Hydration of Acetylenes Catalyzed by Rhodium(III) Chloride Complexes

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Abstract: Aqueous acid solutions of some rhodium(III) chloro complexes, $[Rh(H_2O)_{6-n}Cl_n]^{(n-3)-}$, catalyze the hydration of acetylenes under mild conditions. The substitution inert cationic species are completely inactive; the activity then increases with substitution lability up to a maximum at $n = 5$, while the hexachloro complex is inactive. A ligand water molecule is thus required for the hydration process. The kinetics and mechanism of the system, which is similar to a ruthenium(III)-catalyzed system previously reported, are discussed.

There is currently a great deal of interest in reactions catalyzed by transition metal complexes in solution. Complexes of the group VIII metals seem to be particularly active, and a review by one of us[1] was concerned especially with the range of reactions catalyzed by rhodium complexes. Solutions of the commercially available $RhCl_3 \cdot 3H_2O$ can act as catalysts for the hydrogenation, isomerization, and polymerization of olefins and the polymerization of acetylenes.[1] In ethanol–benzene solution phenylacetylene is catalytically polymerized,[2] and in ethanol solution disubstituted acetylenes are converted to hexasubstituted benzenes with complexes of the formula $[(\text{acetylene})RhCl]_n$ also isolated.[3] We report in this paper that aqueous acid solutions of some rhodium(III) chloride complexes catalyze the hydration of acetylenes. The kinetics and mechanism of the reaction are similar to those reported for a corresponding ruthenium(III) chloride catalyzed system[4] and show the importance of a coordinated water molecule on the metal ion for the hydration process.

Experimental Section

Rhodium(III) trichloride was obtained as $RhCl_3 \cdot 3H_2O$ from Platinum Chemicals. $Na_3RhCl_6 \cdot 12H_2O$ was a product of K and K Laboratories. Rh(III) solutions containing the complexes $[Rh(H_2O)_{6-n}Cl_n]^{(n-3)-}$ were prepared and characterized as described earlier[5] using the methods and data of Wolsey and coworkers.[6] Acetylene (99.6% minimum) was a Matheson product; phenylpropiolic acid from Aldrich Chemical Co. was recrystallized from ethanol.

Kinetic measurements for the C_2H_2 system were made by following gas uptake at constant pressure using the apparatus and procedure described earlier.[5] The partial pressure of acetylene was varied from about 100 to 700 mm and the corresponding concentration in 3 M HCl solution estimated from the solubility data of Seidell[7] assuming the solubility to be the same as in pure water.

Acetaldehyde, the product from hydration of acetylene, was separated from the reaction mixture by distillation and identified in the distillate by gas chromatography using a 50/80 Porapak Q column (Varian Aerograph) which was particularly effective for removing the dominant water constituent.

Visible and ultraviolet spectra were recorded on a Perkin-Elmer 202 spectrophotometer, and infrared spectra were recorded on a Perkin-Elmer 21 using KBr disks.

Results

A red solution of $RhCl_3 \cdot 3H_2O$ in 3 M HCl ($\lambda_{\max}$ 404 mμ (ϵ 67) and 511 mμ (ϵ 74)), which contains predominantly the $[Rh(H_2O)Cl_5]^{2-}$ species,[6] absorbed acetylene at conveniently measurable rates from 50 to 65°. A linear rate of gas uptake was observed for several hours. In a typical experiment at 60°, acetylene, at 1 atm total pressure, was taken up by a 0.0125 M Rh(III) solution and converted to acetaldehyde at a rate of 2.3×10^{-5} M sec^{-1}; the rate of uptake was constant for at least 3 hr. The visible absorption spectrum of the red solution remained unchanged throughout the linear uptake region, and no other organic products were detected over this period. Experiments under the same conditions but without $RhCl_3 \cdot 3H_2O$ gave no measurable uptake.

The kinetics of the catalyzed reaction were examined in 3 M HCl. Varying [Rh] between 0.0125 and 0.0375 M and $[C_2H_2]$ between 3.8×10^{-3} and 2.17×10^{-2} M showed that the reaction was first order in each reactant, the rate law being

$$-d[C_2H_2]/dt = k[C_2H_2][Rh(III)] \qquad (1)$$

Values of k are summarized in Table I. Measurements over the temperature range 50–65° yielded a good Arrhenius plot and the activation parameters $\Delta H^{\ddagger} = 22.3 \pm 0.4$ kcal mole^{-1} and $\Delta S^{\ddagger} = 3 \pm 1$ eu.

In similar experiments using solutions of the solid substrate phenylpropiolic acid, CO_2 was evolved presumably due to decarboxylation of the hydration product $C_6H_5COCH_2CO_2H$, a β-keto acid. The kinetics of this reaction were followed by measuring the linear rate of CO_2 evolution, and the rate law corresponded to an expression such as (1). In 3 M HCl at 60° a rate constant of 2.1×10^{-3} M^{-1} sec^{-1} was estimated for this reaction.

A few experiments were carried out to determine the effect of H^+ and Cl^- on the hydration rate of acetylene itself, and the data are also summarized in Table I. At a constant acidity of 3.0 M, Cl^- has little effect over the range 1.0–3.0 M when the 5:1 chloro complex re-

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[1] B. R. James, *Coord. Chem. Rev.*, **1**, 505 (1966).

[2] P. Teyssie, F. Tripier, A. Isfendiyaroglu, B. Francois, V. Sinn, and J. Parrod, *Compt. Rend.*, **261**, 997 (1965).

[3] P. M. Matilis, J. Graham, and S. McVey, Abstracts, 2nd International Symposium on Organometallic Chemistry, Madison, Wis., 1965, p 2.

[4] J. Halpern, B. R. James, and A. L. W. Kemp, *J. Am. Chem. Soc.*, **83**, 4097 (1961).

[5] B. R. James and G. L. Rempel, *Can. J. Chem.*, **44**, 233 (1966).

[6] W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, **2**, 463 (1963).

[7] A. Seidell, "Solubilities of Organic Compounds," Vol. 2, 3rd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1941, p 71.

Table I. Kinetic Data for the Hydration of Acetylene at 60° Using $RhCl_3 \cdot 3H_2O$

[Rh] × 10^2, M	C_2H_2, mm	[C_2H_2] × 10^2, M	Medium	Rate of C_2H_2 uptake × 10^5, M sec^{-1}	k × 10^2, M^{-1} sec^{-1}
1.25	630	2.0	3 M HCl	2.30	9.2
2.50	630	2.0	3 M HCl	4.36	8.7
3.75	630	2.0	3 M HCl	6.47	8.6
1.25	119	0.4	3 M HCl	0.46	9.2
1.25	203	0.65	3 M HCl	0.71	8.8
1.25	405	1.3	3 M HCl	1.35	8.4
1.25	630	"2.0"	2 M HCl, 1 M $HClO_4$	2.60	10.4
1.25	630	"2.0"	1.5 M HCl, 1.5 M $HClO_4$	2.76	11.0
1.25	630	"2.0"	1 M HCl, 2 M $HClO_4$	2.82	11.3
1.25	630	"2.0"	2 M HCl, 1 M LiCl	2.00	8.0
1.25	630	"2.0"	1 M HCl, 2 M LiCl	1.81	7.3
1.25	630	2.0	3 M HCl	2.20	8.8[a]
1.25	630	2.0	5 M HCl	0.79	3.2[a]
1.25	. . .	10.0[b]	3 M HCl	0.26	0.2[b]

[a] Using $Na_3RhCl_6 \cdot 12H_2O$. [b] Using $C_6H_5C{\equiv}CCO_2H$.

Table II. Kinetic Data at 60° for the Hydration of Acetylene Using the Complexes $[Rh(H_2O)_{6-n}Cl_n]^{(n-3)-}$ (C_2H_2 = 630 mm)

n	[Rh] × 10^2, M	Medium: HCl, M	Medium: $HClO_4$, M	Rate of C_2H_2 uptake × 10^5, M sec^{-1}
0	1.25	0.00	6.00	0
1	1.25	0.01	6.00	0
2	1.25	0.025	5.98	0
3	1.47	0.04	5.96	3.42
4	1.70	0.08	5.92	4.62
5	1.70	0.20	5.80	6.12
6	1.70	3.50	2.50	0.38

mains the major species.[5] The slightly increased rate in the systems containing perchloric acid is thought to be due to increased solubility of C_2H_2 in these media. H_2 shows increased solubility with increasing [$HClO_4$] in solutions with a constant total concentration of HCl and $HClO_4$.[5] The effect of acid was studied by varying the composition of an HCl–LiCl mixture while maintaining a total concentration of 3.0 M. There is no significant dependence on H^-; small differences in rate could again be due to differences in gas solubility.[8] An experiment using $Na_3RhCl_6 \cdot 12H_2O$ in 3 M HCl, which contains mainly the $[Rh(H_2O)Cl_5]^{2-}$ species, gave essentially the same reaction rate obtained for 3 M HCl solutions of the trichloride; in 5 M HCl the hexachloro salt gives a solution containing appreciable amounts of the $[RhCl_6]^{3-}$ species,[5] and the linear rate of uptake was only about one-third that observed for the pentachloroaquo species in 3 M HCl. To examine more closely the relative activity of the various chloroaquorhodium(III) complexes, we have studied the reactivity of a range of solutions with varying Cl^- at a total acidity (HCl + $HClO_4$) of 6.0 M. Where reaction occurred, linear rates were again observed, and the data obtained are summarized in Table II; the complex listed as being present is the major component.[6] The activity of the $[Rh(H_2O)Cl_5]^{2-}$ species in 0.2 M HCl–5.80 M $HClO_4$ is about twice that in the 3 M HCl media, and this is likely due to an increase in the C_2H_2 solubility by about 2. The cationic species show no reactivity; activity is observed for the neutral $Rh(H_2O)_3Cl_3$ species, and this increases to a maximum for a solution containing mainly the 5:1 chloro species. The hexachloro complex is very much less active even allowing for the probable lower solubility of C_2H_2 in 3.50 M HCl–2.50 M $HClO_4$ compared to that in the other media listed.

The linear rate of reaction of the $RhCl_3 \cdot 3H_2O$–3 M HCl solution with C_2H_2 does fall off after longer periods, and a brown solid is slowly produced; after 8 hr the rate is about half the initial rate and after 24 hr the rate is only $^1/_{20}$th of the initial rate. The solid present at the end of such 24-hr experiments was collected, washed with water and ether, and dried. We have been unable to characterize this solid; it contains rhodium and could be a mixture of species, some polymeric. Strong infrared absorption bands were observed at 3400, 2900, 1670, 1620, 1450, 1380, and 1330 cm^{-1}.

Discussion

The kinetics of the C_2H_2 system, the acetaldehyde production, and the spectrophotometric observations are consistent with a Rh(III)-catalyzed hydration according to eq 2 and 3. The low activity of the $[RhCl_6]^{3-}$ complex indicates that the hydration reaction (3) involves a ligand water molecule. The relative activity of the other species reflects the substitution lability of these complexes for reaction 2, ranging generally from the rather high lability of $[Rh(H_2O)Cl_5]^{2-}$ to the inertness of the cationic species.[9–11] The kinetic data indicate an SN2-type mechanism for reaction 2 with acetylene replacing chloride for the formation of an intermediate π complex. Steric factors are likely to be involved in the greatly reduced rate (a factor of about 40) observed for the phenylpropiolic acid system. These Rh(III)-catalyzed systems are very similar to those previously reported for Ru(III)-catalyzed systems.[4,12] For acetylene itself, $RhCl_3 \cdot 3H_2O$ in 3 M HCl is about three times

$$\mathrm{Rh^{III}} + \mathrm{C_2H_2} \xrightarrow{k} \mathrm{Rh^{III}(C_2H_2)} \qquad (2)$$

$$\begin{tikzcd} \mathrm{Rh^{III}(C_2H_2)} \arrow[r, "\text{fast}", "\mathrm{H_2O}"'] & \mathrm{Rh^{III}} + \text{“}\mathrm{CH_2{=}CH(OH)}\text{”} \arrow[d] \\ & \mathrm{CH_3CHO} \end{tikzcd} \qquad (3)$$

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[8] J. F. Harrod and J. Halpern, *Can. J. Chem.*, 37, 1933 (1959).

[9] W. Robb and G. M. Harris, *J. Am. Chem. Soc.*, 87, 4472 (1965).

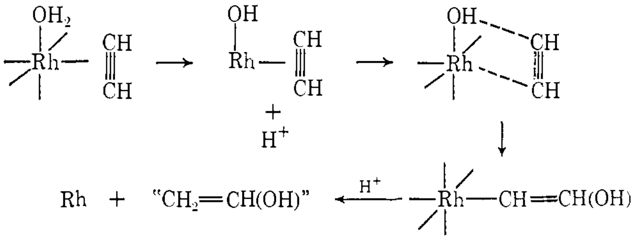
[10] K. Swaminathan and G. M. Harris, *ibid.*, 88, 4411 (1966).

[11] W. Robb and M. M. De V. Steyn, *Inorg. Chem.*, 6, 616 (1967).

[12] A. L. W. Kemp, Ph.D. Thesis, University of Chicago, 1964.

more reactive than the corresponding system involving ruthenium(III) chloride, where a similar dependence on the chloride concentration, due to the distribution of chloro complexes present, was observed. The Arrhenius parameters in the 3 M HCl media are very similar to those obtained for the Ru(III) system ($\Delta H^{\ddagger} = 21.4$ kcal, $\Delta S^{\ddagger} = -1.5$ eu)[12] and are in the normal range for a reaction between an ion and a neutral molecule.[13]

After formation of the π complex, the following scheme involving faster steps seems plausible.



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The steps involved are of a rather general type that has been postulated for a whole range of catalytic reactions including hydrogenation, polymerization, isomerization, and oxidation of olefins and the hydration of acetylenes.[14-16] The coordinated water ligand will be somewhat acidic and is probably somewhat more so in $[Rh(H_2O)Cl_5]^{2-}$ than in the corresponding iridium complex[17] $[Ir(H_2O)Cl_5]^{2-}$ ($K_a \sim 10^{-10}$). The acidity of a $[Rh(H_2O)Cl_4(C_2H_2)]^-$ complex is likely to be greater than that of $[Rh(H_2O)Cl_5]^{2-}$, and the ionization probably occurs with the acetylene complex. The essential acid independence of the kinetics is consistent with this. The concentration of the hydroxy species will be very small in the acid media used. Nucleophilic attack by the coordinated OH^- at the C atom finally yields the σ complex I (in effect, an "insertion" reaction of the CH≡CH moiety into the Rh–OH bond), which is then decomposed by electrophilic attack by a proton at the C atom attached to the metal to regenerate the Rh(III) catalyst and give the hydration product. The reaction scheme corresponds closely to that postulated for the ethylene reduction of metal ions.[18,19] Here, however, a two-electron transfer to the metal from the organo group in the σ complex gives rise to the oxidation–reduction process; presumably the more unsaturated nature of the resulting olefinic organo ligand in the acetylene system prevents this electron transfer.

The eventual falloff in the hydration rate was also observed in the Ru(III)-catalyzed system, and this was due to the formation of less active Ru(III) and Ru(II) carbonyl complexes;[20] the mechanism of their formation was not established, but the system was an early example of the decarbonylation of an organic oxygen-containing compound by platinum metal complexes,[21] and it seems that such reactions go through unstable acyl or aldehyde intermediates.[21] No rhodium carbonyl species were detected in the present work; in the longer experiments rhodium was present only as catalytic $[Rh(H_2O)Cl_5]^{2-}$ in solution and in the uncharacterized solid which showed no infrared absorption due to a Rh bonded CO stretch. However, intermediate rhodium carbonyls may be involved, and Maitlis and coworkers have reported[22,23] that interaction of $[Rh(CO)_2Cl]_2$ with acetylenes gives rise to a complex mixture of products containing organic trimers, quinones, and a range of metal complexed cyclopentadienones and quinones, some not containing a Rh–CO grouping. The infrared of our solid product indicates that unsaturated carbonyl compounds could be present.

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(13) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1963, p 149.

(14) J. Halpern, *Ann. Rev. Phys. Chem.*, **16**, 103 (1965).

(15) J. Halpern, Proceedings of the 3rd International Congress on Catalysis, North Holland, Amsterdam, 1965, p 146.

(16) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 578.

(17) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 151 (1957).

(18) P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964).

(19) B. R. James and G. L. Rempel, *Can. J. Chem.*, **46**, 571 (1968).

(20) J. Halpern, B. R. James, and A. L. W. Kemp, *J. Am. Chem. Soc.*, **88**, 5142 (1966).

(21) M. Baird, C. Nyman, and G. Wilkinson, *J. Chem. Soc., A*, 348 (1968), and references therein.

(22) P. M. Maitlis and S. McVey, *J. Organometal. Chem.*, **4**, 254 (1965).

(23) P. M. Maitlis, S. McVey, and J. W. Kang, Proceedings of the 1st International Symposium on New Aspects of the Chemistry of Metal Carbonyls and Derivatives, Venice, 1968, D2.