Isomerism in the Metal Derivatives of 8-Hydroxyquinoline

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Summary The existence of geometrical isomers of the zinc, iron(II), aluminium and indium derivatives of 8-hydroxyquinoline is demonstrated by the detection of fine structure in the integrated ion-current curves obtained by the evaporation of small samples of the metal chelates into the ion source of a mass spectrometer.

THE metal derivatives of 8-hydroxyquinoline are sufficiently volatile to permit the recording of their mass spectra at temperatures between 200 and 500°. The introduction of the metal chelates into the ion source of the mass spectrometer must be made using a direct insertion probe which allows evaporation of the substance to be made very close to the ionising beam of electrons.[1,2] During the recording of such spectra the sample pressure within the ion source may vary so that it is not possible to relate peak height at any specific m/e value to the concentration of metal chelate. If however the ion current at any specific m/e value can be recorded for the whole time during which a small amount of sample is being evaporated from the probe it is then possible to relate the integrated ion current at this m/e value to the weight of sample evaporated.

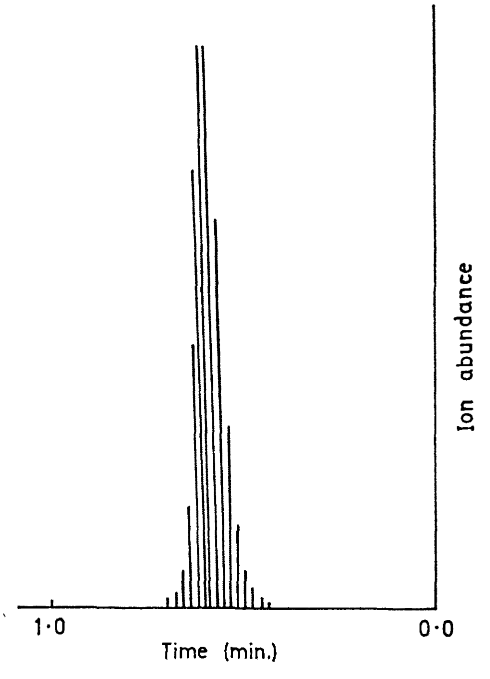

FIGURE 1. *Integrated Ion-current curve of copper 8-hydroxyquinolinate on* $CuOx_2^+$ *peak at* 250°.

The techniques by which this may be achieved using an A.E.I. MS9 double-focussing mass spectrometer have been described previously[3] and very small amounts of substances in the subnanogram range have been detected. Because of instrumental requirements the record of the course of evaporation which is obtained consists of a series of measurements of the ion current at the chosen m/e value taken at one second intervals. A typical record is shown in Figure 1. The envelope of the separate ion-current measurements, the single vertical lines in the diagram, is proportional to the integrated ion current and is related to the amount of sample evaporated. It is only possible to produce such a record with a sample substance which does not evaporate at an appreciable rate at room temperature under high vacuum conditions but which will evaporate rapidly at a temperature attainable within the ion source of the instrument.

It is then possible to focus on the appropriate m/e value before any ion current is being produced and when the sample is in the cool part of the vacuum system. The sample is then lowered into the heated ion source, where it evaporates and becomes ionised. Any m/e value characteristic of the substance may be chosen, but it is advantageous to use a value corresponding to an ion which carries a substantial proportion of the total ion current. The mass spectra of the metal derivatives of 8-hydroxyquinoline are very simple (Figure 2) and it is frequently possible to use the molecular ion peak for integration. In other cases, the m/e value of the peak corresponding to the ion MOx_2^+ (where M = metal and Ox = residue of the 8-hydroxyquinoline group) may be used. When the sample consists of a single substance the integrated ion-current curve has the form shown in Figure 1 but where there are two species in the sample, both of which provide an ion at the same m/e value and which evaporate at different rates, the integrated ion-current curve may show structure. This situation is most commonly encountered when the sample consists of a pair of geometrical isomers and has been demonstrated for a number of organic compounds exhibiting isomerism.[4] The reason for this structure is that the process really consists of a fractional vacuum sublimation into the ion source, with the mass spectrometer acting as a detector. Small differences in the heat of evaporation of the two isomers are being exploited and it is significant that there is an optimum temperature for the resolution of the isomers.

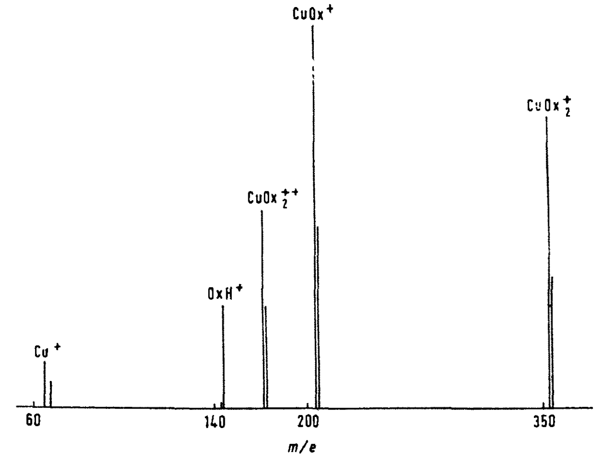

FIGURE 2. *Mass spectrum of Copper 8-hydroxyquinolinate at* 250°.

Although 8-hydroxyquinoline is an unsymmetrical chelating agent and the 8-hydroxyquinolinates of bivalent and tervalent metals should be capable of existing in two geometrical isomeric forms, the existence of such isomers has not previously been demonstrated. The integrated ion-current curve shown in Figure 1 is the record obtained upon evaporating copper 8-hydroxyquinolinate and shows no fine structure. There can be three reasons for the failure to demonstrate two isomeric forms. The copper atom may be tetrahedral in this structure so that no isomerism is possible; the difference in the heat of evaporation between the two isomers may be small; or only one isomer may be formed under the conditions of preparation.

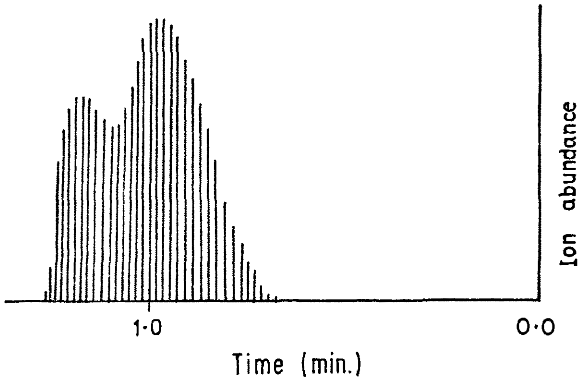

FIGURE 3. *Integrated ion-current curve at zinc 8-hydroxyquinolinate on* $ZnOx_2^+$ *peak at* 400°.

Figure 3 shows the integrated ion-current curve obtained on evaporating zinc 8-hydroxyquinolinate. The two peaks are almost completely resolved, suggesting the existence of two distinct species. This is only possible if the molecule of zinc 8-hydroxyquinolinate is planar. The ionisation cross-section for a pair of isomers must be closely similar so that a measurement of the relative proportions of the two isomers may be made by comparing peak areas. The ratio for zinc 8-hydroxyquinolinate is 3 : 2. It is not possible, however, to predict from the experimental evidence which peak corresponds to which isomer.

Figure 4 illustrates the record obtained upon evaporating iron 8-hydroxyquinolinate, and here the two peaks are clearly resolved and the isomer ratio is 2 : 3. A partial separation was obtained with cobalt 8-hydroxyquinolinate but no structure was obtained on records given by the 8-hydroxyquinoline derivatives of magnesium, nickel, cadmium, or bismuth.

Although the 8-hydroxyquinolinates of tervalent metals were much less volatile than those of the bivalent metals it was possible to obtain records with aluminium, samarium, and indium. Figure 5 illustrates the integrated ion current curve obtained upon evaporating aluminium 8-hydroxyquinolinate. The peaks are not completely separated, but the existence of two isomers is clearly demonstrated. A similar trace was obtained with indium 8-hydroxyquinolinate. No structure was observed in the records obtained for the 8-hydroxyquinolinates of gallium, samarium, gadolinium, or titanium.

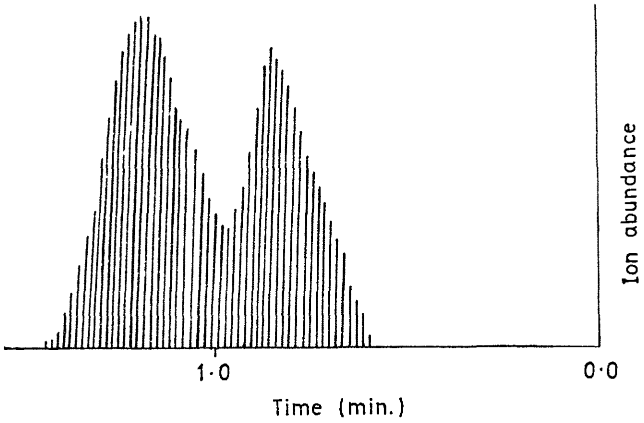

FIGURE 4. *Integrated ion-current curve of iron 8-hydroxyquinolinate on* $FeOx_2^+$ *peak at* 390°.

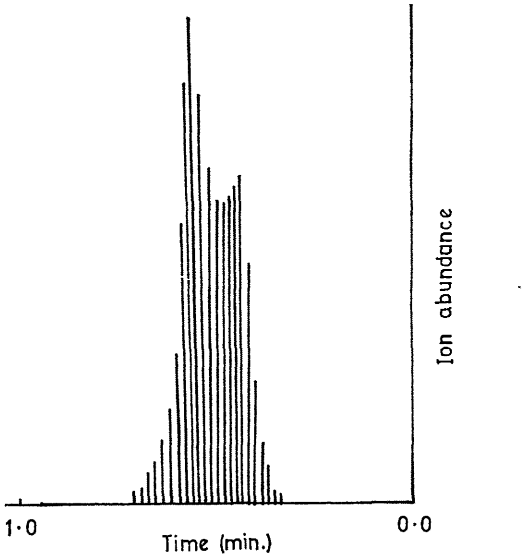

FIGURE 5. *Integrated ion-current curve of aluminium 8-hydroxyquinolinate on* $AlOx_2^+$ *peak at* 400°.

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[1] A. E. Jenkins, J. R. Majer, and M. J. A. Reade, *Talanta*, 1967, **14**, 1213.
[2] J. R. Majer, M. J. A. Reade, and W. I. Stephen, *Talanta*, 1968, **15**, 373.
[3] A. E. Jenkins and J. R. Majer, "Mass Spectrometry" (Proceedings of the Symposium on M.S., Enfield, 1967), Butterworths, London, 1968, p. 253.
[4] J. R. Majer and R. Perry, *J. Chem. Soc.* (*A*), in the press.