3{\cdot}CO{\cdot}CH{\cdot}CO$ can form a stable neutral.

The occurrence of a delayed consecutive reaction (4) requires rather special conditions in the framework of the quasiequilibrium theory of mass spectra. The lifetimes of contributing parent ions ABC^+ must be nearly the same as their primary dissociation product AB^+, *i.e.*, about 1 μsec. Therefore, the rates k_1 and k_2 must be competitive over a fairly large range of parent ion energies. For the class of compounds studied here, the density of states for AB^+ will not be significantly less than for ABC^+; consequently, it is necessary that the activation energies be quite close and that the primary neutral not carry away much energy. The toluene calculations mentioned earlier[3] for consecutive acetylene loss from tropylium ion indicate that no consecutive metastables will be observed if activation energies differ by much more than 1 ev. For toluene, this is the case, and process (3) is well described by a QET treatment as proceeding exclusively *via* process (4).

There is, of course, also the possibility of long-lived energetic states of the parent ion, where incomplete internal conversion delays the primary reaction. According to Dougherty,[4] bond cleavage from a radical cation at slower rates occurs from low-lying doublets. Ottinger[2] has also found some consecutive metastables in hydrocarbons where the primary and secondary activation energies are known to differ by more than three volts. Moreover, the peak size is almost invarient with delay time, indicating a very flat decay curve. This seems strong evidence for long-lived high-energy states in some molecules. In the absence of detailed information on fragmentation mechanisms and energetics for these chelate molecules, we cannot determine which of these interpretations correctly rationalizes the occurrence of abundant consecutive metastable transitions.

A study of chelates from different acetylacetone derivatives shows changes in decomposition patterns. The major metastables are shown in Table 2. In spite of varying paths, there is still an indication that some loss from the ligand preceeds loss of the ligand itself. Though consecutive mestastables have been demonstrated only for $Al(hfa)_3$, it seems likely that the entire class of compounds will show delayed consecutive dissociations. It is suggested that this is a general decomposition scheme for metal acetylacetonates.

TABLE 2

Decomposition paths and metastables for cobalt complexes of hexafluoracetylacetone (hfa), trifluoroacetylacetone (tfa), and benzoyltrifluoracetone (bta)

	m^*_{obs}
$Co(hfa)_3$, L = hfa	
$Co(L_2 - CF_3)^+ \rightarrow CoF(L_2 - 2CF_3)^+$	310·2
$CoF(L_2 - 2CF_3)^+ \rightarrow CoF(L - CF_3)^+$	131·8
$Co(L_2 - CF_3)^+ \rightarrow CoF(L - CF_3)^+$	115·5
$Co(tfa)_3$, L = tfa	
$Co(L_2 - CF_3) \rightarrow Co(L_2 - CF_3 - C_2H_2O)^+$	218·0
$Co(L_2 - CF_3 - C_2H_2O)^+ \rightarrow CoL^+$	176·9
$Co(L_2 - CF_3) \rightarrow CoL^+$	151·8
$Co(bta)_3$, L = bta	
$Co(L_2 - CF_3)^+ \rightarrow Co(L_2 - CF_3 - 44)$	336·6
$Co(L_2 - CF_3 - 44)^+ \rightarrow CoL^+$	199·7
$Co(L_2 - CF_3) \rightarrow CoL^+$	178·8

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