Exchange Reaction and the Formation of New Organometallic Compounds in the Ion Source of a Mass Spectrometer

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THE alkali-metal derivatives of β-diketones (ML) can react with rare-earth chelates (RL_3):[1,2]

$$ML + RL_3 \longrightarrow MRL_4 \text{ (association)}$$

$$\left.\begin{array}{l} M'L + MRL_4 \longrightarrow ML + M'RL_4 \\ M'L' + ML \longrightarrow M'L + ML' \end{array}\right\} \text{(exchange)}$$

We report that during the evaporation of metal chelates into the ion source of a mass spectrometer more extensive rearrangements may take place and more complex reactions leading to the formation of new metal chelates may occur. These reactions are demonstrated most simply by the simultaneous evaporation of two different metal chelates into the ion source and the comparison of the resulting mass spectrum with that of the metal chelates recorded separately. These reactions occur whenever metal chelates are evaporated. The new peaks in the combined mass spectra, absent in the individual mass spectra, are not instrumental artefacts. In some cases the existence of the complex metal chelates revealed by this method has been confirmed by preparation and isolation. The reactions detected may be divided into two types, ligand interchange reaction in which a complete β-diketone residue or other ligand is transferred from one metal atom to another and association reaction in which complex metal chelates containing two different metal atoms are formed.

The mass spectra of the alkali metal derivatives of β-diketones exhibit peaks due to polymeric ions of the form $M_xL_y^+$ and sublimation studies have indicated that such polymerisation probably occurs during evaporation. When a mixture of the sodium derivative of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl octane-4,6-dione and the potassium derivative of 1,1,1,2,2-pentafluoro-6,6-dimethylheptane 3,5-dione was evaporated at a temperature of 220° into the ion source of an A.E.I. MS9 mass spectrometer, the combined mass spectrum revealed peaks due to the exchange of the alkali metal atoms. In addition there was a peak at *m/e* 602 due to an ion containing both metal atoms and both ligands [$NaK(C_{10}H_{10}O_2F_7)(C_9H_{10}O_2F_5)^+$]. This confirms the suggestion that polymeric ions arise from species produced by reactions occurring during evaporation and are not the result of the evaporation of a polymer present in the original solid.

When a mixture of the sodium and magnesium derivatives of ethyl trifluoroacetoacetate was evaporated into the ion source at a temperature of 220°, the combined mass spectrum revealed a peak at *m/e* 390 corresponding to the ion $Mg(C_6H_6O_3F_3)_2^+$ of very low intensity. The principal ions in the spectrum were at *m/e* 413 and 596 corresponding to the species $NaMg(C_6H_6O_3F_3)_2^+$ and $NaMg(C_6H_6O_3F_3)_3^+$ and indicated the existence of a complex metal chelate having the structure $NaMg(C_6H_6O_3F_3)_3^+$. This was confirmed by synthesising the compound directly by the action of ethyl trifluoroacetoacetate on a mixture of magnesium hydroxide and sodium acetate. Ligand interchange was demonstrated by evaporating a mixture of the magnesium derivative of ethyl trifluoroacetoacetate and the sodium derivative of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione into the ion source at a temperature of 220°. In addition to the peaks of the polymeric ions of the sodium derivative there was a second series of peaks due to the formation of the sodium derivative of ethyl trifluoroacetoacetate and subsequent polymerisation. Simultaneous ligand interchange and association reactions resulted in the appearance of peaks at *m/e* 932 [$NaMg(C_{10}H_{10}O_2F_7)_3{}^+$], *m/e* 820 [$NaMg(C_6H_6O_3F_3)(C_{10}H_{10}O_2F_7)_2{}^+$] and at *m/e* 708 [$NaMg(C_6H_6O_3F_3)_2(C_{10}H_{10}O_2F_7){}^+$].

Similar results have been obtained with mixtures of sodium and strontium derivatives and sodium and barium derivatives of 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione, the mass spectra indicating the existence of the complex chelates $NaSr(C_8H_{10}O_2F_3)_3$ and $NaBa(C_8H_{10}O_2F_3)_3$.

The alkali-metal interchange and association reactions of the alkali-metal and rare-earth metal derivatives have been discussed previously[1] but the study was restricted to β-diketones containing fluorine atoms. When a mixture of sodium oxinate and the holmium derivative of 1,1,1-trifluoropentane-2,4-dione was evaporated 230° all possible interchange and association reactions occurred (Table 1). The existence of complex metal chelates containing both alkali metals and rare-earth metals and having 8-hydroxyquinoline as the ligand is demonstrated. Similar results were obtained with samarium oxinate and the sodium derivative of 1,1,1,2,2-pentafluoro-6,6-dimethylheptan-3,5-dione. The existence of similar complex metal chelates in which 8-hydroxyquinoline was the only ligand species was demonstrated by the appearance of peaks due to the ions $NaSm(C_9H_6NO)_3{}^+$ and $NaGd(C_9H_6NO)_3{}^+$ in the mass spectra of mixtures of sodium oxinate and samarium oxinate and of sodium oxinate and gadolinium oxinate respectively.

Mass spectrum of $Na(C_9H_6NO) + Ho(C_5H_4O_2F_3)_3$

m/e 176 [$Na(C_5H_4O_2F_3)$]; 309 [$Ho(C_9H_6NO)$]; 462 [$Ho(C_9H_6NO)(C_5H_4O_2F_3)$]; 597 [$Ho(C_9H_6NO)_3$]; 606 [$Ho(C_9H_6NO)_2(C_5H_4O_2F_3)$]; 615 [$Ho(C_9H_6NO)(C_5H_4O_2F_3)_2$]; 629 [$HoNa(C_9H_6NO)_2(C_5H_4O_2F_3)$]; 638 [$HoNa(C_9H_6NO)(C_5H_4O_2F_3)_2$]; 647 [$HoNa(C_5H_4O_2F_3)_3$]; 791 [$HoNa(C_9H_6NO)(C_5H_4O_2F_3)_3$]; 800 [$HoNa(C_5H_4O_2F_3)_4$]; 805 [$HoNa_2(C_9H_6NO)_2(C_5H_4O_2F_3)_2$]; 814 [$HoNa_2C_9H_6NO)(C_5H_4O_2F_3)_3$]; 823 [$HoNa_2(C_5H_4O_2F_3)_4$]; 935 [$HoNaC_9H_6NO)_2(C_5H_4O_2F_3)_3$; 944 [$HoNa(C_9H_6NO)(C_5H_4O_2F_3)_4$]; 953 [$HoNa(C_5H_4O_2F_3)_5$]; 958 [$HoNa_2(C_9H_6NO)_2(C_5H_4O_2F_3)_3$]; 967 [$HoNa_2(C_9H_6NO)(C_5H_4O_2F_3)_4$].

Ligand interchange was also found in the mass spectrum obtained when a mixture of the erbium derivative of 1,1,1-trifluoro-4-(2-thienyl)butane-2,4-dione and the samarium derivative of 2,2,6,6-tetramethylheptane-3,5-dione was evaporated at 250°. All possible ligand–metal combinations were formed, but no association reactions were observed. The importance of selecting metal chelates with approximately the same volatility was shown by the simultaneous evaporation of samarium oxinate and the holmium derivative of 1,1,1-trifluoropentane-2,4-dione. Samarium oxinate is considerably less volatile and the only interchange revealed by the mass spectrum was that producing holmium oxinate. No peaks due to ions containing samarium were observed.

When a mixture of the copper and chromium derivatives 1,1,1-trifluoropentane-2,4-dione was evaporated at 220° an association reaction took place as indicated by the appearance in the mass spectrum of peaks due to the ions $CuCr(C_5H_4O_2F_3)_4{}^+$ and $CuCr(C_5H_4O_2F_3)_3{}^+$.

When a mixture of the copper and holmium derivatives of 1,1,1-trifluoropentane-2,4-dione were evaporated an association reaction leading to the formation of $CuHo(C_5H_4O_2F_3)_4{}^+$ was detected by the appearance of a peak due to the ion $CuHo(C_5H_4O_2F_3)_3{}^+$. In this new complex metal chelate and in the analogous compound containing chromium described above, the copper is assumed to be in a lower-valent state.

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[1] R. Belcher, J. R. Majer, R. Perry, and W. I. Stephen, *J. Inorg. Nuclear Chem.*, 1969, **31**, 471.

[2] J. R. Majer and R. Perry, *Chem. Comm.*, 1969, 271.