Thermochimica Acta, 93 (1985) 57-60
Elsevier Science Publishers B.V., Amsterdam

THERMAL DECOMPOSITION OF SILVER ARYLCARBOXYLATES

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ABSTRACT

The process of thermal decomposition of silver(I) complexes with benzoic acid and its para-derivatives has been investigated with the purpose of identification of solid phase intermediate products an isothermic calcination of complexes at the temperatu of appropriate effectsand their X-ray phase and i.r. spectroscop investigation have been carried out.It is shown that all complex decompose single-typly by a radical mechanism.Anhydrous complexe form a free metal and organic compounds.

INTRODUCTION

A big interest presents an exposure of regulatity between the structure and thermal decay of silver complexes,study of an influence of metal nature and substitutes of ligands on the course of thermal decomposition.However,in literature the works dedicated t a thermal analysis of silver complexes are rathe scant.In literature have been studied only thermal and photochemical transformations of silver benzoate in a gas and liquid phases/1/.

The results of synthesis,thermogravimetric,X-ray powder analyses and X-ray structural investigations of silver arylcarboxylate are listed in this work.

MEASURING METHODS

Synthesis of complexes.The investigated complexes synthesized by means of interaction of freshly-prepared solutions of sodium salt of the appropriate acids with silver nitrates in an aqueous medium at pH solution 6-7.The composition of complexes is determined by the method of an element analysis:$Ag(C_6H_5COO)$ (I), $Ag(p\text{-}HOC_6H_4COO)\ H_2O$ (II),$Ag(p\text{-}H_2NC_6H_4COO)\ H_2O$(III),$Ag(p\text{-}CNC_6H_4COO$ $1/4\ p\text{-}CNC_6H_4COOH$ (IV),$Ag(p\text{-}O_2NC_6H_4COO)\ H_2O$ (V),$Ag(p\text{-}ClC_6H_4COO)$ (VI),$Ag(p\text{-}BrC_6H_4COO)$ (VII).

Thermogravimetry.The process of thermal decomposition has been investigated in the atmosphere air on the Hungarian MOM-model with

Proceedings of ICTA 85, Bratislava

electronic registering devices at an interval of temperatures 20-1000°C at a rate of heating furnace 10°C/min.An aluminium oxide was used as an ethalone.With the purpose of exposure of the intermediate and final solid phase products an isothermal calcination of complexes at different temperatures and their X-ray powder and X-ray phase investigations have been carried out.

X-ray analysis.The structures are deciphered by a method of heavy atom and refined isotropically and anisotropically by least square procedure.For the investigated compounds of three-dimensional set of intesities obtained on a fourcircle diffractometr "Syntex $P2_1$"(θ:2θ scan technique, λ Mo-K_α -radiation).Allcalculations were olone on the programmes of "XTL Syntex" and "X-ray-75". The X-ray powder investigation is carried out on a diffracometer Dron-2(λCu-K_α -radiation,V=32 kv,I=20 ma).

RESULTS AND DISCUSSION

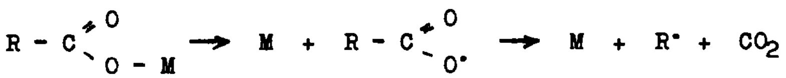
The results of a structural investigation/2/ have showed that the crystal structures of complexes I and II consist of the insulated binuclear molecules(Fig.).A general configuration and character of packing in both structures(I and II) do not considerably differ.A configuration of dimeric molecule determines by a formation of the octatermed rings with a participation of two atoms of Ag.Crystallization water forms a H-bond with a hydroxyl group of p-hydroxybenzoic acid.

Deciphering of thermogrammes of the investigated complexes has showed that a process of thermolysis proceeds in the main single--typely in three stages:1)a removal of complementary ligands,2) a decomposition of salt,3)a burning out of organic compounds and a formation of metal.The data on thermilysis of complexes are listed in the Table.It was discovered that at a rather low temerature (190-350°C) irrespective of ligands as an intrmediate solid phase product forms a free metal.An analysis of literary and personal data gives us ground to assume that a reaction of decomposition of silver carboxylates proceeds by a radical mechanism.It is also pointed out in literature that thermal and photochemical transformations of silver arylcarboxylates proceed by a radical mechanism with a formation of polyphenyls in a marked quantity.However, a formaton of biphenils and the more so,as polyphenyls is not observed at a reaction of phenyl radicals in gas and liquid phases.

Table.Principal thermographic date of the complexes

Complex	Temperature range, °C, (DTA)	t_{max}, °C (DTA)	Mass loss %		Solid state products composition
			Found	Calc.	
I	200-265	250			
	265-290	275	43.2		Ag + (C)
	305-455	375	52.7	52.8	Ag
II	35-75		4.4	3.3	adsorb.water
	75-115	95	10.8	9.9	Ag(p-HOC_6H_4COO)
	160-200	190	13.6		Ag + (C)
	200-285	240			
	285-315	295	38.0		Ag + (C)
	315-650	395,540	60.3	60.3	Ag
III	80-115	95	7.3	6.9	Ag(p-$H_2NC_6H_4COO$)
	135-180	165	31.2	32.5	
	180-225	190	47.1		Ag + (C)
	300-355	310			Ag + (C)
	525-700	575	59.6	58.8	Ag
IV	40-85	65	4.0	5.9	Ag(p-CNC_6H_4COO)
	320-380	350	47.5	47.7	Ag
V	100-205	165	7.0	6.2	Ag(p-O_2N-C_6H_4COO)
	205-310	270	46.7	44.0	Ag
VI	280-320	285			
		310			Ag
VII	280-330	295			Ag + (C)
	455-590	540			Ag + (C)
	540-720	685			Ag

Possibly that this is a result of a topochemical reaction between phenyl radicals in a solid state. An arrangement in a crystal lattice of the molecules of silver benzoates, as well as other carboxylates must promote proceeding of a similar reaction. Thus, the fact of polyphenyls formation under a thermolysis of silver carboxylates is in good agreement with a structural peculiarity of the latters. The reactions of a thermolysis of silver carboxylates can be presented by a following scheme:



$$R-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O-M} \longrightarrow M + R-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O^{\bullet}} \longrightarrow M + R^{\bullet} + CO_2$$

Therefore, these reactions present rich sources of radicals and free atoms of silver which is confirmed by our X-ray powder analysis of the products of thermolysis.

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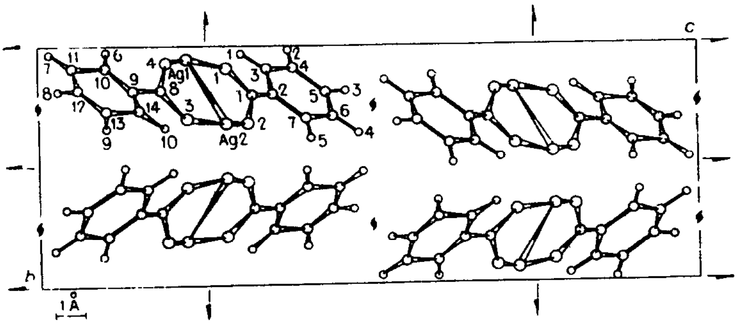

Fig. The Crystal structure of I.