Mass Spectra of Butatriene- and 1, 4-Dimethylbutatriene(hexacarbonyl)di-iron and Related Compounds

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Until recently, only few reports on mass spectrometric study of olefin complexes have appeared.1a,b) Fragmentation process and structure of metastable species in the unsubstituted and substituted butatriene iron carbonyl complexes,2a,b,3) $C_4H_4Fe_2(CO)_6$ (I) and $C_4H_2(CH_3)_2{\cdot}Fe_2(CO)_6$ (II) are our present interest. The mass spectra of these complexes revealed that the fragmentation proceeds at first to eliminate six CO groups consecutively and leaves (butatriene)Fe_2^+ which further gave fragment ions of $C_2H_nFe_2^+$, Fe_2^+, $C_2H_nFe^+$ (n= 0, 1, 2, 3, 4), and Fe^+ (Figs. 1 and 2). Previously, di-iron pentacarbonyl structure was proposed2a) for these butatriene complexes. This mass spectrometric results clearly shows the hexacarbonyl structure to be the correct one.*1 The appearance of a strong peak at m/e 112 is in agreement with the independent observation made by King*2 which indicates the presence of a relatively strong iron-iron bond in the complex. In the spectra of I and II, a weak broad peak was observed at m/e 278.8 and 306.3 which showed the occurrance of a meta-stable ion, $C_4H_4Fe_2(CO)_5^+$ and $C_4H_2(CH_3)_2Fe_2(CO)_5^+$, respectively by elimination of one mole of neutral CO molecule. The calculated values, 278.4 and 306.0, were obtained by the equation $M=M_2^2/M_1$, where M stands for m/e of a new peak due to the meta-stable ion, M_1, for the parent peak, and M_2 for M_1 − mass of CO(28).

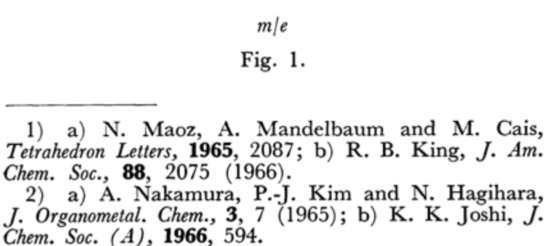


Fig. 1.

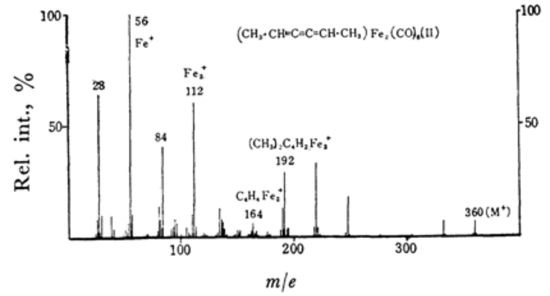
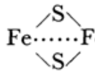


Fig. 2.

An attempted measurement of the mass spectrum of the hexapentaene iron carbonyl complex3) ($C_6H_4Fe_3(CO)_{7-8}$) failed to show its parent peak.*3 However, it exhibited a peak at m/e 168 assigned to a metal atom cluster, Fe_3^+. No strong peak was observed at m/e 112(Fe_2^+). In the mass spectrum of bis-methylthio(hexacarbonyl)di-iron, peaks assignable to $Fe_2(SCH_3)_2^+$, $Fe_2S_2^+$, and Fe_2^+ were observed but, again no parent peak.*3 Stability of  $\mathrm{Fe}\overset{\diagup S \diagdown}{\underset{\diagdown S \diagup}{\cdots\cdots}}\mathrm{Fe}$ system is clearly demonstrated.

A mono-nuclear iron carbonyl complex, diacetyldianil iron tricarbonyl,4) $PhN{=}C(CH_3){-}C(CH_3){=}$

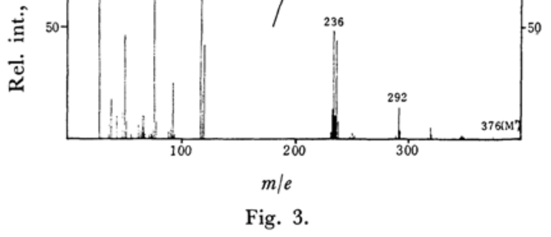


Fig. 3.

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1) a) N. Maoz, A. Mandelbaum and M. Cais, *Tetrahedron Letters*, **1965**, 2087; b) R. B. King, *J. Am. Chem. Soc.*, **88**, 2075 (1966).

2) a) A. Nakamura, P.-J. Kim and N. Hagihara, *J. Organometal. Chem.*, **3**, 7 (1965); b) K. K. Joshi, *J. Chem. Soc. (A)*, **1966**, 594.

3) A. Nakamura, This Bulletin **38**, 1868 (1965).

*1 A very brief communication for the revision of the structure has been reported: A. Nakamura, P-J. Kim and N. Hagihara, *J. Organometal. Chem.*, in press.

*2 A brief report of R. B. King also described mass spectrum of I; *cf.* Ref. 1b.

4) S. Otsuka, T. Yoshida and A. Nakamura, to be published.

*3 The failure to detect any parent peak in these compounds may be ascribed to their intrinsic property or may be due to the unsuitable condition of the measurement.

$NPh\cdot Fe(CO)_3$, showed a series of peaks of which m/e corresponds to $Fe(CO)_n$(diacetyldianil)$^+$, $n=$ 0, 1, 2, 3, and complex mutiple peaks around m/e 236, (diacetyldianil)$^+$. In accordance to its mononuclear structure it showed no 112 peak-(Fe_2^+) (Fig. 3).

Experimental

Preparation and purification of butatriene-iron carbonyl complexes[2a,b,3] and tricarbonyl(diacetyldianil)iron[4] were performed as described in the literature.

The mass spectra were obtained by use of a Hitachi high resolution mass spectrometer Model RMU-7HR working at 80 eV of electron energy. Temperature of ionization chamber was 100°C.

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