

THE THERMAL DECOMPOSITION OF SOME RHODIUM(II) CARBOXYLATE COMPLEXES*

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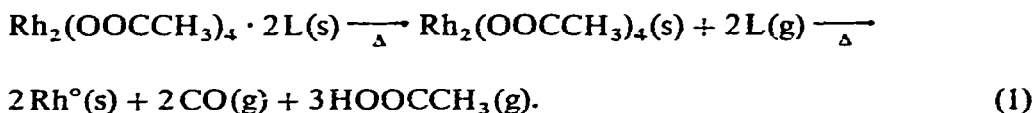
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ABSTRACT

Rhodium(II) propionate, benzoate, trichloroacetate and trifluoroacetate have been prepared and studied by several thermoanalytical techniques. The thermal decomposition products of the propionate and benzoate complexes were determined using thermogravimetric analysis and mass spectrometry. Properties of the trifluoroacetate complex were studied by mass spectrometry and magnetic measurements. Several adducts of the complexes were prepared.

INTRODUCTION

Studies involving the thermal decomposition of rhodium(II) acetate and several of its adducts have recently been reported in the literature^{1,2}. The decomposition sequence was found to be



When L is dimethylsulfoxide or diethylsulfide the donor species comes off stepwise producing a stable monoadduct as the first step in the decomposition².

It is of interest to note that the rhodium is reduced in the decomposition sequence to the free metal and no oxide is formed even if the reaction is carried out in air. With the preparation of other dimeric rhodium(II) carboxylates, our goal was to determine if the metal and free acid were general products in the decomposition reactions or if the products were a function of the carboxylate ligands.

EXPERIMENTAL

The syntheses of the rhodium(II) carboxylates of propionic, benzoic, trichloroacetic, and trifluoroacetic acids were carried out by similar processes. Specifically,

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2.0 g of rhodium(III) chloride hydrate were dissolved in 100 ml of absolute ethanol and then saturated with the desired anhydrous sodium carboxylate. The resulting solution was refluxed thirty minutes to two hours. The solution, which had a strong ester smell, turned from red to green in the propionate and benzoate preparations and to a deep brown-green color in the trichloro- and trifluoroacetate preparations. Upon cooling, the mixture was filtered to remove the excess carboxylate salt. In the benzoate case, blue-green needles were obtained by the slow evaporation of the reaction mixture. The needles were found to be fairly insoluble in cold ethanol, water or benzene, however, they were soluble in acetone from which they were recrystallized in high yield.

Anal. Calc. for rhodium(II) benzoate: C, 48.72; H, 2.92. Found: C, 48.81; H, 3.09.

The best method found for preparing the other carboxylates was to evaporate the reaction mixture and dissolve the residue in water. The water solution was extracted with dichloromethane until the extract was colorless. The dichloromethane was allowed to evaporate and the resulting crystals were recrystallized from other solvents depending upon the compound involved. The rhodium(II) trifluoroacetate was soluble in a variety of solvents including benzene from which it was recrystallized. When necessary further purification was obtained by sublimation which occurs at $\sim 350^\circ\text{C}$ at one atmosphere pressure.

Purification of the trichloroacetato- and propionato-rhodium(II) compounds was accomplished by recrystallization from acetone.

Anal. Calc. for rhodium(II) propionate: C, 28.94; H, 4.05. Found: C, 30.19, 30.01; H, 4.01, 4.14. *Calc.* for rhodium(II) trichloroacetate: C, 11.23; Cl, 49.74. Found: C, 12.00; Cl, 48.61.

The thermogravimetric analysis (TGA) curves were recorded on a DuPont Thermogravimetric Analyzer Model 950. All the samples were run at a heating rate of $20^\circ\text{C}/\text{min}$ and under a flowing dry nitrogen atmosphere.

Magnetic measurements were made by means of the Faraday method using a Cahn RG Electrobalance and an Alpha Model 9500 six inch electromagnet with Faraday pole pieces. Mercury thiocyanatocobaltate(II) ($\chi_A = 16.44 \times 10^{-6}$ cgs)³ was employed as a calibrant and a field strength of 8000 G was used. The electrobalance and the sample which was held in a small quartz boat suspended by a quartz fiber were completely enclosed in a glass case and hangdown tube permitting atmospheric control. All samples were run in air.

The magnetic susceptibilities were calculated from the formula:

$$\chi'_M = M \cdot \chi_A - \chi_{M(\text{corr.})} \quad (2)$$

where χ'_M is the corrected molar susceptibility, M is the molecular weight, $\chi_{M(\text{corr.})}$ is the diamagnetic correction for the ligands and χ_A is the gram susceptibility of the unknown compound; χ_A was calculated from:

$$\chi_A = \chi_{\text{Std.}} \frac{(\Delta m_u - \Delta m_c)}{(\Delta m_s - \Delta m_c)} \cdot \frac{m_s}{m_c} \quad (3)$$

(χ_{Std} is the gram susceptibility of the standard, m_s and Δm_s are the weight of the standard and its change in weight upon application of the magnetic field, m_u and Δm_u are the weight of unknown and its change in weight in the magnetic field, Δm_c is the change in weight of the boat when the field is applied). The effective magnetic moment in Bohr Magnetons was computed from

$$\mu_{eff} = 2.839[\chi'_M T]^{0.5} \quad (4)$$

where T is the absolute temperature. The diamagnetic corrections were estimated from Pascal's constants⁴.

The mass spectra of the gaseous decomposition products were obtained on an Atlas Model CH-4 mass spectrometer made by Mess and Analysen Technical GMBH, Bremen, Germany. A Pyrex tube containing the sample was placed in a stainless steel furnace attached to the inlet system of the instrument. The furnace was evacuated and then heated until the decomposition occurred. The gases were led directly into the inlet system which was maintained at 125°C. Decomposition products were identified by either comparison with known spectra taken under the same conditions or by their appearance potentials. The mass spectrum of rhodium(II) trifluoroacetate was recorded on an LKB Model 9000 mass spectrometer at an ion voltage of 70 eV with a source temperature of 250°C and a probe temperature of less than 200°C.

RESULTS AND DISCUSSIONS

The preparation of rhodium(II) benzoate is described here for the first time. The other rhodium(II) carboxylates have been prepared previously^{5,6,7} although the method of preparation may have been somewhat different. Rhodium(II) benzoate, as it is crystallized from acetone, is in the form of deep blue-green needles. The desolvated form which is yellow-green in color can be made by heating a crushed sample in a vacuum oven for about two hours. The thermogravimetric analysis curve in Fig. 1 shows that the solid is stable up to 350°C where the decomposition takes place rapidly. The grayish residue is undoubtedly an oxide of rhodium, however,

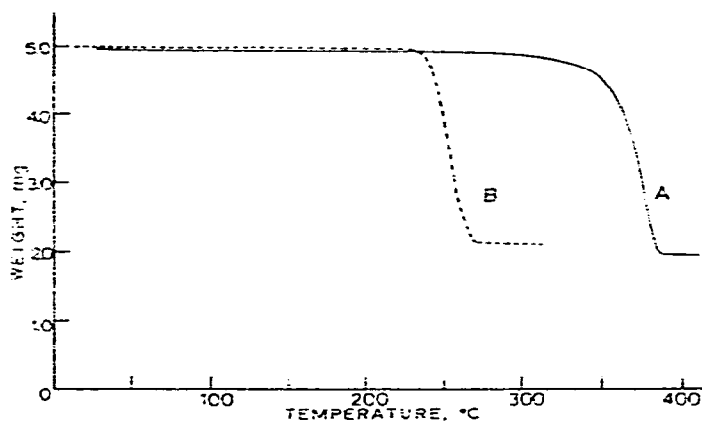


Fig. 1. Thermogravimetric analysis curve of: A, rhodium(II) benzoate and B, rhodium(II) propionate.

the percent of residue was not repeatable and cannot be used to identify which oxide is present. The mass spectrum of the gases from the thermal decomposition is shown in Fig. 2. The peaks at $m/e = 78$, 44, and 18 were identified by appearance potentials

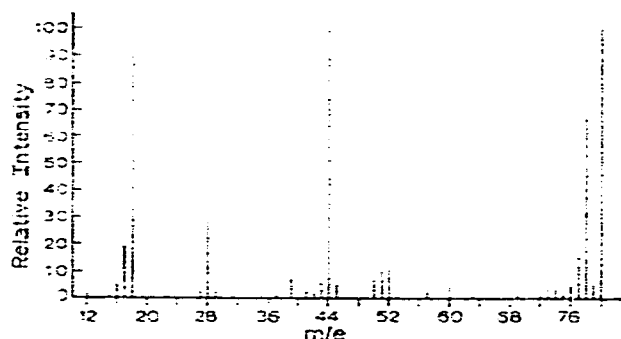


Fig. 2. Mass spectrum of the gases from the thermal decomposition of rhodium(II) benzoate.

as due to benzene, carbon dioxide, and water, respectively. There was no evidence of any benzoic acid, toluene or biphenyl as reaction products. The large amount of water appearing in the mass spectrum is probably not a product of the decomposition reaction but a result of moisture embedded in the stainless steel furnace and inlet system. The water appears to play a part in forming the reaction products under these conditions. The initial step in the decomposition reaction is believed to be the decarboxylation of the benzoate ligand forming the phenyl radical which can then abstract a hydrogen atom from water leading to the formation of benzene, $m/e = 78$, and OH, $m/e = 17$. The products of the decomposition found by mass spectrometry indicate that the pathway is not as simple as that found for rhodium(II) acetate². In the benzoate case there appears to be several competing reactions dependent on conditions leading to different products.

The thermogravimetric analysis curve of rhodium propionate is shown in Fig. 1. The residue weight is equal to that expected for rhodium metal. The mass spectra of the decomposition gases (see Fig. 3) shows the major peak to be $m/e = 28$ which

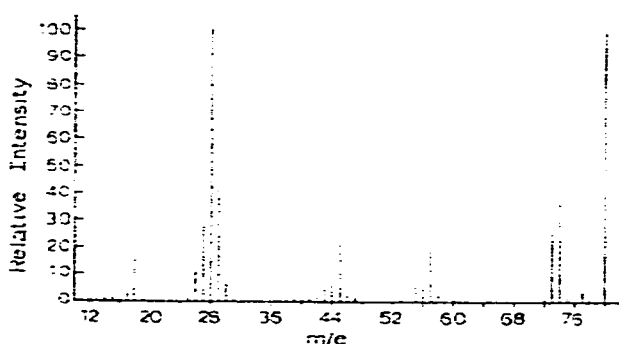


Fig. 3. Mass spectrum of the gases from the thermal decomposition of rhodium(II) propionate.

is due to carbon monoxide and ethylene. The peaks at $m/e = 27$, 29, 57, 73, and 74 correspond to the following fragments of propionic acid: $[\text{CH}_2=\text{CH}]^+$, $[\text{CH}_3-\text{CH}_2]^+$,

$[\text{CH}_2\text{-CH}_2\text{-C=O}]^+$, $[\text{CH}_2\text{-CH}_2\text{-COOH}]^+$, and $[\text{CH}_3\text{-CH}_2\text{-COOH}]^+$, respectively. Although the results are not conclusive the most probably pathway for the decomposition of rhodium(II) propionate is as follows:



Rhodium(II) trifluoroacetate sublimes before decomposition. This property was used to find its molecular weight by utilization of the solid probe on the LKB Model 9000 mass spectrometer. The highest observed m/e value is 658 which corresponds to the expected molecular weight of the rhodium(II) trifluoroacetate dimer indicating that the dimeric structure is present even in the gaseous form. The manner in which this compound decomposes in the mass spectrometer is interesting (see Fig. 4). The dimer breaks down in a set pattern losing one carboxylate group at a

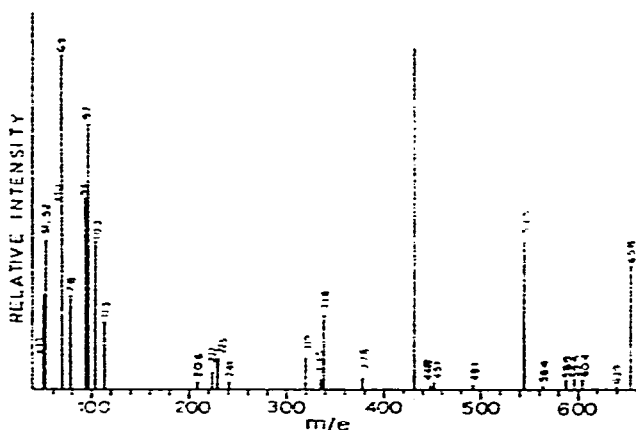


Fig. 4. Mass spectrum of rhodium(II) trifluoroacetate.

time leading to the formation of: $\text{Rh}_2(\text{OOCF}_3)_3^+$, $m/e = 545$; $\text{Rh}_2(\text{OOCF}_3)_2^+$, $m/e = 432$; and $\text{Rh}_2(\text{OOCF}_3)^+$, $m/e = 319$. The intensity of the peak corresponding to $\text{Rh}_2(\text{OOCF}_3)_2^+$ suggests that this ion is quite stable. Some of the other interesting products in the mass spectrum are $(\text{Rh}_2\text{OF})^+$, $m/e = 241$; $(\text{Rh}_2\text{F})^+$, $m/e = 225$; $(\text{Rh}_2\text{O})^+$, $m/e = 222$; and $(\text{Rh}_2)^+$, $m/e = 206$.

Rhodium(II) trichloroacetate was the last of the series to be prepared and although some of its other properties were extensively studied, a study of its thermal decomposition was not undertaken.

Many of the properties and reactions of these rhodium(II) carboxylates are very similar to those of rhodium(II) acetate. The magnetic moments given in Table I measured at room temperature vary somewhat from the desolvated rhodium(II) acetate moment of 0.16 B.M.; however, they indicate that the strong interaction between the two rhodium atoms is still present.

The colors of the products of the reaction of rhodium(II) carboxylates with some selected donor ligands are given in Table II. With most of the donor ligands the colors are very similar to those for the acetato-compound. The trichloro- and trifluoroacetato compounds are more susceptible to degradation by nucleophiles with decom-

TABLE I

MAGNETIC DATA FOR SOME RHODIUM(II) CARBOXYLATES AT 298°K

Compound	χ_M' (cgs)	χ_M (corr.) (cgs)	μ_{eff} (B.M.)
$\text{Rh}_2(\text{OOCCH}_2\text{CH}_3)_4$	$\pm 22.6 \div 10^{-6}$	-162.4×10^{-6}	0.165
$\text{Rh}_2(\text{OOC}_6\text{H}_5)_4$	$\pm 32.4 \times 10^{-6}$	-259.8×10^{-6}	0.28
$\text{Rh}_2(\text{OOCF}_3)_4$	-3.6×10^{-6}	-155.4×10^{-6}	
$\text{Rh}_2(\text{OOCCL}_3)_4$	$\pm 70.0 \times 10^{-6}$	-321.0×10^{-6}	0.41

position taking place with prolonged or repeated exposure. There are, however, obvious dissimilarities in Table II between the compounds formed by the reaction of dimethylsulfoxide with the acetato, propionato, and benzoato, and the trichloro- and trifluoroacetato compounds. The former group forms an orange adduct complex with dimethylsulfoxide which, as discussed earlier, results from the metal-sulfur bonding⁷. The latter two form a deep blue solution upon addition of dimethylsulfoxide. With the removal of the excess ligand, a greenish tar-like substance remains which the thermogravimetric analysis curve in Fig. 5 indicates is not a true adduct

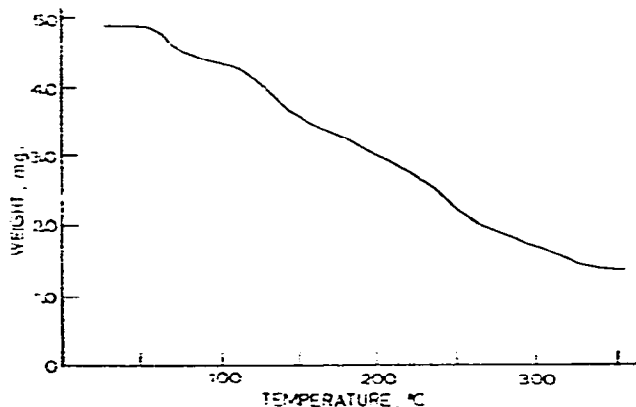


Fig. 5. Thermogravimetric analysis curve of the product resulting from the reaction of dimethylsulfoxide with rhodium(II) trichloroacetate.

as in the case of rhodium(II) acetate^{1,2,7}. The indication is that this is a degradation product in which the cage structure has been destroyed. The color of the initial solution indicates two possibilities, either the dimethylsulfoxide does not add to the axial positions or the bonding through the oxygen atom instead of the sulfur atom.

It is obvious from this investigation that the decomposition products depends on the structure of the carboxylate ligand. In the case of the acetate and propionate complexes the free acids and rhodium metal are the major products whereas the decomposition of the benzoate complex produces an oxide of rhodium and no free acid. It appears that the weakest bond in the carboxylate ion is broken and initiates the decomposition process. For the aliphatic carboxylates the α -carbon-hydrogen bond is the most probable bond to break. The mechanism we would like to propose

TABLE II
COLOR OF REACTION PRODUCT OF RHODIUM(II) CARBOXYLATES WITH SOME SELECTED LIGANDS

Compound	Color of desolvated form	Color of reaction products with ligand					
		2 H ₂ O	2 N(CH ₃ CH ₃) ₃	2 Pyridine	2 Triphenylphosphine	2 S(CH ₂ CH ₃) ₂	2 DMSO
Rh ₂ (OOCCH ₃) ₄	Green	Green	Purple	Rose-pink	Yellow-orange	Burgundy	Orange
Rh ₂ (OOCCH ₂ CH ₃) ₄	Green	Green	Rose-violet	Rose-pink	Yellow-orange	Burgundy	Orange
Rh ₂ (OOCCH ₂ CH ₂) ₄	Yellow-green	Blue-green	Rose-violet	Rose-pink	Yellow-orange	Rose-red	Orange
Rh ₂ (OOCCH ₂ CF ₃) ₄	*Green at high temperatures; blue-green at room temperature; purple at 77°K	Blue	Rose-red	Red-orange	Yellow-orange	Rose-red	Blue in solution
Rh ₂ (OOCCH ₂ Cl) ₄	Green	Blue	Rose-red	Red-pink	Orange	Burgundy	Blue in solution

*This affect may be due to rapid absorption of water by the molecule

for this type of reaction will be illustrated using the acetate case. The first step is the loss of a proton from the α -carbon which protonates an oxygen of one of the other acetate groups. An α -lactone can then be formed with the reduction of one of the metal ions. The α -lactone is unstable to dissociation to CO and formaldehyde. At these temperatures, formaldehyde is highly reactive to decomposition and is capable of further reduction of the rhodium and the protonation of the remaining two acetate groups leading to another CO molecule and two other acetic acid molecules.

This reaction is in contrast to the benzoate complex where there is not an α hydrogen and the bond between the carboxyl carbon and the ring carbon is the weakest. The phenyl radical is thus formed which is capable of abstracting a hydrogen atom from water as discussed earlier. However, total mechanistic interpretation in the case is difficult because of the several competing reactions which take place leading to the variation in the oxide composition as observed.

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