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Mechanism of Interaction of Dimethylgold(III) Chelates Vapour with Hot Surface

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Abstract. By the electron impact mass-spectrometric method, the temperature dependence of the gas phase structure was investigated at the thermal decomposition of dimethylgold chelate vapour of the general formula $(\text{CH}_3)_2\text{AuL}$, where $\text{L} = (\text{RC}(\text{X})\text{CHC}(\text{Y})\text{R}')$; $\text{R} = \text{CH}_3, \text{C}(\text{CH}_3)_3$; $\text{R}' = \text{CH}_3, \text{C}(\text{CH}_3)_3, \text{CF}_3$; $\text{X} = \text{O}, \text{NH}$; $\text{Y} = \text{O}, \text{S}$ in vacuum and deuterium environment at temperatures up to 350 °C and the saturated vapour pressure by $10^{-4} - 10^{-2}$ Torr. The threshold temperature of the stability of complexes vapour was determined. From the temperature dependence of the rate constant of decomposition processes the effective activation energy was obtained. It was shown that the initial act of the complexes destruction is break of the chelate cycle. The following decomposition process complexes adsorbed at the surface lead to HL , L and CH_3L , methane and ethane by competitive inside- and intermolecular processes. The presence of deuterium (or hydrogen) in the reaction zone causes to decrease onset temperatures for all investigated compounds.

1. INTRODUCTION

Recent publications are indicative of the successful application of acetylacetonate of such metal as nickel and copper /1/, cobalt /2/ and noble metals /3/ as initial reagents for metall film preparation by MOC CVD method. The way of obtaining of the gold film with use dimethylgold acetylacetonate had been describe /4/. However, the literature lacks data on the stability and chemical features of dimethylgold chelates applied. There is no information on the detail mechanism of the thermal decomposition of complexes. The aim of the present work is to study the mechanism of the thermal decomposition process a number of dimethylgold (III) chelates, as far as by varying the substituent and donor atoms of the ligand over a wide range, it is possible to change the electronic structure and the thermal property of complexes. The gas phase composition of thermolysis products of the complexes vapour reflects the process of the gold film formation. Therefore the temperature dependence of the gas phase composition was investigated in this report.

2. EXPERIMENTAL

The dimethylgold(III) complexes with β -diketone and their analogues of the general formula $(\text{CH}_3)_2\text{Au}(\text{RC}(\text{X})\text{CHC}(\text{Y})\text{R}')$, where $\text{R} = \text{CH}_3, \text{C}(\text{CH}_3)_3$; $\text{R}' = \text{CH}_3, \text{CF}_3, \text{C}(\text{CH}_3)_3$; $\text{X} = \text{O}, \text{NH}$; $\text{Y} = \text{O}, \text{S}$, were produced by the technique described in [5]. The composition of the gas phase was determined by the electron impact mass spectrometric method with use of a mass spectrometer MI-1201 and the gaseous input /6/, being the open type reactor of ideal mixing. The complexes at given temperatures of the vapour source, appropriate to the saturated vapour pressure by $10^{-4} - 10^{-2}$ Torr, by the system of pipelines arrived to the heating chamber. The molecular beam of products from the reactor arrived directly to the ion source of the mass spectrometer. To separate the useful signal the interrupter of molecular beam was used. Input of the

other gases is stipulated directly to the reactor. The measurements of the gas phase composition were conducted at fixed temperatures of the reactor at the mode of steady concentrations. To avoid the influence of the surface nature on the process of the thermal decomposition of complexes, the reaction took place at the already generated gold film by the decomposition of the investigating compound.

3. RESULTS AND DISCUSSION

3.1 Thermolysis of $(\text{CH}_3)_2\text{Au}(\text{CH}_3\text{C}(\text{X})\text{CHC}(\text{Y})\text{CH}_3)$ vapour ($\text{X}, \text{Y} = \text{O}, \text{O} - (\text{aa}); \text{O}, \text{S} - (\text{taa}); \text{O}, \text{NH} - (\text{kaa}); \text{NH}, \text{S} - (\text{tkaa})$)

The analysis of mass spectra of these and down investigated complexes vapours has shown the certain generality of ways the destruction under electron impact. In mass spectra of complexes there are molecular ion peaks $[(\text{CH}_3)_2\text{AuL}]^+$ and $[\text{CH}_3\text{AuL}]^+$, $[\text{AuL}]^+$, $[\text{AuH}]^+$, Au^+ peaks and organic ion peaks $[\text{L}]^+$ and $[\text{HL}]^+$ and their fragments. In Fig. 1(a-d) the temperature dependence of ion peak intensities of $(\text{CH}_3)_2\text{Au}(\text{aa})$, $(\text{CH}_3)_2\text{Au}(\text{taa})$, $(\text{CH}_3)_2\text{Au}(\text{kaa})$ and $(\text{CH}_3)_2\text{Au}(\text{tkaa})$ complexes is shown reflecting the change in the gas phase composition at output of thermal reactor. Up to temperatures characteristic for each complex the relative intensities of peaks in mass spectra do not change. Above these temperatures the reduction of the intensities of the metal-containing ion peaks and growth of uncoordinated metal ion peaks takes place. The analysis of mass spectra of the products revealed that the HL, CH_3L , CH_4 , C_2H_6 molecules and non-coordinated radicals of the ligand L were basically formed. It is necessary to note that in the mass spectra of non-coordinated ligand radical formed by the thermolysis, in addition to $(\text{CH}_3)_2\text{Au}(\text{taa})$, the $[\text{L}-\text{H}]^+$ ions uncoordinated proton are registered instead of the $[\text{L}]^+$ ion fragments in the mass spectra of the complexes. We observed the formation of the radicals of some ligands for the destruction of the O,N- and N,S-analogues of dimethylgold acetylacetonates. The concentration ratio essentially depends on the type of atoms of the chelate cycle. The gold-containing products of the thermolysis corresponding to the ion peaks $[\text{C}_2\text{H}_5\text{Au}]^+$ and their fragments, are observed only for $(\text{CH}_3)_2\text{Au}(\text{tkaa})$ complexes. As the result of thermal decomposition of complexes the gold film was formed at the reactor wall. The easily taken off carbon film at the gold film surface was founded for all complexes decomposition. The nature of the donor atoms influences the temperature range of the complexes decomposition. According to the received data at the interaction with a surface the thermal stability of the complexes increases depending on the composition of the chelate cycle (X, Y) in the $(\text{O}, \text{S}) < (\text{O}, \text{O}) < (\text{S}, \text{NH}) < (\text{O}, \text{NH})$ row.

3.2 Thermolysis of $(\text{CH}_3)_2\text{Au}(\text{RC}(\text{O})\text{CHC}(\text{O})\text{R}')$ vapour ($\text{R}, \text{R}' = \text{CH}_3, \text{CF}_3 - (\text{tfa}), \text{R} = \text{R}' = \text{C}(\text{CH}_3)_3 - (\text{dpm})$)

Fig. 2 shows the similar results for the β -diketonates of the dimethylgold complexes. The principal products of the reaction are the most characteristic ones for the complexes described above. The type of the ligand substitutes as well as the central atom's surrounding influences the concentration ratio of the thermal decomposition products and the temperature range of the reaction. For these compounds the radical of ligand there are not in the gas phase product of thermolysis. Comparing the destruction temperature of acetylacetonate complexes $(\text{CH}_3)_2\text{Au}(\text{aa})$ and the data in Fig. 2, it is easy to see that the replacement of one CH_3 group by CF_3 in a ligand causes to decrease of the temperature of decomposition of the complexes. The replacement of both methyl substituents by $\text{C}(\text{CH}_3)_3$ shifts the reaction to the higher temperature range. On the other hand, if the concentration ratio of organic products of thermal decomposition complexes with (aa)- and (tfa)-ligand differs not very much, the dimethylgold compound with (dpm)-ligand differs more essentially. It especially concerns the concentration of the $\text{CH}_3(\text{dpm})$ molecule. For the $(\text{CH}_3)_2\text{Au}(\text{tfa})$ complexes metal-containing products formed by eliminating COF at the temperatures above 125°C are observed.

Figure 1: Temperature dependence of gas phase composition at thermolysis of acetylacetonate derivatives of dimethyl gold(III) ($(\text{CH}_3)_2\text{Au}(\text{aa})$ a), ($(\text{CH}_3)_2\text{Au}(\text{taa})$ b), ($(\text{CH}_3)_2\text{Au}(\text{kaa})$ c), and ($(\text{CH}_3)_2\text{Au}(\text{tkaa})$ d) vapour: $[(\text{CH}_3)_2\text{AuL}]^+$ (1), $[\text{HL}]^+$ (2), $[\text{CH}_3\text{L}]^+$ (3), $[\text{C}_2\text{H}_6]^+$ (4), $[\text{CH}_4]^+$ (5), $[\text{L-H}]^+$ (6), $[\text{L}]^+$ (7), $[\text{C}_2\text{H}_5\text{Au}]^+$ (8).

Figure 2: Temperature dependence of gas phase composition at thermolysis of $(\text{CH}_3)_2\text{Au}(\text{tfa})$ a) and $(\text{CH}_3)_2\text{Au}(\text{dpm})$ b) vapour : $[(\text{CH}_3)_2\text{AuL}]^+$ (1), $[\text{HL}]^+$ (2), $[\text{CH}_3\text{L}]^+$ (3), $[\text{C}_2\text{H}_6]^+$ (4), $[\text{CH}_4]^+$ (5), $[\text{Au}(\text{CH}_3\text{COCHCF}_2)]^+$ (6).

Figure 3: Temperature dependence of gas phase composition at thermolysis of $(\text{CH}_3)_2\text{Au}(\text{ktfa})$ a) and $(\text{CH}_3)_2\text{Au}(\text{iktfa})$ b) vapour : $[(\text{CH}_3)_2\text{AuL}]^+$ (1), $[\text{HL}]^+$ (2), $[\text{CH}_3\text{L}]^+$ (3), $[\text{C}_2\text{H}_6]^+$ (4), $[\text{CH}_4]^+$ (5), $[\text{L-H}]^+$ (6), $[(\text{CH}_3)_2\text{Au}(\text{CH}_3\text{CSCH}_2\text{F})]^+$ (7), $[(\text{CH}_3)_2\text{Au}(\text{CH}_3\text{CSCCF})]^+$ (8).

3.3 Thermolysis of $(\text{CH}_3)_2\text{Au}(\text{CH}_3\text{C}(\text{X})\text{CHC}(\text{Y})\text{CF}_3)$ vapour ($\text{X}, \text{Y}=\text{O}, \text{NH} - (\text{ktfa})$, $\text{X}, \text{Y}=\text{S}, \text{NH} - (\text{tkfta})$)

Fig. 3 shows the thermolysis data for the vapour of the compounds. The principal products of the reaction are the most characteristic ones for the complexes described above, their concentration ratio depends on the atom composition of chelate cycle. The main distinction of the thermal destruction of the present compounds from the complexes described above is the higher production of the ligand radicals. Besides, for complexes with (tkfta) metal-containing products are observed (Fig. 3b). These products are formed by elimination of the CF_2CNH and CF_2NH_2 radical ligand fragments. The replacement of an oxygen atom by a sulfur atom results in the essential decrease of the temperature range of the thermal decomposition of the complexes. The thermal decomposition total process of the complexes can be described by the following scheme:

3.4 Thermolysis dimethylgold chelates in the deuterium

The presence of deuterium in the reaction zone reduces the temperature range of reaction for all investigated complexes and preserves the qualitative composition of the organic products. The interaction of molecules of the complexes with deuterium causes the increase of the total concentration of free ligands - ($[\text{HL}]$, $[\text{DL}]$, $[\text{D}(\text{RCXCDYR}')]$), ethane - ($[\text{C}_2\text{H}_6]$, $[\text{C}_2\text{H}_5\text{D}]$, $[\text{C}_2\text{H}_4\text{D}_2]$) and the reduction of the overall content of ($[\text{CH}_3\text{L}]$, $[\text{CH}_3(\text{RCXCDYR}')]$) methyl-ligand and ($[\text{L}]$, $[\text{RCXCDYR}']$) radicals. Methane do not contain deuterium and its concentration tends to reduce for all complexes. In gas phase there are HD molecules also. Under these conditions, gold-containing products described above for the appropriate complexes are not observed in the gas phase. The total thermal decomposition process of the complexes in deuterium is described by the following scheme:

where $\text{L}(\text{D}) = \text{RC}(\text{X})\text{CDC}(\text{Y})\text{R}'$.

The analysis of received data showed the temperature range and kinetics of the complexes decomposition depends on the ligand type. Decomposition onset temperature of complexes vapour are listed in Table 1. At the variations of initial concentrations of the complexes in the reaction zone the started limits of temperature range of their destruction does not change and the temperature curves of the reaction products, except for methane and ethane, are transformed to each other by a simple change of the ion current intensity scale. It is witness the thermal decomposition process of complexes may be described by a kinetic equation of the first order to the initial component. The relative concentration of methane and ethane products increase by various rate with the growth of the initial vapour pressure of complexes. The rate constant of the thermal decomposition of dimethylgold chelates vapour were calculated from the temperature dependence of molecular ion peak intensities using the equation /8/. The effective activation energy and preexponential factor of the Arrhenius equation are given in Table 2.

The relative intensities of the metal-containing ion peaks at thermal decomposition of the complexes, excepting the cases mentioned above do not change with temperature within the investigated range. The qualitative composition of the thermolysis products shows certain general laws. Near the onset temperature, metal-containing products are not found in the gas phase of thermal decomposition products. The main organic products of the reaction are the free HL ligands, the radicals of the L ligand and CH_3L ligand. The ethane and methane molecules are found in the thermal decomposition products of all complexes. The quantitative ratio of the thermolysis products depends essentially on the ligand type. A visual carbon film

Table 1: Decomposition onset temperatures of $(\text{CH}_3)_2\text{AuL}$ complexes in condensed and vapour states

Compound	Temperature, °C			
	DTA / He	DTA / H ₂	vapour	vapour
	[9]	[9]	in vacuum	in D ₂
$(\text{CH}_3)_2\text{Au}(\text{aa})$	145	125	92	56
$(\text{CH}_3)_2\text{Au}(\text{taa})$	77	--	70	40
$(\text{CH}_3)_2\text{Au}(\text{kaa})$	190	160	275	100
$(\text{CH}_3)_2\text{Au}(\text{tkaa})$	--	--	145	80
$(\text{CH}_3)_2\text{Au}(\text{tfa})$	140	125	70	45
$(\text{CH}_3)_2\text{Au}(\text{dpm})$	200	160	125	--
$(\text{CH}_3)_2\text{Au}(\text{ktfa})$	250	150	200	150
$(\text{CH}_3)_2\text{Au}(\text{tktfa})$	--	--	135	85

Table 2: Effective values of Arrhenius parameters for dimethylgold chelates vapour thermolysis

Compound	Temperature, °C	Activation energy, kJ/mol	Preexp. factor, s ⁻¹
$(\text{CH}_3)_2\text{Au}(\text{aa})$	95 - 150	93.2 ± 6.7	$8.2 * 10^{12}$
$(\text{CH}_3)_2\text{Au}(\text{taa})$	70 - 150	79.4 ± 7.5	$5.8 * 10^{11}$
$(\text{CH}_3)_2\text{Au}(\text{kaa})$	275 - 350	137.5 ± 7.9	$6.8 * 10^{12}$
$(\text{CH}_3)_2\text{Au}(\text{tkaa})$	145 - 220	92.0 ± 8.3	$2.1 * 10^{11}$
$(\text{CH}_3)_2\text{Au}(\text{tfa})$	70 - 130	79.2 ± 7.1	$7.8 * 10^{11}$
$(\text{CH}_3)_2\text{Au}(\text{dpm})$	125 - 170	115.3 ± 8.7	$8.6 * 10^{14}$
$(\text{CH}_3)_2\text{Au}(\text{ktfa})$	200 - 280	92.4 ± 5.8	$1.1 * 10^{10}$
$(\text{CH}_3)_2\text{Au}(\text{tktfa})$	135 - 210	86.1 ± 7.5	$6.3 * 10^{10}$

has been found at the surface of a gold film resulted by decomposition of the complexes, irrespective to the environment (hydrogen or vacuum) it was formed in. The analysis of the thermal behaviour of the thermolysis products shows the qualitative preservation of the gas phase composition but their quantitative ratio depends strongly on the ligand type. This fact testifies the presence of the competitive reactions at the thermal decomposition process of the complexes. The observed result permits to assume the general scheme of thermal decomposition of dimethylgold(III) chelates:

The first stage of the thermal decomposition process on the complexes adsorbed at the surface is the thermal activation of molecules and the break of the donor atom-metal bond. The subsequent acts of destruction are the inside molecular processes, leading to the formation of free ligand (a), methyl-ligand (b) and ligand radicals (c) according to the scheme (III). The alkyl-derivatives of gold indicated in the scheme are the intermediate products. The analysis of thermolysis product in deuterium showed the deuterium attack γ -CH proton. As the result proton and deuterium molecule exchange seats and HD molecule is formed. The molecule of complex is excited and the temperature range of complex decomposition is reduced. The following act of complex destruction take place according to the scheme (III). Methane, ethane and carbon are formed as a result of the secondary reactions during the destruction of these intermediate products or their interaction with each other and with the initial molecules of the complexes. The appropriate channel of the secondary reaction depends on the structure of intermediate products and the orientation of the falling complex in the process of adsorption. From these prerequisites it is possible to offer a number of the alternate secondary reactions:

The influence of alkylgold derivatives to the thermal decomposition process of the complexes was studied by the number of $(\text{CH}_3)_2\text{Au}(\text{kaa})$ samples obtained at various intervals of store after synthesis.

Figure 4: Temperature dependence of gas phase composition at thermolysis of mixture $(\text{CH}_3)_2\text{Au}(\text{kaa})$ and $\text{C}_2\text{H}_4\text{Au}$ vapour : $[(\text{CH}_3)_2\text{Au}(\text{kaa})]^+$ (1), $[\text{HL}]^+$ (2), $[\text{CH}_4]^+$ (3), $[\text{C}_2\text{H}_6]^+$ (4), $[\text{C}_2\text{H}_4\text{Au}]^+$ (5), $[\text{C}_2\text{H}_2\text{Au}]^+$ (6).

At the sublimation of these compounds, besides the molecules of the complex in the gas phase, the alkylgold molecules were registered, which corresponded to the $[\text{C}_2\text{H}_4\text{Au}]^+$ ion peaks and its fragments in the mass spectrum. Fig. 4 shows the results of this experiment. Analysis of the temperature dependence of the composition of the gas phase products shows that the decomposition of the complexes occurs at temperatures 180 °C below the temperature of decomposition of the pure complexes (Table. 1). The thermal decomposition products are the free ligand, ethane and methane, but there are not the methyl-ligand and the ligand radical characteristic for the vapour destruction of the pure complex. The weak temperature dependence of $[\text{C}_2\text{H}_4\text{Au}]^+$ peak is to pay attention on. This fact confirms the catalysis effect of the adsorbed

alkylgold compounds at the surface. At the thermolysis of this mixture vapour the low decomposition temperature, higher output of ethane than methane, the absence of a number of products in comparison with the thermolysis of pure vapour of the given complex confirms the influence of the alkylgold compounds on the thermal decomposition of the investigated complexes.

4. CONCLUSION

The initial stage of the thermal decomposition process of dimethylgold(III) chelates is the break of donor atom-metal bond of the chelate cycle. At the subsequent stage of the complex destruction the free ligand (HL), ligand radical (L) and methyl-ligand (CH_3L) are formed in the gase phase by the competitive inside molecular process. As the result of this process intermediate alkylgold products are produced. The decomposition and interaction of intermediate alkylgold compounds and their collision with molecules of initial complexes produce methane and ethane in gase phase and the gold film at the surface. The temperature range and kinetics of the thermal decomposition vapour of investigated compounds depends on the ligand type. The type of the substituent and donor atom of the ligand determine the probability of some course of the thermal decomposition of complexes.

References

- [1] Van Hemmert R.L., Spendlove L.B., Sievers R.E., *J. Electrochem. Soc.* **112** (1965) 1123-1127.
- [2] Jablonowski E.I., *Cobalt* **14** (1962) 28-33.
- [3] Rand M.I., *J. Electrochem. Soc.* **120** (1973) 686-689.
- [4] Uvarova N.M., Polikarpov V.V., Druzhkov O.N. and Postnikova T.K., Metal β -diketonates (Nauka, Moscow, 1978) pp. 14-15 (in Russian).
- [5] Zharkova G.I., Igumenov I.K. and Zemskov S.V., *Koord. Khim.* **6** (1980) 720-727 (in Russian).
- [6] Grankin V.M. and Semyannikov P.P., *Pribori i tekhnika experimenta* **4** (1991) 129-132 (in Russian).
- [7] Semyannikov P.P., Zharkova G.I., Grankin V.M. et al., *Metaloorg. Khim.* **1** (1988) 1105-1113 (in Russian).
- [8] Bykov A.F., Semyannikov P.P., Igumenov I.K., *J. Thermal Analysis.* **38** (1992) 1463-1475