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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

XVIII *. PRODUCTS OF ADDITION OF HYDROGEN AND DEUTEROEXCHANGE IN MASS SPECTRA OF SOME π-COMPLEXES OF TRANSITION METALS

G.A. NURGALIEVA, YU.S. NEKRASOV, D.V. ZAGOREVSKII, and D.N. KURSANOV *

Institute of Organoelement Compounds of the Academy of Sciences of the U.S.S.R., Vavilov st. 28, Moscow 117334 (U.S.S.R.)

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Summary

In the mass spectra of some π-complexes of transition metals, obtained by their simultaneous evaporation with organic molecules and deuteroanalogues, protonated (deuterated) molecular and fragment ions have been discovered. They are formed as a result of ion—molecule reactions in the ionization chamber of the mass spectrometer at pressures of 10^{-5}—10^{-4} mmHg as well as during the interactions of neutral molecules.

In the mass spectra of many π-complexes of transition metals, besides ions which are products of intramolecular dissociation of molecules under electron impact, there occur secondary fragments appearing as a result of thermolysis [1] or ion—molecule reactions in the ionization chamber [2]. The superposition of secondary ions on molecular and fragment ions may lead to distortion of the results of the determination of the quantity of an isotope label in organometallic compounds using the mass spectrometric techniques.

In this work we have studied the processes of addition of hydrogen atoms and deuteroexchange of some π-complexes of transition metals (Ia—e) taking place under various conditions of mass-spectral experiments. Earlier [2—6], during the study of ion—molecule reactions of π-complexes of transition metals with organic compounds, the formation of secondary ions having a new metal—ligand bond was observed. However, the reactions of addition or substitution of a ligand are not the only type of processes taking place in gas phase mixtures of these compounds under electron impact at pressures of 10^{-4}—10^{-5} mmHg in

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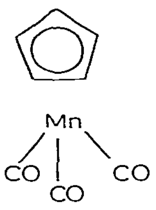
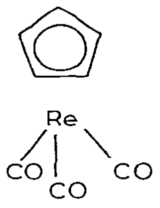
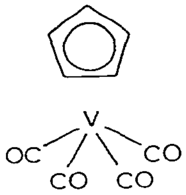
* For part XVII see ref. 6.



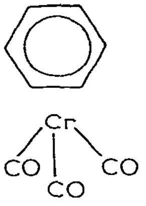
(Ia)



(Ib)



(Ic)



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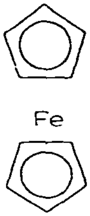

(Ie)

the ionization chamber. During the simultaneous evaporation of complexes Ia—e with the compounds IIa—d (IIa, AcAcH; IIb, PPh_3; IIc, H_2O; IId, I_2) the formation of hydrogenated (protonated) ions of π-complexes is observed (Table 1).

We can assume three possible mechanisms of the formation of protonated ions: 1) the interaction of neutral molecules of the complex and the organic compound with further ionization of the hydrogenated product (reaction 1); 2) ion—molecule reaction of the neutral molecule of the complex with the molecular or protonated molecular ion of the compound IIa—d (reaction 2); 3) ion—molecule reaction with the transition of hydrogen from the neutral organic molecule to the molecular or fragment ions of the complex (reaction 3). In the case of the first or the second mechanism one should expect the formation of protonated molecular and fragment ions with an approximately

TABLE 1

THE RATIO OF THE TOTAL INTENSITY OF PROTONATED (HYDROGENATED) MOLECULAR AND FRAGMENT IONS TO THE INTENSITY OF THE CORRESPONDING PRIMARY IONS (IN %) IN MASS SPECTRA OF Ia—d

Mixture	Intensity (%)			
	M^+	$M^+ - CO$	$M^+ - 2\,CO$	$M^+ - 3\,CO$
AcAcH + $C_5H_5Mn(CO)_3$	—	—	2·9	6·8
AcAcH + $C_5H_5Re(CO)_3$	1·9	4·9	—	—
AcAcH + $C_5H_5V(CO)_4$	24	—	—	3·6 [a]
AcAcH + $C_6H_6Cr(CO)_3$	7·0	—	—	—
PPh_3 + $C_5H_5Mn(CO)_3$	128	137	230	114
H_2O + $C_5H_5FeC_5H_5$	4·3			0·6 [b]
I_2 + $C_5H_5Mn(CO)_3$	132	230	144	137
I_2 + $C_5H_5Re(CO)_3$	—	—	—	2·3

[a] For ion $C_5H_5V^+$. [b] For ion $C_5H_5Fe^+$.

equal degree of hydrogenation, while in the third case the formation of protonated molecular ion is not necessary and the degree of the hydrogenation of fragmentary ions may be different. From Table 1, which shows the ratios between the intensities of protonated and unprotonated ions, it is seen that the degree of hydrogenation of molecular and fragment ions is not the same in all cases. This is especially pronounced in the mass spectra of the mixtures of the complexes Ia—d with acetylacetone which proves that mechanism 3 takes place in these cases, that is the transition of the mobile hydrogen atom from the neutral molecule of acetylacetone to molecular or fragment ion. An unexpectedly high contribution of protonated ions is observed in the mass spectra of mixtures of complexes with iodine. This is related to the intense character of the reaction of the complex with HI which is always present in the mass spectrometer during iodine evaporation (the ratio of the intensities HI^+/I^+ is equal to 1).

$$C_5H_5Mn(CO)_3 + HI \xrightarrow{-I} C_5H_5Mn(CO)_3H \xrightarrow[-2e]{+e} C_5H_5Mn(CO)_3H^+ \qquad (1)$$

$$C_5H_5FeC_5H_5 + H_3O^+ \rightarrow (C_5H_5)_2FeH^+ + H_2O \qquad (2)$$

$$C_5H_5Re(CO)_2^{+\cdot} + AcAcH \rightarrow C_5H_5Re(CO)_2H^+ + AcAc^\cdot \qquad (3)$$

Reactions of deuteroexchange in the gas phase are another type of secondary processes. During the simultaneous evaporation in the mass spectrometer of Ia with various deuterated molecule (Table 2) an increase of weight of $C_5H_5Mn(CO)_3^+$ and $C_5H_5Mn^+$ is observed. On the contrary, the simultaneous introduction into the ionization chamber of cyclopentadienyltricarbonylmanganese vapour with the deuterium label and "non-labelled" compounds decreases the deuterium contents in the metal-containing ions.

It can be assumed that the hydrogen atom exchange takes place as a result of the interaction of the neutral molecules of π-complex and the organic compound before their ionization. However, such transformations have not been observed in the corresponding solutions of π-complexes even during refluxing. This indicates that deuteroexchange is caused by ion—molecule interactions. The unequal degree of deuteroexchange in the molecular and fragment ions (Table 2) also supports the suggested mechanism.

Unlike the unsubstituted complexes Ia—e, for some of their functional derivatives, carboxylic acids and their amides, amines, carbinols etc., containing mobile hydrogen atoms in the substituent, deuteroexchange precedes ionization. For example, the formation of deuterated molecular and fragment ions

TABLE 2

THE AMOUNT OF DEUTERIUM (IN ATOM %) IN IONS $C_5H_5Mn(CO)_3^+$ AND $C_5H_5Mn^+$ IN THE MASS SPECTRUM OF Ia OBTAINED DURING SIMULTANEOUS EVAPORATION WITH DIFFERENT DEUTEROLABELLED COMPOUNDS

Ion	Deuterolabelled compound				
	CD_3OD	CD_3I	$(CD_3)_2CO$	$(CD_3)_2SO$	D_2O
$C_5H_5Mn(CO)_3^+$	0.9	1.0	0.06	—	—
$C_5H_5Mn^+$	0.7	1.3	0.3	1.1	0.1

with an equal amount of label is observed in the mass spectrum of $C_5H_5FeC_5H_4$-COOH obtained with the aid of apparatus preliminary "washed" with heavy water. On the contrary the content of deuterium in the labeled hydroxy group of carbinol $(C_5H_4CH_2OH)_2Fe$ decreases in time even without preliminary evaporation of water in the mass spectrometer. The degree to which the secondary processes take place as well as the nature of the compounds formed depends on the experimental conditions. For instance, the cross-section of ion-molecule reactions increases when the energy of the ionizing electrons decreases [2]. In some cases (during the simultaneous evaporation of cyclopentadienyltricarbonylmanganese (Ia) and CD_3I or CD_3OD) we observed a considerable increase in the deutero-exchange degree when the ionizing chamber temperature was increased.

Thus hydrogenation and deuteroexchange in the gas phase is characteristic of some of the π-complexes. This hampers the isotope analysis of compounds of this class. It should be noted that the study of the secondary processes described was carried out by simultaneous evaporation of the complex with organic and inorganic compounds, the pressures of the latter being increased. However, these reactions can also take place under the usual conditions of obtaining a mass spectrum as a result of the interaction of π-complex ions with its neutral molecules or with the background substances in the spectrometer. In this case the degree of the secondary processes depends on the amount of the evaporated substance as well as the amount and composition of the residual background of the apparatus. That is why the successful solving of the problems of the isotope analysis of π-complexes of transition metals by mass spectrometry requires preliminary experiments aimed at studying their behaviour in the mass spectrometer both under extreme and usual conditional of measuring a mass spectrum.

Experimental

Mass spectra were recorded with a MS-30 apparatus (with the data processing system DS-50) and a MX-1303 apparatus. The evaporation of an organometallic compound was carried out from the direct inlet system, and the volatile organic and inorganic compounds from the glass input system. The "washing" of the apparatus consisted of evaporation of small amounts ($\approx$0.4 ml) of deutero-labelled compounds into an ionization chamber. After the pressure in the ion source was reduced to 10^{-6}—10^{-7} mmHg, the π-complex was introduced and its mass spectrum registered. The experiment was conducted at ionizing voltages of 70, 50, 30, 20 and 12 V. The range of the temperature variation in the ionization chamber was from —70 up to 250° C. The reproduction of the relative intensities of the peaks in the mass spectrum was not worse than 3% relative. The results were processed by the AELITA and ISOMETA [8,9] programs using a Nova 2/10 computer.

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