Exchange Reactions in the Ion Source of a Mass Spectrometer

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METAL chelates, ML_3 (M = rare-earth metal; L = residue of a fluoro-β-diketone), *e.g.* prepared in the presence of an alkali-metal carbonate contain a tetrakis-metal chelate, $M'ML_4$ (M' = alkali-metal).[1] These chelates are formed in solutions of low dielectric constant by reaction of the tris-chelate, ML_3, and the alkali-metal derivative of the β-diketone $M'L'$ (L' = second residue of a different fluoro-β-diketone).

$$ML_3 + M'L' \rightleftharpoons MM'L_3L'$$

This reaction was shown (by u.v. spectrophotometry) to be reversible, the tetrakis-chelate dissociating in solutions of high dielectric constant (*i.e.* EtOH). Although the tris- and tetrakis-chelates could be readily distinguished by their u.v. spectra, introduction of spectroscopically pure samples of the tris-chelates of rare-earth metals into the ion source of the mass spectrometer, gave spectra which

TABLE 1

Formation of tetrakis-complexes within the source of the mass spectrometer

β-Diketone	Rare-earth metal (M)	Alkali metal (M′)	Formation of tetrakis-chelates ($MM'L_4$)
$\mathrm{MeCO\cdot CH_2Ac}$	Ho, Er, Sm	Li, Na, K	—
$\mathrm{PhCO\cdot CH_2\cdot COPh}$	"	"	—
$\mathrm{Bu^tCO\cdot CH_2\cdot COBu^t}$	"	"	—
$\mathrm{CF_3\cdot CO\cdot CH_2\cdot Ac}$	Eu, Gd, Cy, Ho, Er	Li, Na, K, Rb, Cs	+
$\mathrm{CF_3\cdot CO\cdot CH_2\cdot CO\cdot CF_3}$	Y	Cs	+
$\mathrm{CF_3\cdot CO\cdot CH_2\cdot CO\cdot C_4H_3S}$	Y, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb	Li, Na, K, Rb, Cs	+
$\mathrm{Bu^t\cdot CO\cdot CH_2\cdot CO\cdot CF_3}$	Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb	"	+
$\mathrm{Bu^tCO\cdot CH_2\cdot CO\cdot C_2F_5}$	Y, Sm, Dy, Ho, Er	"	+
$\mathrm{Bu^tCO\cdot CH_2\cdot CO\cdot C_3F_7}$	"	"	+

showed peaks corresponding to ions from a tetrakis-chelate containing both the rare-earth metal and a sodium atom. Since flame photometry showed that sodium was absent in the original tris-chelate sample the production of the tetrakis-chelate must have occurred upon the filament or the plates of the spectrometer source. Table 1 summarises the reactions observed with various rare-earth metal chelates. These observations were confirmed by first introducing into the ion source a sample of the β-diketonate of potassium or rubidium and, when the sample had apparently been pumped away (by the disappearance of its mass spectrum), a sample of a tris-rare-earth metal chelate was introduced. The mass spectrum now contained peaks due to ions containing both the rare-earth metal and the alkali-metal. Further, an exchange reaction was demonstrated in which, when a tetrakis-metal chelate [*e.g.* $\mathrm{NaHo(CF_3CO\cdot CHAc)]_4}$ was introduced into the ion source followed by a sample of an alkali-metal derivative (*e.g.* $\mathrm{CF_3CO\cdot CHKAc}$) the mass spectrum showed peaks due to ions from the tetrakis-chelate $\mathrm{KHo(CF_3CO\cdot CHAc)_4}$. Thus, before studying the mass spectra of rare-earth metal chelates the alkali-metal contamination of the surfaces within the ion sources was removed by the introduction of a large sample of the parent diketone or any other similar diketone; we used trifluorothenoylacetone.

The mass spectra of the alkali-metal derivatives of β-diketones when recorded separately showed, in addition to peaks corresponding to the expected molecule ions $(M\,L)^+$, peaks at greater *m/e* values corresponding to the ions, M'_2L^+, $M'_2L_2^+$, $M'_2L_3^+$, and $M'_3L_3^+$, these are as intense in some cases as those due to the monomer (Figure 1). Whether these structures exist in the solid phase or whether they are formed in the evaporation process is unknown although the same spectra are produced from samples before and after vacuum sublimation; and elemental composition of the sample is unaltered by sublimation. The polymeric ions are not formed by the replacement of a second alkali-metal atom in the β-diketone as each ligand still retains a single hydrogen atom attached to the central carbon atom.

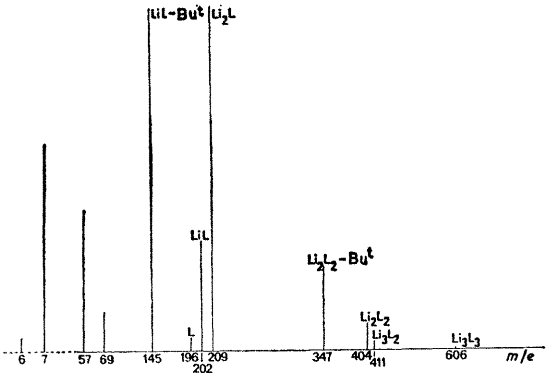

FIGURE. *Polymeric ions of alkali-metal chelates.*

TABLE 2

Formation of polymeric ions within the source of the mass spectrometer

β-Diketone (L)	Ion $MM'L^+$	Detected	Ion $MM'L_2{}^+$	Detected
	M	M′	M	M′
$\mathrm{Bu^tCO\cdot CH_2\cdot COC_2F_5}$	Li	Li	Li	Li
	Li	Na	Li	Na
	Na	Na	Na	Na
	Na	K	Na	K
	K	K	K	K
$\mathrm{Bu^tCO\cdot CH_2\cdot COCF_3}$	Na	Na	Na	Na
	Na	K	Na	K
	K	K	K	K

Exchange reactions between different alkali-metal chelates can also occur within the ion source of the spectrometer. If a sample of the alkali-metal derivative of a β-diketone is introduced into the ion source, the spectrum recorded and the mass spectrometer pumped until the spectrum of the sample has disappeared, when a second sample of a different alkali-metal derivative of the same β-diketone is introduced into the ion source, the mass spectrum recorded exhibits peaks due to ions which contain both alkali metals. Table 2 summarises the results obtained with pairs of alkali-metal chelates and lists polymeric ions containing two different alkali metal atoms.

Thus our results show that in studies of the alkali-metal derivatives of β-diketones in the gas phase (*i.e.* by mass spectrometry or gas chromatography) care must be taken to exclude the possibility of alkali-metal exchange upon surfaces.

(*Received, January 23rd, 1969; Com.* 102.)

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[1] R. Belcher, J. R. Majer, R. Perry and W. I. Stephen, *J. Inorg. Nuclear Chem.*, in the press.