THE REACTIONS AND KINETICS OF RHODIUM(II) ACETATE WITH CARBOXYLIC ACIDS

A Thesis

Presented to

the Faculty of the Department of Chemistry College of Arts and Sciences University of Houston

> In Partial Fulfillment of the Requirements for the Degree Master of Sciences

> > bу

Garland R. Barnes August, 1970

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ABSTRACT

The reaction of rhodium(II) acetate with excess carboxylic acids were followed by ¹H nuclear magnetic resonance spectroscopy. The reaction was found to be a stepwise exchange of deuteroacetate for the acetate cage. The rate constants measured have a ratio of approximately 1:0.75:0.5:0.25 for $k_1:k_2:k_3:k_4$. The ratio is due to a statistical effect depending on the number of "exchange" sites available on the reaction species.

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INTRODUCTION

In recent years there has been an interest in compounds with homonuclear metal-metal interactions. Special interest has been given in this laboratory to the dimeric carboxylates of the transition metal ions, the general structure of which is shown in Figure 1. In these dimers the two



Figure 1. Model of $M_{2}(OOR)_{4}$

metal ions are found in close proximity to each other and are bridged by four carboxylate groups. The metal-metal interaction varies from weak, antiferromaganetic spin-spin coupling to strong sigma bonding, and in some cases, also, pi and delta bonding depending on the properties of the metal involved.

There are six transition metal ions for which this type of metal carboxylate structure has been established by X-ray crystallography. Tetrabenzoatodirhenium chloride (1), tetra-n-butyratodiruthenium chloride (2), and the acetates of copper(II) (3), chromium (II) (4), molybdenum(II) (5), and rhodium(II) (6) have been found to possess the dimeric structure. Other carboxylates of these metal ions exist , but their structures have not yet been determined by X-ray.

An extensive study of a selected group of rhodium(II) carboxylates has been done by Kitchens and Bear (7). In the above study emphasis was placed on the thermal, magnetic, and spectroscopic properties and also the building of a theoretical model to explain the observed properties and reactions of the rhodium(II) carboxylates. Primarily, interest was placed on the properties of reaction products of rhodium(II) acetate with several donor-type ligands. Also, the "exchange" reaction in which rhodium(II) trifluoroacetate is formed by the reaction of rhodium(II) acetate with excess trifluoroacetic acid was studied by nuclear magnetic resonance spectroscopy.

The hydrate, $Rh_2(OOCCH_3)_4 \cdot 2H_20$, was first prepared in 1962 by Cherynaev, <u>et al</u> (8) by the action of acetic acid on ammonium hexchlororhodate(III) in the aqueous-ethanol solution. X-ray analysis by Porai-Koshits and Antsyshkina (6) has shown the metal-metal distance to be about 2.45Å which is shorter than the 2.6901Å (9) found in metallic rhodium. Magnetic susceptibility measurements by Belova (10) showed that the compound is diamagnetic, but its susceptibility varies with temperature.

In 1963, Johnson, <u>et al</u> (11) reported the preparation of anhydrous or desolvated rhodium(II) acetate by the action of glacial acetic acid on freshly precipitated rhodium(III) hydroxide. They found rhodium(II) acetate to be stable indefinitely in the solid form, aqueous solutions, and a wide variety of organic solvents, but that the cage structure is destroyed quite readily by strong acids.

Desolvated rhodium(II) acetate is thermally stable up to a procedural decomposition temperature of about 250°C (7). At this point it decomposes rapidly yielding a residue consisting of rhodium metal. It reacts with

electron pair donor type ligands to form adducts of the composition, $Rh_2(OOCCH_3)_4 \cdot 2L$ as reported by Chernyaev and co-workers (10,12). They reported compounds of this type with the following ligands: ammonia, pyridine, acetamide, guandinium halides, thiourea, and potassium nitrite. They found that the complexes with the neutral-type molecules are nonelectrolytes where as those of the guandinium halides and potassium nitrite are three-ion electrolytes. With inorganic salts, compounds of the type $Rh_2(OOCCH_3)_4 \cdot MX$ and $Rh_2(OOCCH_3)_4 \cdot 4NY$ (where MX is KC1 or NH_4C1 and NY is KC1, KBr, NH_4C1 or NH_4Br) are formed. The latter type of complexes are reported to be five-ion electrolytes. Johnson, <u>et al</u> (11), also reported the preparation and properties of some 1:2 adducts using the following ligands: water, tetrahydrofuran, acetonitrile, dimethylsulfoxide, dimethylsulfide, trimethylamine, ammonia, nitric oxide, pyridine, and ethylenediamine.

More recently the haloacetato-complexes of rhodium(II) have been prepared by Winhaus and Ziegler (13). Probably the most interesting reported compound is that by Maspero and Taube (14) of the aquorhodium(II) ion. It is a dimer with a bond between the two rhodium ions, but since it lacks the added stability due to the carboxylate bridges as found in rhodium(II) acetate, it is easily oxidized in the presence of air.

Kitchens and Bear (7) reported the formation of 1:2 type adducts as well as a new type adduct of the formula $Rh_2(OOCCH_3)_4$ ·L from the reaction of rhodium(II) acetate with donor type ligands. Some of the ligands used were water, diethylsulfide, dimethylsulfoxide, pyridine and ethyl amines. An interesting feature was noted from the spectroscopic data.

Compared to the spectral data of the desolvated rhodium(II) acetate the peak maxima shifted towards the ultraviolet with adducts formed from ligands of different electron donor ability. Magnetic susceptibility studies on the adducts show that they are diamagnetic. The stabilities were determined from the procedural decomposition temperatures and ranged from 75°C for diethylamine to 170°C for pyridine.

The data presented such as calorimetric measurements, magnetic susceptibility and spectroscopic measurements substantiates the stability of the 1:2 type adducts where the ligands occupy the terminal positions along the rhodium-rhodium axis. With the rhodium(II) acetate dimer containing two ligands per molecule, this makes each rhodium ion have a coordination number of six. Then the stability of the adducts formed depends on the donor ability of the ligands which, upon addition to the complex, tend to stabilize the system and thus increase the attraction between the two rhodium ions.

Kitchens and Bear (7) also reported the preparation and properties of some rhodium(II) carboxylates of propionic, benzoic, trichloroacetic, and trifluoroacetic acids. All of the compounds were found to be quite stable. The benzoate and propionate are stable to above 300 and 200°, respectively, and the trifluoroacetate sublimes before decomposition at about 350°C and one atmosphere. Many of the properties of the carboxylates were similar to those of rhodium(II) acetate, and magnetic measurements indicated that the strong interaction between the two rhodium atoms was still present.

Reactions of this type have created an interest in this laboratory to study further the reaction between rhodium(II) acetate and carboxylic acids. The reaction of rhodium(II) benzoate with trifluoroacetic acid was investigated, but the preliminary data lends itself to such a complicated form that no results were obtained. The reaction of rhodium(II) acetate with trifluoroacetic acid has been reported to yield the corresponding rhodium(II) trifluoroacetate (11). It is an exchange reaction in which the acetate cage is exchanged for a trifluoroacetate cage. More recently, Bear, Kitchens, and Willcott (15) have reported the kinetics of the exchange reaction between trifluoroacetic acid and rhodium(II) acetate. The exchange reaction was followed by ¹H nuclear magnetic resonance spectroscopy. It was thought that each substitution involved essentially the same process and that all the rates would be similar. This was not the case, however, and it was found that the second substitution (k_2) was twice as large as k_1 and that k_3 and k_4 were much smaller than would be expected. The fact that k₂ was twice as large as k_1 indicated a possible trans-effect in that step of the reaction. It was stated that the trans-effect was probably due to an increase in the pi bonding between the pi orbitals of the carboxyl groups of the trifluoroacetate and the d_{xv} orbitals of the rhodiums due to polarization of the pi system by the fluorine atoms. The results was a kinetic labelization of the acetate group in the trans position. If the trans-effect is in fact the result of the polarization caused by the fluorines of the trifluoroacetate, then elements with less polarzation effect should tend to cause the rate constants to be more nearly the same.

This work was undertaken to investigate further kinetics of the exchange reaction by ¹H nuclear magnetic resonance spectroscopy between carboxylic acids and rhodium(II) acetate. The acid chosen for this study was deuteroacetic acid.

EXPERIMENTAL

Rhodium(II) acetate was prepared by two methods. One method involved refluxing 80 ml of glacial acetic acid with 2.0 grams of freshly precipitated rhodium(III) hydroxide for eighteen hours. The resulting green solution was evaporated to dryness on a rotary evaporator and the residue extracted with boiling acetone. The solution was allowed to evaporate slowly, and the resulting deep green crystals were recrystallized from either acetone or water. The method was lengthy and results in a poor yield based on the amount of rhodium(III) chloride hydrate used in the precipitation of the hydroxide. A better yield was obtained by combining 2.0 grams of rhodium(III) chloride hydrate and 100 ml of absolute ethanol saturated with anhydrous sodium acetate and refluxing until the solution turned a deep blue-green color (about two to three hours at 80°C). The mixture was filtered and allowed to evaporate slowly. The resulting blue crystals were then recrystallized from water or acetone. The desolvated form of rhodium(II) acetate was obtained by heating crushed crystals in a vacuum oven at 120° for two to three hours. Carbon and hydrogen analyses were performed by Huffman Laboratories, Inc., Wheatride, Colorado. The deuteroacetic acid used as a solvent was obtained from Dr. M. R. Willcott.

The exchange reaction was followed by ¹H nuclear magnetic resonance spectrometry using a Varian Model HA-100 instrument. The probe temperature was 32°C. In a typical experiment, two to four milligrams of anhydrous rhodium(II) acetate was weighed into a 5 millimeter nmr tube and 0.33 milliliters of deuteroacetic acid was added. The solution was then mixed using a Vortex mixer. Tetramethylsilane was added to act as an internal reference. As soon as dissolution was completed (about 20 minutes), the spectra were recorded as a function of time and the kinetic data were obtained by integration of the signals. All of the spectra were obtained at 50 cycles per second with a 250 second sweep time.

It was noted from the first experimental run that very little reaction, if any, occurred until the sample was heated above the probe temperature of 32°C. It was determined that after heating the sample in a constant temperature oil bath at $68.5^{\circ}C\pm0.05^{\circ}C$ for ten minutes, enough reaction had occurred to make a noticeable difference in the nmr spectrum. A cycle was established so that the sample (while remaining in the nmr tube) 1) was placed in the constant temperature bath for ten minutes, 2) removed and placed in the nmr probe, 3) the spectrum obtained and integrated, then 4) removed from the probe and placed back in the constant temperature bath to start the next cycle. The time for each cycle was measured to determine if it remained constant over a period of several runs. If the nmr was properly tuned and the instrument conditions were not changed, an average cycle took 20 to 22 minutes. In order to determine if the reaction continued after it was removed from the constant temperature bath, a sample was allowed to remain in the probe after going through six cycles. While the sample remained in the probe, spectra were obtained 1) just after removal from the constant temperature bath, 2) at ten minute intervals for 30 to 40 minutes, and

3) after being in the probe for one and a half hours and no reaction was observed. The reaction then was a function of the time the sample was heated. So the data obtained was recorded as such.

RESULTS AND DISCUSSION

When rhodium(II) acetate was exposed to an excess of some carboxylic acids, an "exchange" reaction occurred to some degree. The reaction of rhodium(II) acetate with trifluoroacetic acid has been reported (7,11). The acetate cage exchanged with a trifluoroacetate cage and eventually led to the formation of rhodium(II) trifluoroacetate.

The first step in the reaction was the dissolution of the rhodium(II) acetate in the trifluoroacetic acid. This resulted in trifluoroacetic acid adding to the axial positions of the rhodium(II) acetate cage. The adduct formation was a fast and reversible process and was directly involved in the exchange in that it was probably solvent in the axial position which substituted for the acetate cage.

The various possible reaction steps for the exchange are shown in Figure 2.* Since the trifluoroacetic acid was in large excess, the reverse reactions were considered negligible. The equation governing the reaction rates shown in Table 1 were programmed in an analog computer in terms of methyl proton concentrations. The rate constants obtained from the computer confirmed k_5 , k_6 and k_7 to be zero and that k_2 was twice as large as k_1 due to a trans effect. The conclusion was that the exchange was a simple stepwise process, and simultaneous substitution of two trifluoroacetic acid molecules for two acetate groups did not occur.

The interest here lies in the pathway of this type of "exchange." Reactions between rhodium(II) acetate and dichloroacetic acid were investi-

^{*}The mechanism shown here is for the reaction with deuteroacetic acid but can be used to explain the mechanism for the reaction with trifluoroacetic acid.

Figure 2. Reaction Steps for the Exchange Between Rhodium(II) Acetate and Deuteroacetic Acid



TABLE 1

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DATEC

$$= \frac{dA}{dt} = k_1 [A] + k_5 [A]$$

$$= \frac{dA}{dt} = -k_1 [A] + k_5 [A]$$

$$= \frac{dB}{dt} = -k_1 [A] + k_2 [B] + k_6 [B]$$

$$= \frac{dC}{dt} = -k_2 [B] - k_5 [A] + k_3 [C] + k_7 [C]$$

$$= \frac{dD}{dt} = -k_3 [C] - k_6 [B] + k_4 [D]$$

$$= \frac{dE}{dt} = -k_4 [D] - k_7 [C]$$

$$= \frac{d[HAc]}{dt} = -k_1 [A] - k_2 [B] - k_3 [C] - k_4 [D] - 2k_5 [A]$$

.

gated, but the data obtained was insufficient to elucidate a pathway for the exchange. Also, the reaction between rhodium(II) benzoate with trifluoroacetic acid was investigated. In this reaction, benzoic acid was formed indicating an "exchange" type reaction like that between rhodium(II) acetate and trifluoroacetic acid. However, the reaction was either too fast and occurred before the sample could be prepared and placed in the nmr probe, or the parent peaks were concealed by the lines due to benzoic acid. It was impossible to interpret the spectra obtained. In all cases, the reactions were followed by ¹H nuclear magnetic resonance spectroscopy. In using this method the methyl proton concentration can be followed easily if there is no interference by absorptions due to the solvent.

Deuteroacetic acid is a non-interfering solvent, and its reaction with rhodium(II) acetate can be followed by nuclear magnetic resonance spectroscopy. A blank sample with only deuteroacetic acid was obtained, and the spectrum was a five line pattern (Figure 3). This pattern can be attributed to the splitting pattern of deuteroacetic acid-d₂ present in the deuteroacetic acid-d₃ used.

After dissolution of rhodium(II) acetate in deuteroacetic acid the tube containing the sample was placed in the nuclear magnetic resonance spectrometer probe. With tetramethylsilane as an internal standard, a resonance appeared at 1.87δ (A) downfield and was identified as the methyl protons of rhodium(II) acetate. Another resonance was apparent further downfield at 1.98δ (B) and it was the five line pattern due to deuteroacetic acid-d₃ and deuteroacetic acid-d₂. The nuclear magnetic resonance spectrum at this point is shown in Figure 3. It

Figure 3. Sample nmr Spectra at t = 0

A = Parent Compound

B = Deuteroacetic Acid

•



was necessary to heat the sample to instigate the reaction. Once this was done and as the reaction proceeded, (A) gradually disappeared and the resonance for free acetic acid appeared at the same position where line (B_2) of resonance (B) appeared. This resonance (B_2) increased due to the formation of acetic acid. None of the other four lines of (B) were noted to increase in intensity as the reaction proceeded. At t = 0 the ratio of line (B_4 : B_2), see Figure 3, was measured from the integrated area. As the reaction proceeded, (B_2) increased in intensity and the ratio (B_4 : B_2) changed as a function of time. This ratio and the original ratio of (B_4 : B_2) were used to calculate the amount of acetic acid formed since t = 0. This had a normalization effect in that it put the acetic acid concentration at zero percent and the parent concentration (A) at 100 percent, at t = 0. The reaction proceeded until the completely exchanged rhodium(II) deuteroacetate was formed (Figure 4).

From the nuclear magnetic resonance data, a pathway for the "exchange" reaction can be proposed. When desolvated rhodium(II) acetate was placed in an excess of deuteroacetic acid, the first step was an adductlike addition of deuteroacetic acid to the axial positions forming a blue solution (see Figure 2). This solution process required about twenty minutes (depending on the amount of solvent and sample used) and should be completed before the solution was placed in the probe. As the solution was heated, the parent rhodium(II) acetate (A in Figure 2) decreased following pseudo-first order kinetics. The first order plot Figure 4. Sample nmr Spectra at t = 160 minutes

A = Parent Compound

B = Deuteroacetic Acid



of $\ln \frac{a^{\prime}}{a^{\prime}-x}$ versus time* for the disappearance of A (where a' was the initial concentration of A in protons and xwas the number of protons of A decomposed at time t) is given in Figure 5. The calculated values for this plot are found in Table 2. The rate constant for the disappearance of A was $k_1 = 0.0243$ /minute at 68.5°C. Under the reaction conditions of a large excess of deuteroacetic acid, k_{-1} would be negligible and the acetate cage that was replaced forms a molecule of free acetic acid.

A plot of methyl proton concentration obtained from the integrated nmr signal versus time for the parent compound (A) and free acetic acid (B_2) formed from the reaction is given in Figure 6 and the calculated values are in Table 3. The relationship of the curves to one another is that one is just the reverse of the other. This indicated that for each step of the exchange reaction there was one molecule of free acetic formed. So, from Figure 2 for every molecule of B formed, there was one molecule of (B_2) formed, and likewise for every molecule of C, D, and E formed, there was one molecule of (B_2) formed of (B_2) formed for each.

Since each substitution involved essentially the same process, all rates should be the same. However, there is a statistical effect to account for. This is: when deuteroacetic acid reacted with A there were four "exchange" sites available, with B there were 3 "exchange" sites available, with C there were two "exchange" sites available and only one available with D. The results of this statistical effect was a decrease

*This is the time the sample has been heated.

Figure 5. First Order Plot for the Disappearance of Rhodium(II) Acetate (A) in the Exchange Reaction with Deuteroacetic Acid



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Figure 6. Relative Methyl Proton Concentration of the Species Present in the Reaction Mixture Versus Time as Calculated from nmr Data.

Q = Acetic AcidH = A + B + C + D



TABLE	2
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		<u>a'</u> a'-x	
Time (min)]	2	3
0	1.00	1.06	1.00
10	1.12	1.15	1.03
20	1.19	1.32	1.16
30	1.32	1.47	1.35
 . 40	1.45	1.67	1.45
50	1.72	1.69	1.67
60	1.64	1.96	2.13
70	1.82	2.27	2.44
80	2.27	2.32	2.70
90	2.78	2.70	3.12
100	3.70	2.78	3.03
110	3.81	3.22	
120	4.35	3.70	3.85
130	4.61	3.70	4.21
140	5.50	4.17	4.90
150		5.56	4.89
160	·	5.78	6.02

FIRST ORDER PLOT DATA FOR THE DISAPPEARANCE OF RHODIUM(II) ACETATE

	Pare	nt Comp	ound	Ac	etic A	cid
		Rel	ative Com	ncentra	tion	
Time (min)	1	· 2	3	1	2	3
0	100	100	100	0	0	0
10	. 89	97	87	11	4	13
20	84	86	76	16	14	24
30	[•] 74	76	68	26	24	32
40	68	68	59	32	32	41
50	60	60	58	40	40	42
60	61	51	47	39	49	53
7 0 ·	50	44	41	50	56	59
80	44	43	37	56	57	. 63
90	37	35	32	63	65	68 ·
100	33	36	27	67	64	73
110	28	31	26	72	69	74
120	26	27	23	74	73	77 ·
130	24	27	22	76	73	78
140	21	24	14	79	76	86
150	21	23	18 .	79	77	82
160	18	20	17	82	80	83

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PERCENT METHYL PROTON CONCENTRATION CALCULATED FROM EXPERIMENTAL DATA

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in rate constants for each successive step in the reaction. Assuming no change in metal-acetate bond energies upon deuteroacetate substitution, the ratio should be 1.0:0.75:0.50:0.25.

The equations governing the reaction rates shown in Table 1* were programmed in terms of molar concentration on an analog computer. The values of the rate constants used were obtained from the statistical ratio. From the resulting computer drawn curves in Figure 7, the 'relative concentration of each species A, B, C, D, and E (see Table 4) were calculated for time t. The total methyl proton concentration calculated from the computer drawn curves were compared to the methyl proton concentration obtained experimentally and there was a close fit to the experimental data as shown in Figure 8. This substantiated the statistical effect which caused a decrease in the rate constants for each successive step in the reaction.

This further substantiated the results of a kinetic study name by Bear, Kitchens, and Willcott (15) in that they reported k_2 of the reaction between rhodium(II) acetate and trifluoroacetic acid was twice as large as k_1 due to polarization of the pi system by the fluorides. The results was a kinetic labelization of the acetate group in the trans position. Elements with a less polarization effect should have less effect in a kinetic labelization of the acetate group in the trans position and thus, the rate constants should be more nearly the same. This was found to be the case, based on the experimental results reported in this work with the reaction of rhodium(II) acetate and deuteroacetic acid.

^{*}These equations are the same as those proposed for the reaction between rhodium(II) acetate and trifluoroacetic acid--assuming no simultaneous substitution of two groups at a time.

Figure 7. Relative Methyl Proton Concentration of the Substituents of the Reaction Mixture Versus Time as Obtained from the Computer Integration of the Equations in Table 1



TABLE 4	
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	Species Percent				
Time (min)	А	В	С	D	Total (A+B+C+D)
0	100.				100.
10	67.50	21.60	2.10	0.05	91.25
20	44.00	30.75	7.20	0.50	82.45
30	29.50	31.20	12.10	1.50	74.30
40	20.00	27.60	15.50	3.00	66.10
50	14.00	23.25	17.20	4.50	58.95
60	10.00	18.45	17.80	6.00	52.25
70	8.50	14.85	17.00	7.35	47.70
80	6.50	11.10	16.00	8.40	42.00
90	5.00	8.55	14.20	9.10	36.85
100	5.00	6.15	12.70	9.50	33.35
110	5.00	4.50	11.00	9.95	30.45
120	5.00	3.15	9.40	9.95	27.50
130	- 5.00	2.70	8.00	9.70	25.40
140	5.00	1.65	6.70	9.45	22.80
150	5.00	1.50	5.60	8.95	21.05
160	5.00	1.05	4.60	8.50	19.15

PERCENT METHYL PROTON CONCENTRATION OF SUBSTITUENTS IN THE REACTION MIXTURE CALCULATED FROM COMPUTER DATA

Figure 8. Comparison of the Relative Methyl Proton Concentration of the Reaction Mixture (A + B + C + D) as Calculated from nmr Data and the Relative Methyl Proton Concentration of the Reaction Mixture Obtained from the Computer Integration of the Equations in Table 1 Versus Time.

o = nmr Data

- = Computer Data



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In conclusion, the mechanism for the substitution of deuteroacetic acid for the acetate ion in rhodium(II) acetatewas shown to be a stepwise process. The first substitution occurred according to pseudo first order kinetics with a rate constant of 0.024/minute at 68.5°C. The second substitution was three-fourths as fast as the first due to the statistical affect--likewise, the third substitution was one-half as fast as the first and finally the fourth substitution was one-fourth as fast as the first.

It was possible that simultaneous substitution of two deuteroacetate groups at a time could occur. However, it would seem that the chance of simultaneous substitution would be less likely to occur as compared to the stepwise process previously mentioned. Also, the results reported by Bear, Kitchens, and Willcott (15) substantiated the single stepwise exchange with only a difference in rates due to a trans effect. The trans effect would not be expected in the reaction between rhodium(II) acetate and deuteroacetic acid because of the similarities between deuterium and hydrogen atoms.

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