Formation and Properties of Some Chlorocarbonyl Complexes of Ruthenium(II) and Ruthenium(III)[1]

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Abstract: Carbon monoxide was found to react with chlororuthenate(III) and chlororuthenate(II) complexes in aqueous hydrochloric acid solutions to form the carbonyl derivatives $Ru(CO)Cl_5^{2-}$, $Ru(CO)(H_2O)Cl_4^{2-}$, and $Ru(CO)_2Cl_4^{2-}$, according to reactions 1, 11, and 13. The kinetics of these reactions were examined, and the products were isolated as their ammonium salts and characterized. The neutral derivatives $Ru(CO)Cl_2(PPh_3)_3$ and $Ru(CO)_2Cl_2(PPh_3)_2$ were obtained by addition of triphenylphosphine to solutions of the corresponding anions. $Ru(CO)(H_2O)Cl_4^{2-}$ was also prepared by homogeneous reduction of $Ru(CO)Cl_5^{2-}$ with H_2. This reaction was found to be autocatalytic due to catalysis by $Ru(CO)(H_2O)Cl_4^{2-}$. The latter was also found to be a catalyst for the exchange of D_2 with H_2O and for the hydration of acetylene. It was also found that ruthenium carbonyl chloride complexes are formed during the ruthenium(III)-catalyzed hydration of acetylenes and that their formation is accompanied by a fall off of catalytic activity.

In the course of an investigation of the catalysis of the hydration of acetylenes by ruthenium(III) chloride complexes, preliminary results of which have previously been reported,[4] it was noted that prolonged continuation of the reaction resulted in a decrease in rate and ultimate cessation of reaction, the cause of which could be traced to formation of the catalytically inactive ruthenium carbonyl complex, $Ru(CO)_2Cl_4^{2-}$. It was further found that this complex, as well as certain other carbonyl complexes of ruthenium, could also be formed by direct reaction of carbon monoxide with aqueous solutions of ruthenium(III) and ruthenium(II) chlorides. The studies described in this paper relate to the kinetics of these reactions, the characterization of the products, and the examination of their catalytic properties.

Experimental Section

Solutions of ammonium chlororuthenate(III) and chlororuthenate(II) salts in aqueous hydrochloric acid were prepared from Johnson Matthey Specpure ammonium aquochlororuthenite, $(NH_4)_2Ru(H_2O)Cl_5$, and standardized, as described earlier.[5,6] The gaseous acetylenes, CO, H_2, and N_2 were Matheson Co. CP grade reagents, the H_2 being passed through a Deoxo catalytic purifier before use. D_2 was obtained from the Stuart Oxygen Co. and the D_2–H_2O exchange measurements were made as previously described.[7]

Kinetic measurements were made by following uptake of the gaseous reactant (CO, H_2, or acetylene) at constant pressure using the apparatus and procedure described earlier.[8] Concentrations of CO, H_2, and acetylene were computed in each case from the solubility data of Seidell[9] assuming the solubility to be the same as in pure water.

The procedure for the isolation of the inorganic carbonyl products depended on the preparation. $Ru(CO)_2Cl_4^{2-}$ produced during the catalytic hydration of acetylenes was precipitated as the ammonium salt by evaporation of the aqueous HCl solution at room temperature following removal of the organic products by ether extraction. The products of the direct reactions with CO, *i.e.*, $(NH_4)_2Ru(CO)Cl_5$, $(NH_4)_2Ru(CO)(H_2O)Cl_4$, $(NH_4)_2Ru(CO)_2Cl_4$, and $Ru(CO)_2Cl_2$, were obtained simply by evaporation of the solutions. These products were dried over P_2O_5 *in vacuo* and their melting points, infrared spectra, and chemical compositions determined. To establish that no decomposition had occurred it was confirmed that the spectrum of a sample of the dried product when redissolved in aqueous HCl agreed with that of the original solution. The dried product was also decomposed by gentle heating and the liberation of CO confirmed gas chromatographically.

The triphenylphosphine derivatives, $Ru(CO)Cl_2(PPh_3)_3$ and $Ru(CO)_2Cl_2(PPh_3)_2$, were prepared by addition of triphenylphosphine to solutions of the products, $Ru(CO)(H_2O)Cl_4^{2-}$ and $Ru(CO)_2Cl_4^{2-}$, respectively. The mixtures were shaken under nitrogen at 80° for 24 hr, completion of the reactions being indicated by disappearance of the colors of the anionic ruthenium complexes. The insoluble triphenylphosphine derivatives were separated by filtration and purified by repeated recrystallization from hot benzene, after excess triphenylphosphine had been removed by ether extraction.

Infrared spectra were recorded with a Perkin-Elmer 21 or Beckman IR-7 spectrophotometer using KBr disks. Visible and ultraviolet spectra were recorded with a Cary 14 spectrophotometer. Melting points were determined with a calibrated Fisher-Johns apparatus.

Microanalyses were performed by Mr. W. Saschek, Department of Chemistry, University of Chicago; Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; and A. Bernhardt, Mulheim, Germany.

Results and Discussion

Formation of $Ru(CO)Cl_5^{2-}$ by Reaction of CO with Ruthenium(III) Chloride. Aqueous solutions of ruthenium(III) chloride, containing 1 to 7 *M* HCl, were found to absorb CO at conveniently measurable rates in the temperature range 65–80°, the total uptake of CO corresponding closely to 1 mole of CO per mole of ruthenium(III) (Figure 1). The absorption of CO was accompanied by a change in the color of the solution from orange-brown to deep red, the spectrum of the final solution being depicted in Figure 2. The solution was stable in air and yielded, on evaporation, a red

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(1) This work was supported through grants from the National Research Council of Canada, the National Institutes of Health of the U. S. Public Health Service, and the Petroleum Research Fund, administered by the American Chemical Society.

(2) University of Chicago.

(3) University of British Columbia.

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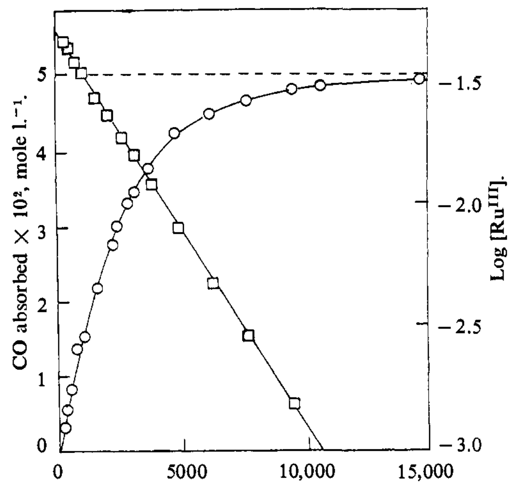

Figure 1. Kinetic plots for the formation of $Ru^{III}(CO)$ by reaction 1 (5.0×10^{-2} *M* Ru^{III}, 4.2×10^{-4} *M* CO, 5.0 *M* HCl, 80°): ○, CO absorbed; □, log [Ru^{III}]. The broken line corresponds to the uptake of 1 mole of CO per mole of Ru^{III}.

solid whose analysis was consistent with the formula $(NH_4)_2Ru(CO)Cl_5$. *Anal.* Calcd for $CH_8OCl_5N_2Ru$: C, 3.50; H, 2.35; Cl, 51.68; N, 8.17; Ru, 29.63. Found: C, 3.51; H, 2.50; Cl, 50.85; N, 8.20; Ru, 29.07.

$(NH_4)_2Ru(CO)Cl_5$ was found to be thermally stable up to at least 350°. Its infrared spectrum exhibited strong peaks at 3145 and 1400 (attributable to the N-H stretching and bending modes of NH_4^+) and 2059 cm^{-1} (attributable to CO stretching).

In the range of HCl concentrations of these experiments, ruthenium(III) is present predominantly as a mixture of the species $Ru(H_2O)_2Cl_4^-$, $Ru(H_2O)Cl_5^{2-}$, and $RuCl_6^{3-}$.[10] The stoichiometry of the reaction with CO is thus represented by

$$Ru(H_2O)Cl_5^{2-} + CO \longrightarrow Ru(CO)Cl_5^{2-} + H_2O \qquad (1)$$

together with corresponding equations for the formation of $Ru(CO)Cl_5^{2-}$ (subsequently abbreviated as Ru^{III}-(CO)) from the other ruthenium(III) complexes.

At constant HCl concentration the formation of $Ru^{III}(CO)$ was found to obey the second-order rate law.

$$-d[Ru^{III}]/dt = d[Ru^{III}(CO)]/dt = k_1[Ru^{III}][CO] \qquad (2)$$

At constant CO concentration the reaction thus exhibited pseudo-first-order kinetic behavior. Values of k_1 were determined using eq 2 from the slopes of first-order plots such as that depicted in Figure 1, the stoichiometric relation

$$[Ru^{III}] + [Ru^{III}(CO)] = [Ru^{III}]_{initial} \qquad (3)$$

being used to compute [Ru^{III}] from the observed CO uptake. The values of k_1 thus obtained are summarized in Tables I and II.

Because of the presence of several different chloro complexes of ruthenium(III) these values of k_1 must be considered as composite rate constants containing contributions from reaction 1 as well as from the reactions of the other chlororuthenium(III) complexes. The dependence of the rate on the Cl$^-$ concentration, depicted in Table II, may reflect some differences in these contributions. Unfortunately the accompanying variation in ionic strength and other medium effects, including those affecting the solubility of CO which were not corrected for, preclude a detailed interpretation of these results. The increase in k_1 with increasing H$^+$ concentration, at constant [Cl$^-$], appears to represent a real trend the significance of which, however, is not clear. Somewhat similar effects of varying the concentrations of H$^+$ and Cl$^-$ have previously been observed on the catalytic activity of ruthenium(III) for the oxidation of hydrogen[5] and for the hydration of acetylenes.[4]

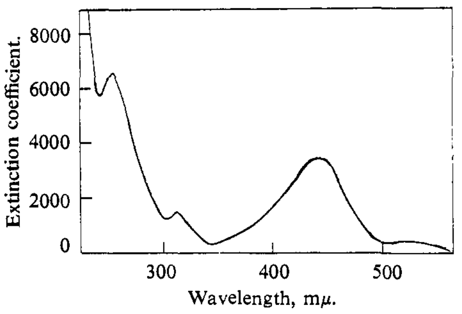

Figure 2. Absorption spectrum of $Ru(CO)Cl_5^{2-}$ in 5 *M* HCl.

Table I. Summary of Kinetic Data for Reaction 1 (3.3 *M* HCl)

Temp, °C	[Ru^{III}], *M*	CO, mm	[CO] × 10⁴, *M*	k_1, *M*$^{-1}$ sec^{-1}
80	0.0125	450	3.8	0.61
80	0.0167	450	3.8	0.65
80	0.0250	450	3.8	0.65
80	0.0375	450	3.8	0.61
80	0.0500	450	3.8	0.61
80	0.0250	161	1.4	0.66
80	0.0250	249	2.1	0.68
80	0.0250	349	2.9	0.59
85	0.0167	380	3.2	0.92
75	0.0167	510	4.3	0.41
70	0.0167	560	4.7	0.18
65	0.0167	600	5.2	0.13

Table II. Kinetic Data for Reaction 1 at 80° (0.0125 *M* Ru^{III})

[HCl], *M*	[LiCl], *M*	CO, mm	[CO] × 10⁴, *M*	k_1, *M*$^{-1}$ sec^{-1}
1.1	4.3	403	3.4	0.44
2.2	3.2	423	3.6	0.53
3.3	2.1	450	3.8	0.63
4.4	1.0	479	4.0	0.84
5.4	0.0	509	4.3	1.05
1.1	0.0	403	3.4	0.19
2.2	0.0	423	3.6	0.39
4.4	0.0	479	4.0	0.72
5.4	0.0	509	4.3	0.77
6.2	0.0	537	4.5	0.64
7.3	0.0	583	4.9	0.67
1.1	1.0	410	3.4	0.33
1.1	2.0	410	3.4	0.49
1.1	3.0	410	3.4	0.52
1.1	5.0	410	3.4	0.44
1.1	6.0	410	3.4	0.34
1.1	7.0	410	3.4	0.20

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[10] D. A. Fine, Ph.D. Dissertation, University of California, Berkeley, 1960.

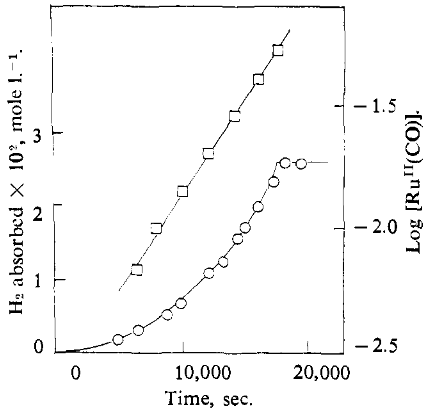

Figure 3. Kinetic plots for the reduction of $Ru^{III}(CO)$ to $Ru^{II}(CO)$ by H_2 according to reaction 4 (5.0×10^{-2} *M* $Ru^{III}(CO)$, 3.6×10^{-4} *M* H_2, 5.0 *M* HCl, 80°): ○, H_2 absorbed; □, log $[Ru^{II}(CO)]$.

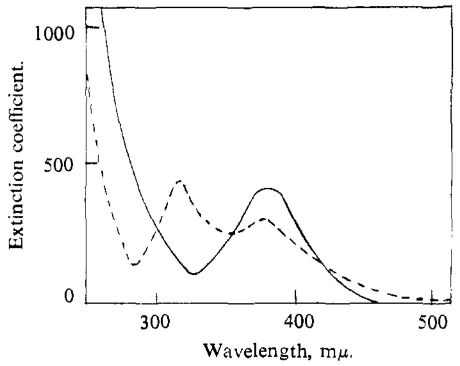

Figure 4. Absorption spectra of $Ru(CO)_2Cl_4^{2-}$ (———) and $Ru(CO)(H_2O)Cl_4^{2-}$ (- - - -) in 5 *M* HCl.

Measurements of k_1 at 3.3 *M* HCl, over the temperature range 65–85° (Table I), yielded a good Arrhenius plot from which the following activation parameters were determined: $\Delta H_1^* = 24$ kcal/mole, $\Delta S_1^* = 7$ eu.

Formation of $Ru(CO)(H_2O)Cl_4^{2-}$ and $Ru(CO)Cl_2(PPh_3)_3$ by Reduction of $Ru(CO)Cl_5^{2-}$. Solutions of $Ru^{III}(CO)$ at 80° readily took up gaseous hydrogen, the total uptake corresponding to 0.5 mole of H_2 per mole of $Ru^{III}(CO)$ (Figure 3). The uptake was accompanied by a change in the color of the solution from red to pale green, the spectrum of the final solution being depicted in Figure 4. Evaporation of the solution yielded a green air-stable solid which decomposed at about 260° with evolution of CO, and whose analysis was consistent with the formula $(NH_4)_2Ru(CO)(H_2O)Cl_4$. *Anal.* Calcd for $CH_{10}O_2Cl_4N_2Ru$: C, 3.69; H, 3.09; Cl, 43.54; N, 8.63; Ru, 31.21. Found: C, 4.23; H, 3.21; Cl, 43.58; N, 8.72; Ru, 30.39. The infrared spectrum exhibited strong peaks at 1950 (assigned to CO), 3140 and 1400 (assigned to NH_4^+), and 3480 and 1610 cm⁻¹ (assigned to H_2O).

The stoichiometry of the reaction with H_2 may thus be written as

$$2Ru(CO)Cl_5^{2-} + H_2 + 2H_2O \longrightarrow 2Ru(CO)(H_2O)Cl_4^{2-} + 2H^+ + 2Cl^- \quad (4)$$

Reduction of $Ru^{III}(CO)$ to $Ru(CO)(H_2O)Cl_4^{2-}$ (subsequently designated as $Ru^{II}(CO)$) could also be effected readily by Ti(III). Addition of H_2O_2 resulted in reoxidation to $Ru^{III}(CO)$. There was some indication of slight disproportionation of $Ru(CO)(H_2O)Cl_4^{2-}$ to form the dicarbonylruthenium(II) complex to be described later. Addition of triphenylphosphine to a solution of $Ru^{II}(CO)$ resulted in the precipitation of a brown solid (mp 70–72°) which exhibited an infrared peak at 1950 cm⁻¹ (assigned to ν_{CO}) and whose chemical analysis and properties were consistent with those expected for $Ru(CO)Cl_2(PPh_3)_3$ formed according to reaction 5. *Anal.* Calcd for $C_{55}H_{45}OCl_2P_3Ru$: C, 66.90; H, 4.59; Cl, 7.18; P, 9.41. Found: C, 67.11; H, 4.74; Cl, 7.64; P, 9.11.

$$Ru(CO)(H_2O)Cl_4^{2-} + 3PPh_3 \longrightarrow Ru(CO)Cl_2(PPh_3)_3 + H_2O + 2Cl^- \quad (5)$$

Catalytic Properties of $Ru^{II}(CO)$. The autocatalytic behavior of reaction 4 can be ascribed to homogeneous catalysis by the product $Ru^{II}(CO)$ and fitted (at constant $[H_2]$) by the rate law

$$d[Ru^{II}(CO)]/dt = 2k_2'[Ru^{II}(CO)] \quad (6)$$

which yields, on integration

$$\ln [Ru^{II}(CO)] = \ln [Ru^{II}(CO)]_{initial} + 2k_2't \quad (7)$$

The linear plot of log $[Ru^{II}(CO)]$ *vs.* time in Figure 3 is in accord with this and yields $k_2' = 7.9 \times 10^{-5}$ sec⁻¹ at 80°, 5.0 *M* HCl, 3.6×10^{-4} *M* H_2. While not definitely established in this case, it is considered likely by analogy with the mechanisms of the homogeneous catalytic activation of H_2 by ruthenium(III) chloride and related complexes[5,7] that the catalytic mechanism involves the heterolytic splitting of H_2 by $Ru^{II}(CO)$, *i.e.*

$$Ru^{II}(CO) + H_2 \xrightarrow{k_2} Ru^{II}(CO)H^- + H^+ \quad (8)$$

$$Ru^{II}(CO)H^- + 2Ru^{III}(CO) \xrightarrow{\text{fast}} 3Ru^{II}(CO) + H^+ \quad (9)$$

The assumption, accordingly, of first-order kinetic dependence on $[H_2]$, *i.e.*, $k_2' = k_2[H_2]$, yields the second-order rate constant, $k_2 = 0.22\ M^{-1}\ sec^{-1}$. In line with this it was also found (as in the related case involving ruthenium(III) chloride as catalyst)[7] that $Ru^{II}(CO)$, in the absence of $Ru^{III}(CO)$ or other reducible substrates, catalyzes homogeneously the isotopic exchange of D_2 with H_2O (to yield principally H_2). Assuming that exchange occurs *via* reaction 8, the value of k_2 computed from the measured exchange rate was found to be 0.18 M^{-1} sec⁻¹. This is in reasonable agreement with the value (0.22 M^{-1} sec⁻¹) deduced from the autocatalytic reduction of $Ru^{III}(CO)$, when allowance is made for a small kinetic isotope effect similar to that ($k_{H_2}/k_{D_2} = 1.12$) found for the corresponding reactions of ruthenium(III) chloride.[7]

$Ru^{III}(CO)$ was also found to be autocatalytically reduced to $Ru^{II}(CO)$ by acetylene, the reduction being followed by further uptake of acetylene owing to catalysis of hydration of the latter by $Ru^{II}(CO)$ (Figure 5). When the reaction was stopped at the end of the autocatalytic stage the spectrum of the solution was found to correspond to that of $Ru^{II}(CO)$. The products of the subsequent hydration of acetylene, as in the case of the corresponding ruthenium(III) chloride catalyzed reaction, were found to be predominantly acetaldehyde along with a small amount of crotonaldehyde. At constant acetylene concentration the $Ru^{II}(CO)$-catalyzed hydration of acetylene exhibited zero-order kinetics for periods of up to at least 1 hr (Figures 5 and 6).

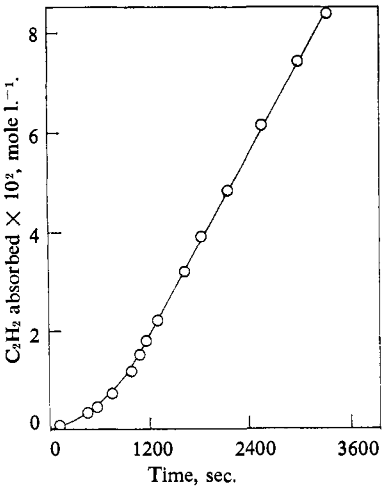

Figure 5. Autocatalytic reduction of $Ru^{III}(CO)$ to $Ru^{II}(CO)$ by acetylene followed by catalytic hydration of acetylene (2.5 × 10^{-2} *M* $Ru^{III}(CO)$, 9.1 × 10^{-3} *M* C_2H_2, 3.0 *M* HCl, 80°).

At 80° and 5 *M* HCl, the reaction was found to be first order in $Ru^{II}(CO)$ and in acetylene according to the rate law

$$-d[C_2H_2]/dt = k_3[Ru^{II}(CO)][C_2H_2] \qquad (10)$$

where $k_3 = 7.4 \pm 0.6 \times 10^{-2}\ M^{-1}\ sec^{-1}$ (Table III). The catalytic activity of $Ru^{II}(CO)$ for the hydration of acetylene is thus about one-eighth that of ruthenium(III) chloride under the same conditions.[11] The dependence of k_3 on the concentration of H^+ and Cl^- was not investigated.

Table III. Kinetic Data for the $Ru^{II}(CO)$-Catalyzed Hydration of Acetylene (5.0 *M* HCl, 80°)

$[Ru^{II}(CO)]$, *M*	$[C_2H_2]$ × 10^3, *M*	Initial rate × 10^5, *M* sec^{-1}	k_3 × 10^2, M^{-1} sec^{-1}
0.050	9.1	3.16	7.0
0.025	9.1	1.57	6.9
0.017	9.1	1.17	7.6
0.008	9.1	0.54	7.4
0.004	9.1	0.27	7.4
0.050	9.1	3.12	6.9
0.050	5.6	1.92	6.9
0.050	12.1	4.12	6.8
0.050	6.7	2.54	7.7
0.050	3.5	1.35	7.8

The rapid reduction of $Ru^{III}(CO)$ by acetylene precluded determination of its catalytic activity for the hydration of the latter.

Formation of $Ru(CO)(H_2O)Cl_4^{2-}$, $Ru(CO)_2Cl_4^{2-}$, $Ru(CO)_2Cl_2$, and $Ru(CO)_2Cl_2(PPh_3)_2$ by Reaction of CO with Ruthenium(II) Chloride. Solutions of ruthenium(II) chloride, prepared by addition of an excess of titanium(III) chloride to an aqueous HCl solution of ruthenium(IV), absorbed up to 2 moles of CO per mole of ruthenium(II) as shown in Figure 7. This absorption occurred in two distinct stages, the first mole of CO being taken up relatively rapidly (~2 hr at 80°) and the second mole much more slowly (~24 hr). The absorption of the first mole of CO was accompanied by a color change from deep blue (attributable to $RuCl_4^{2-}$)[12] to green and the second by a color change from green to yellow. After absorption of 1 mole of CO, the spectrum of the solution was identical with that previously found for $Ru^{II}(CO)$ (Figure 4) suggesting that the first stage of the reaction corresponds to

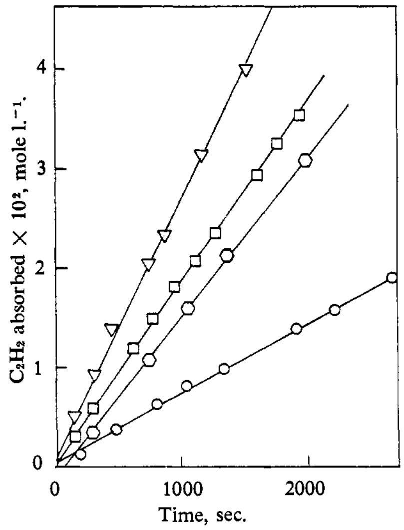

Figure 6. Rate plots for the $Ru^{II}(CO)$-catalyzed hydration of acetylene in 5 *M* HCl at 80°: ○, 8.0 × 10^{-3} *M* $Ru^{II}(CO)$, 9.1 × 10^{-3} *M* C_2H_2; □, 2.5 × 10^{-2} *M* $Ru^{II}(CO)$, 9.1 × 10^{-3} *M* C_2H_2; ▽, 5.0 × 10^{-3} *M* $Ru^{II}(CO)$, 9.1 × 10^{-3} *M* C_2H_2; ○, 5.0 × 10^{-2} *M* $Ru^{II}(CO)$, 5.6 × 10^{-3} *M* C_2H_2.

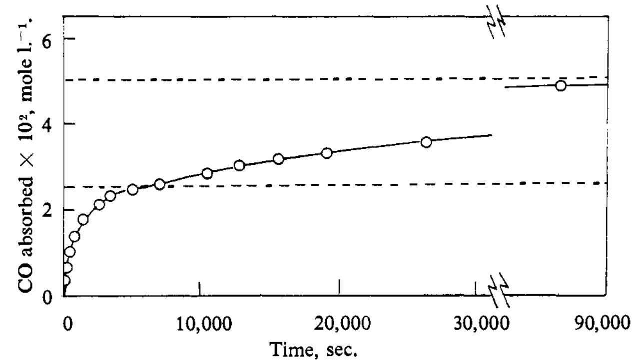

Figure 7. Uptake of CO by a 2.5 × 10^{-2} *M* solution of ruthenium(II) chloride containing 3 *M* HCl (3.8 × 10^{-4} *M* CO, 80°). The broken lines correspond to the uptake of 1 mole of CO and 2 moles of CO, respectively, per mole of Ru^{II}.

$$RuCl_4^{2-} + CO + H_2O \longrightarrow Ru(CO)(H_2O)Cl_4^{2-} \qquad (11)$$

The kinetic data in Table IV reveal that at constant H^+ and Cl^- concentration reaction 11 obeys the rate law

$$d[Ru^{II}(CO)]/dt = k_4[Ru^{II}][CO] \qquad (12)$$

the value of k_4 at 80°, 3.4 *M* HCl being 2 M^{-1} sec^{-1}. Measurement of the temperature dependence of k_4 (Table IV) yielded the activation parameters $\Delta H_4^* = 19$ kcal/mole, $\Delta S_4^* = -5$ eu; k_4 was relatively insensitive to variation of $[H^+]$ at constant $[Cl^-]$, but exhibited a marked inverse dependence on $[Cl^-]$ when the latter was increased by addition of LiCl (Table V). The interpretation of this trend is complicated by the accompanying changes in ionic strength and other medium prop-

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(11) A. L. W. Kemp, Ph.D. Dissertation, University of Chicago, 1964.

(12) C. K. Jørgensen, *Acta Chem. Scand.*, 10, 518 (1956).

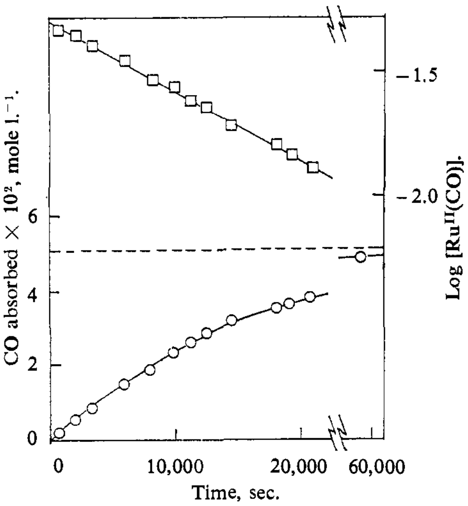

Figure 8. Kinetic plots for the formation of $Ru^{II}(CO)_2$ by reaction 13 (0.05 *M* $Ru^{II}(CO)$, 4.2 × 10^{-4} *M* CO, 5.0 *M* HCl, 80°): ○, CO absorbed; □, log [$Ru^{II}(CO)$]. The broken line corresponds to the uptake of 1 mole of CO per mole of $Ru^{II}(CO)$.

erties which could not be avoided because of failure to find a suitable inert anion to substitute for Cl^- (ClO_4^- is rapidly reduced by Ru^{II}). However, spectral changes accompanying variation of the Cl^- concentration suggest that changes in the distribution of chlororuthenate(II) complexes may be influencing the rate.

Table IV. Summary of Kinetic Data for Reaction 11 (3.4 *M* HCl, 0.1 *M* $TiCl_3$)

Temp, °C	[Ru^{II}], *M*	CO, mm	[CO] × 10^4, *M*	k_4, M^{-1} sec^{-1}
80	0.0090	450	3.8	2.06
80	0.0125	450	3.8	1.94
80	0.0186	450	3.8	1.70
80	0.0250	450	3.8	1.60
80	0.0313	450	3.8	1.76
80	0.0125	157	1.3	2.20
80	0.0125	237	2.0	2.08
80	0.0125	351	3.0	2.20
80	0.0125	450	3.8	2.06
65	0.0125	600	5.2	0.62
70	0.0125	560	4.7	0.87
75	0.0125	510	4.3	1.22
85	0.0125	380	3.2	2.86

Table V. Kinetic Data for Reaction 11 at 80° (0.0125 *M* Ru^{II}, 0.1 *M* $TiCl_3$)

[HCl], *M*	[LiCl], *M*	CO, mm	[CO] × 10^4, *M*	k_4, M^{-1} sec^{-1}
2.4	0.0	428	3.60	3.46
2.4	1.3	428	3.60	2.20
2.4	2.4	428	3.60	1.43
2.4	3.6	428	3.60	1.03
2.4	4.7	428	3.60	0.58
5.2	0.0	503	4.20	1.05
1.5	5.6	410	3.46	0.74
4.7	2.4	485	4.10	0.58
7.1	0.0	575	4.85	0.62

The second stage of the reaction (*i.e.*, the absorption of a second mole of CO) could be reproduced (Figure 8) by starting with a solution of $Ru^{II}(CO)$, prepared as described earlier (reaction 4) by the reduction of $Ru^{III}(CO)$ with H_2 and hence uncontaminated by titanium. The spectrum of the final yellow solution is shown (designated as $Ru(CO)_2Cl_4^{2-}$) in Figure 4. Evaporation of this solution yielded a water-soluble yellow solid which decomposed with evolution of CO above 240° and whose infrared spectrum exhibited strong peaks at 3145 and 1400 (assigned to NH_4^+) and at 2060 and 1991 cm^{-1} (assigned to CO). These observations and the chemical analysis of the compound are consistent with its formulation as $(NH_4)_2Ru(CO)_2Cl_4$. *Anal.* Calcd for $C_2H_8O_2Cl_4N_2Ru$: C, 7.16; H, 2.40; Cl, 42.26; N, 8.35; Ru, 30.30. Found: C, 7.01; H, 2.60; Cl, 42.17; N, 8.68; Ru, 30.03.

The uptake of CO thus apparently corresponds to reaction 13. Because of its slowness, reaction

$$Ru(CO)(H_2O)Cl_4^{2-} + CO \longrightarrow Ru(CO)_2Cl_4^{2-} + H_2O \quad (13)$$

13 was not extensively examined. At constant CO and HCl concentrations the reaction was found to be first order in $Ru^{II}(CO)$ (Figure 8). Assuming also first-order dependence on CO yields a second-order rate constant of 0.17 M^{-1} sec^{-1} at 80° in 5 *M* HCl.

Addition of triphenylphosphine to a solution containing $Ru(CO)_2Cl_4^{2-}$ (subsequently designated as $Ru^{II}(CO)_2$) resulted in precipitation of $Ru(CO)_2Cl_2(PPh_3)_2$, a white solid which decomposed above 280° and whose infrared spectrum exhibited CO stretching bands at 2056 and 1991 cm^{-1}. *Anal.* Calcd for $C_{38}H_{30}O_2Cl_2P_2Ru$: C, 60.60; H, 4.02; Cl, 9.42; P, 8.23. Found: C, 60.47; H, 4.28; Cl, 9.03; P, 8.21. This compound is apparently identical with the compound whose preparation by prolonged treatment of a methanolic solution of $RuCl_3 \cdot xH_2O$ with CO followed by addition of triphenylphosphine has recently been reported by Collman and Roper.[13]

Starting with a solution of $RuCl_3 \cdot 3H_2O$ (instead of $(NH_4)_2Ru(H_2O)Cl_5$) in aqueous HCl, successive treatments with CO, H_2, and CO similarly yielded, in succession, solutions of $Ru^{III}(CO)$, $Ru^{II}(CO)$, and $Ru^{II}(CO)_2$, respectively. Evaporation of the latter solution yielded a yellow solid, which exhibited infrared absorption bands at 2060 and 1991 cm^{-1} (assigned to ν_{CO}) and which decomposed, with evolution of CO, at 270°. This compound was identified as $Ru(CO)_2Cl_2$, a compound previously prepared by Manchot and Konig,[14] which is believed to have a polymeric chloride-bridged structure. *Anal.* Calcd for $C_2O_2Cl_2Ru$: C, 10.51; Cl, 31.01; Ru, 44.47. Found: C, 10.48; Cl, 31.01; Ru, 44.72.

The presence of two infrared bands of approximately equal intensity at about 2060 and 1990 cm^{-1} in $(NH_4)_2Ru(CO)_2Cl_4$, $Ru(CO)_2Cl_2(PPh_3)_2$, and $Ru(CO)_2Cl_2$ suggests that the disposition of the two CO ligands in all these compounds is *cis*. An X-ray powder photograph[15] of $(NH_4)_2Ru(CO)_2Cl_4$ revealed a distorted antifluorite lattice similar to that of $(NH_4)_2PtCl_6$ and analogous salts, indicating that this compound is an ammonium salt of $Ru(CO)_2Cl_4^{2-}$ rather than a mixture of $Ru(CO)_2Cl_2$ and NH_4Cl.

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(13) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **87**, 4008 (1965). The preparation of this compound by still another route has recently been described by T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

(14) W. Manchot and J. Konig, *Ber.*, **57**, 2130 (1924).

(15) Kindly taken and interpreted by Dr. N. F. Bartlett, University of British Columbia.

$Ru(CO)_2Cl_4^{2-}$ was found to exhibit no catalytic activity for the hydration of acetylenes or for the exchange of D_2 with H_2O.

Formation of Ruthenium Carbonyl Complexes during the Hydration of Acetylenes. A common feature of the ruthenium(III) chloride catalyzed hydrations of acetylene and substituted acetylenes described earlier[4] was the tendency of the rate to decrease with time until the reaction ultimately ceased. For acetylene itself this decrease was relatively gradual, the rate falling to about half its initial value after 24 hr (at 50°); for methylacetylene and ethylacetylene the decline in catalytic activity was much more rapid.

The decrease in rate, in each case, was accompanied by a change in the color of the ruthenium complex, the initially orange-brown solution turning first green and finally yellow. In every case the spectrum of the final solution, which was catalytically inactive, corresponded to that of $Ru(CO)_2Cl_4^{2-}$, and evaporation of this solution yielded $(NH_4)_2Ru(CO)_2Cl_4$.[16] The spectrum of the intermediate green solution corresponded to that of $Ru(CO)(H_2O)Cl_4^{2-}$ which, as shown above, was itself a catalyst, although a less efficient one than ruthenium(III) chloride, for the acetylene hydration reaction.

Several experiments were performed with a view to elucidating the origin of the formation of these ruthenium carbonyl complexes during the hydration reactions. The principal products of hydration, acetaldehyde, acetone, and methyl ethyl ketone (from acetylene, methylacetylene, and ethylacetylene, respectively), were ruled out as precursors by showing that they did not react with either ruthenium(III) or ruthenium(II) chlorides under N_2 at 80° over a period of 48 hr. Furthermore, the rates of the ruthenium(III)-catalyzed hydration reactions were found to be unaffected by the addition of these hydration products in large excess. The hydration of ethylacetylene was found to be accompanied by the formation of ethane and methane, the former in an amount corresponding approximately to the amount of ruthenium(III) initially present and the latter in about one-tenth of this amount. No free CO was detected.

These experiments are insufficient to establish the mechanism of the formation of the ruthenium carbonyl complexes which accompanies the hydration of acetylenes and which is at present not understood. Decarbonylation of an intermediate or a by-product of the hydration or (less likely) of impurities present in the acetylenes all constitute possible mechanisms. In related studies it was found[17] that ruthenium(II) chloride in aqueous solution rapidly decarbonylates formic acid to form $Ru^{II}(CO)$. Some indication of formation of $Ru^{II}(CO)$ by decarbonylation of formaldehyde (but not of acetic acid or ethanol) also was obtained. A number of other examples of the formation of metal carbonyl complexes (including complexes of Ru^{II}, Os^{II}, Rh^{I}, and Ir^{I}) by decarbonylation of organic compounds have recently been reported and possible mechanisms of these reactions discussed.[18-22] These reactions are, at best, only partially understood and further work is needed to elucidate them.

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[16] The decrease, with time, of the catalytic activity of ruthenium(II) chloride for the hydrogen transfer reactions of allyl alcohol observed by J. K. Nicholson and B. L. Shaw, *Proc. Chem. Soc.*, 282 (1963), may similarly be due to the formation of catalytically inactive ruthenium carbonyl complexes.

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The Decarbonylation of Formic Acid by Ruthenium(II) Chloride[1]

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Abstract: Ruthenium(II) chloride was found to react with formic acid in aqueous hydrochloric acid solution to form $Ru(CO)(H_2O)Cl_4^{2-}$ according to the reaction $RuCl_4^{2-} + HCOOH \longrightarrow Ru(CO)(H_2O)Cl_4^{2-}$. This paper describes a kinetic study of this reaction in which the dependence of the rate on the concentrations of ruthenium(II), formic acid, hydrogen ion, and chloride ion, as well as on the temperature, was examined. The results suggest that the reaction proceeds through a stepwise mechanism in which the initial step involves the dissociation of a chlororuthenate(II) complex.

We have previously reported[2] that the chlorocarbonylruthenate(II) complexes, $Ru(CO)(H_2O)Cl_4^{2-}$ and $Ru(CO)_2Cl_4^{2-}$ (hereafter designated $Ru^{II}(CO)$ and $Ru^{II}(CO)_2$, respectively), which can also be prepared by direct reaction between CO and ruthenium(II) chloride, are formed as by-products of the ruthenium(III) chloride catalyzed hydration of acetylenic compounds in aqueous HCl solution, presumably by decarbonylation of one of the organic intermediates or by-products of the hydration reaction. In an at-

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[1] This work was supported by grants from the National Science Foundation and from the Petroleum Research Fund, administered by the American Chemical Society.

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