

Formation and Catalytic Properties of Some Ruthenium(II) Halogeno-Olefin Complexes in Solution

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A kinetic study of the complex formation between chlororuthenate(II) species and 1,1-difluoroethylene and vinyl fluoride under mild conditions in aqueous hydrochloric acid solution is described; a two step process involving an initial dissociation of a chloride ligand seems likely for these systems but a detailed discussion is limited by lack of information on the equilibria between chlororuthenate(II) species in solution. The fluoroolefins are not homogeneously catalytically hydrogenated at Ru^{II} due to a competing catalytic hydration process which converts 1,1-difluoroethylene to acetic acid and vinyl fluoride to acetaldehyde. Similarities between the mechanisms of catalytic hydration and hydrogenation are discussed.

Introduction

Aqueous hydrochloric acid solutions of chlororuthenate(II) species are known to homogeneously catalyze the hydrogenation of certain substituted ethylenes.¹ Ethylene and substituted ethylenes complex readily with the chlororuthenate(II)^{1,2} but, in the presence of molecular hydrogen, catalytic hydrogenation was observed only with olefins in which the double bond was activated by the presence of an adjacent carboxylic acid group. This effect was rationalized in terms of the electron-withdrawing power of this substituent favouring a nucleophilic attack of a hydride ligand on the double bond.¹ The use of halogen substituted olefins, particularly fluoro compounds, suggested a further testing of this hypothesis, and here we report the results of these studies. Catalytic hydrogenation of these olefins was not in fact observed, but a catalytic hydration process occurred in the solution.

Experimental Section

Ruthenium(II) chloride solutions were generated by reduction of Johnson Matthey Specpure ammonium aquochlororuthenate with an excess of titanium(III) chloride as previously described.² 1,1-difluoroethylene (99.0% min.) and the vinyl halides (99.9% min) were Matheson products. Hydrochloric acid and other chemicals were of reagent grade.

Kinetic measurements were made principally by following gas uptake at constant pressure using the apparatus and procedure described earlier.³

Organic products of the catalytic reactions were separated from the inorganic components of the reaction by distillation or solvent extraction procedures, and were identified primarily by standard techniques involving gas chromatography, infrared and N.M.R. spectroscopy.

Absorption spectra were recorded with a Cary 14 or Perkin-Elmer 202 Spectrophotometers; infrared spectra of solids were taken with a Perkin-Elmer 21 using KBr discs; mass spectra were recorded on an A.E.I. MS9; ¹H and ¹⁹F N.M.R. spectra were recorded on Varian A 60 and HR 100 instruments. Both Aerograph A 90/P3 and a Beckman GC 2A gas chromatograph units were used for product analysis.

1,1-Difluoroethylene system. Stoichiometry. Blue solutions of ruthenium(II) chloride in 3 M HCl (λ_{\max} , 680 m μ , ϵ 800) were found to absorb 1,1-difluoroethylene at conveniently measurable rates in the temperature range 55°-70°. Typical uptake plots at 60° for three solutions containing different initial ruthenium concentrations are shown in Figure 1 for the conditions noted. The initial part of the uptake shows autocatalytic behaviour, and then the rate becomes constant for an hour or so before slowly falling off. The rate plot is quite different from that observed for the Ru^{II}-ethylene system where a pseudo-first order kinetic plot results for a 1:1 stoichiometric gas uptake.²

The kinetic experiments were usually followed over a period of 3-5 hours. The initial deep blue colour faded with uptake of gas and the final solutions were green; these solutions still exhibited a characteristic peak at 680 m μ and the optical density indicated that once the linear region had been reached in experiments using 1 atm. total pressure, no more than 10% of the original Ru^{II} was still present; at the lowest olefin concentrations up to 40% of the initial Ru^{II} was still present. A solution sample taken after 3 hours reaction time was oxidized on standing in air to yellow chlororuthenate(III) species;⁴ the spectrum obtained (λ_{\max} 350 m μ , ϵ 2300) was identical to that obtained for a standard Ru^{III} solution in 3 M HCl prepared by H₂ reduction of

(1) J. Halpern, J. F. Harrod, and B. R. James, *J. Am. Chem. Soc.*, **83**, 753 (1961); *ibid.*, **88**, 5150 (1966).

(2) J. Halpern and B. R. James, *Canad. J. Chem.*, **44**, 495 (1966).
(3) B. R. James and G. L. Rempel, *Canad. J. Chem.*, **44**, 233 (1966).

Ru^{IV} ,⁵ showing that no Ru^{II} had been lost either by disproportionation or reduction to metal.

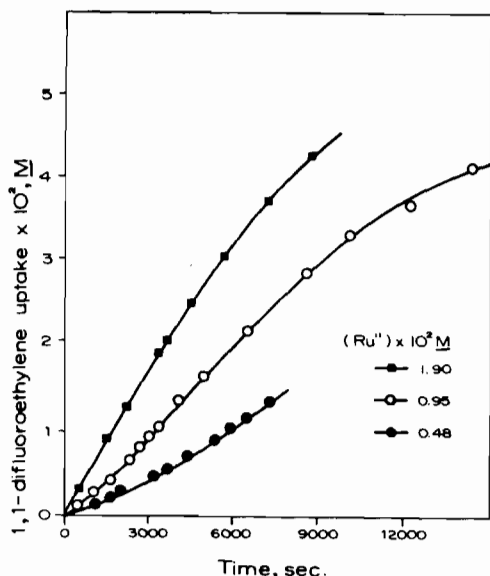


Figure 1. Rate plots for the Ru^{II} 1,1-difluoroethylene system at 60° , 630 mm CF_2CH_2 , 3 M HCl.

Analysis of the aqueous distillate after a 4 hour experiment (olefin absorption ~ 0.15 M) by gas chromatography using a 50/80 Porapak Q column (Varian Aerograph) detected only acetic acid (0.12 M); the *p*-bromophenacyl and nitrobenzyl ester derivatives were then prepared and characterized by their melting points. An ^1H N.M.R. spectrum of the distillate was consistent with the presence of aqueous acetic acid; a ^{19}F N.M.R. spectrum showed no peaks, indicating the absence of F in the organic product. Fluoride was detected qualitatively in the inorganic residue where it could be present as either ruthenium or titanium fluoride complexes. A mass spectroscopic analysis of a gas sample taken at the end of an uptake experiment indicated no mass peaks higher than that of the parent difluoroethylene; there was no evidence for the formation of dimers or higher species.

Kinetics. The kinetics of the reaction have been investigated in the initial region and in the subsequent linear region of the higher rate; the initial slopes could be measured with reasonable accuracy. Table I summarizes the results of experiments at 60° with varying $[\text{Ru}^{\text{II}}]$ and with varying $[\text{CF}_2\text{CH}_2]$; a figure for the solubility of CF_2CH_2 was computed from a ratio of the solubilities at 25° in water of ethylene⁶ and difluoroethylene,⁷ and the solubility of ethylene at 60° .² The initial rates show a good first order dependence on $[\text{Ru}^{\text{II}}]$ but the linear rates show only

an approximate first order dependence. Values of the pseudo first order rate constant k' for the initial reaction were obtained by dividing the rate by the $[\text{Ru}^{\text{II}}]$ and are included in the table. The initial rate could also be followed spectrophotometrically by the disappearance of the 680 m μ peak using a sampling technique⁸ with an initial $[\text{Ru}^{\text{II}}] = 10^{-3}$ M; a good linear log absorbance plot was obtained, confirming the first order dependence on $[\text{Ru}^{\text{II}}]$. The k' value obtained was $0.45 \times 10^{-3} \text{ sec}^{-1}$ which is considered in fair agreement with the values obtained from the corresponding gas uptake experiments ($k' = 0.28 \times 10^{-3} \text{ sec}^{-1}$), considering the differences in $[\text{Ru}^{\text{II}}]$ used and the sampling technique involved for the oxygen sensitive solutions.

The kinetic dependence on the difluoroethylene concentration is shown in Figure 2 for the gas uptake data at 60° . For both the initial and linear rates the dependence is complex corresponding to an order < 1 ; this order decreases with increasing olefin concentration, the rate approaching a limiting value.

The dependence of the initial rate on the concentration of H^+ and Cl^- is shown in Table II. The $[\text{H}^+]$ was varied from 0.5 M to 3.0 M while the $[\text{Cl}^-]$ was varied from 3.35 to 5.35 M; tetrafluoroborate was sometimes added to maintain a constant ionic strength. The $[\text{Cl}^-]$ listed includes the contribution from the added titanium(III) chloride. An inverse dependence on both $[\text{H}^+]$ and $[\text{Cl}^-]$ is apparent.

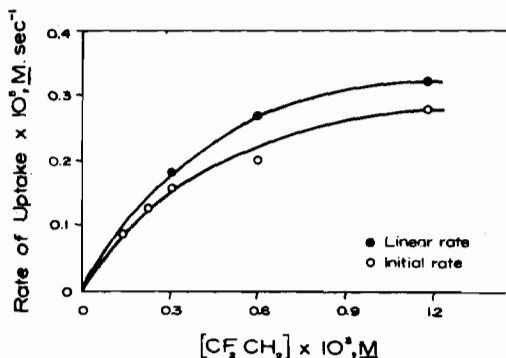
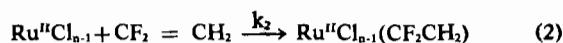
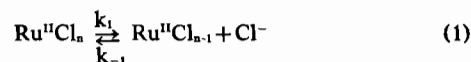


Figure 2. Dependence of rate on the 1,1-difluoroethylene concentration at 60° , $[\text{Ru}^{\text{II}}] = 0.95 \times 10^{-2}$ M, 3 M HCl.

Initial Rates and Initial Reactions. The dependence of the rate on the olefin concentration and the inverse chloride effect suggests, on comparison with the Ru^{II} -ethylene system where similar kinetics were observed,² that the initial reaction involves formation of a complex between Ru^{II} and difluoroethylene via a two step mechanism involving an initial dissociation of chlororuthenate(II) species.



(8) J. Halpern and A. L. W. Kemp, *J. Am. Chem. Soc.*, **88**, 5147 (1966).

(4) D. A. Fine, Ph. D. Dissertation, University of California, Berkeley, 1960.

(5) J. F. Harrod, S. Ciccone, and J. Halpern, *Canad. J. Chem.*, **39**, 1372 (1961).

(6) A. Seidell, « Solubilities of organic compounds », Vol. 2, 3rd Ed., D. Van Nostrand Co., Inc., New York, N.Y. 1961, p. 94.

(7) Matheson Gas Data Book, 4th Ed., Matheson Co., Whitby, Ontario, 1966, p. 185.

Table I. Variation of $[Ru^{II}]$ and $[CF_2CH_2]$ on the rate of reaction between Ru^{II} and 1,1-difluoroethylene. ($3 M HCl$, 60° , added $[Ti^{III}] = 0.11 M$)

$[Ru^{II}]$ $\times 10^2, M$	CF_2CH_2 mm	$[CF_2CH_2]$ $\times 10^3, M$	Rates of uptake $\times 10^5, M. sec^{-1}$		k' (initial) $\times 10^3, sec^{-1}$
			Initial	linear	
0.48	630	1.17	0.13	0.21	0.27
0.95	630	1.17	0.28	0.32	0.29
1.90	630	1.17	0.53	0.58	0.28
0.95	320	0.60	0.20	0.27	0.21
0.95	165	0.31	0.16	0.18	0.17
0.95	120	0.22	0.12	—	0.13
0.95	71	0.13	0.08	—	0.09

Table II. Variation of $[H^+]$ and $[Cl^-]$ on the rate of reaction between Ru^{II} and 1,1-difluoroethylene system (60° , $[Ru^{II}] = 0.95 \times 10^{-2} M$, added $[Ti^{III}] = 0.11 M$).

$[H^+], M$	$[Cl^-], M$	$CF_2CH_2, mm.$	Rates of uptake $\times 10^5, M. sec^{-1}$	
			Initial	linear
3.0	3.35	630	0.28	0.32
1.5	3.35	630	0.42	0.52
3.0	3.35	120	0.13	—
3.0	4.35	120	~0.08	—
3.0	5.35	120	0.06	—
3.0	3.35	120	0.13 ^a	—
3.0	4.35	120	0.11 ^b	—

^a 2 M NaBF₄; ^b 1 M NaBF₄.

A 1:1 complex seems likely and in Figure 1 the linear region does start in a region corresponding very roughly to a 1:1 mole ratio.

Assuming the steady state approximation for the intermediate $Ru^{II}Cl_{n-1}$, the rate law becomes

$$\frac{-d}{dt}[CF_2CH_2] = \frac{k_1 k_2 [Ru^{II}Cl_n][CF_2CH_2]}{k_{-1}[Cl^-] + k_2[CF_2CH_2]} \quad (3)$$

At constant $[Cl^-]$ and $[CF_2CH_2]$,

$$\frac{-d}{dt}[CF_2CH_2] = k'[Ru^{II}Cl_n] \quad (4)$$

where $k' = k_1 k_2 [CF_2CH_2] / \{k_{-1}[Cl^-] + k_2[CF_2CH_2]\}$
thus

$$\frac{1}{k'} = \frac{1}{k_1} + \frac{k_{-1}[Cl^-]}{k_1 k_2 [CF_2CH_2]} \quad (5)$$

The linear plot of $1/k'$ versus $1/[CF_2CH_2]$ in Figure 3 is in accord with this and yields the values $k_1 = 3.3 \times 10^{-4} sec^{-1}$ and $k_2/k_{-1} = 9.7 \times 10^3$.

The inverse dependence of k' on the Cl^- concentration is qualitatively in accord with the proposed mechanism but a quantitative testing of the data (Table II) is not possible, principally because of the effect of varying the Cl^- concentration on the distribution of ruthenium(II) chloride complexes as discussed earlier,^{2,8} and these equilibria have not yet been elucidated. On increasing the Cl^- concentration from 3.35 to 5.35 M the absorbance at 680 μ decreases by about 25% and the decrease in rate with added chloride may result to some extent from the presence of different chloro complexes. Tetrafluoroborate was

used to maintain a constant ionic strength since this anion has been reported⁹ not to complex with Ru^{II} at least up to the maximum concentration of BF_4^- used ($3 \times 10^{-2} M$) by these workers; in the present studies, decreases of up to 15% were observed in the absorption at 680 μ on adding up to 2 M $NaBF_4$, suggesting that tetrafluoroborate might possibly complex weakly with Ru^{II} .

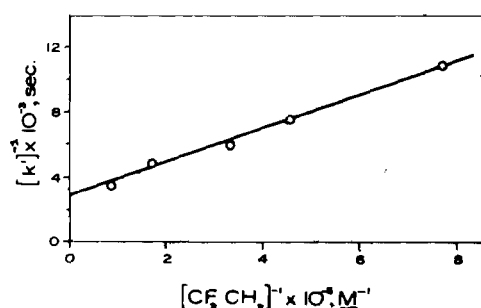


Figure 3. Plot of $[k']^{-1}$ versus $[CF_2CH_2]^{-1}$ at 60° , $[Ru^{II}] = 0.95 \times 10^{-2} M$, $3 M HCl$.

The study of acid dependence of the rate was complicated at lower acidities ($\sim 0.5 M$) by the production of metallic ruthenium. The inverse dependence of the rate on $[H^+]$ from 1.5–3.0 M was similar to that observed in the ethylene system² and may reflect some hydrolytic equilibria involving chlororuthenate(II) complexes, whose reactivity is enhanced through hydrolysis.

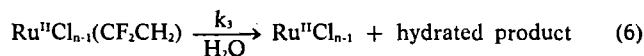
Measurements of the temperature dependence of k' over the range 55–70° (Table III) at the highest partial pressures of CF_2CH_2 (560–665 mm, depending on the temperature) where $k' \sim k_1$, yielded the activation parameters $\Delta H_1^* \sim 29$ kcal/mole, $\Delta S_1^* \sim 13$ eu.

Table III. Temperature dependence of k_1 and k_2 for the 1,1-difluoroethylene system ($[Ru^{II}] = 0.95 \times 10^{-2} M$, added $[Ti^{III}] = 0.11 M$, 760 mm total pressure).

Temperature, °C	$k_1 \times 10^3, sec^{-1}$	$k_2 \times 10^3, sec^{-1}$
55	0.13	0.26
60	0.31	0.39
65	0.57	0.70
69	0.96	0.96

(9) E. Mercer and R. Buckley, *Inorg. Chem.*, 4, 1692 (1965).

Catalytic Hydration Reaction. The experimental results indicate that the subsequent reaction after the initial complex formation is a catalytic hydration process yielding acetic acid. The kinetics are consistent with a mechanism involving decomposition of the olefin complex by H₂O with the liberation of the RuCl_{n-1} species:



Considering the overall reactions indicated by equations 1, 2 and 6, the rate of olefin uptake at any stage can be expressed as follows:

$$-\frac{d}{dt}[\text{CF}_2\text{CH}_2] = k_2[\text{Ru}^{\text{II}}\text{Cl}_{n-1}][\text{CF}_2\text{CH}_2] \quad (7)$$

Assuming a steady state concentration of Ru^{II}Cl_{n-1} gives

$$\frac{-d}{dt}[\text{CF}_2\text{CH}_2] = \frac{k_2[\text{CF}_2\text{CH}_2]\{k_1[\text{Ru}^{\text{II}}\text{Cl}_n] + k_3[\text{Ru}^{\text{II}}\text{Cl}_{n-1}(\text{CF}_2\text{CH}_2)]\}}{k_{-1}[\text{Cl}^-] + k_2[\text{CF}_2\text{CH}_2]}$$

At constant [Cl⁻] and [CF₂CH₂], this becomes

$$\frac{-d}{dt}[\text{CF}_2\text{CH}_2] = k''\{k_1[\text{Ru}^{\text{II}}\text{Cl}_n] + k_3[\text{Ru}^{\text{II}}\text{Cl}_{n-1}(\text{CF}_2\text{CH}_2)]\} \quad (9)$$

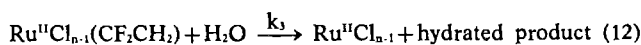
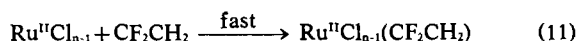
where $k'' = k_2[\text{CF}_2\text{CH}_2] / \{k_{-1}[\text{Cl}^-] + k_2[\text{CF}_2\text{CH}_2]\}$

Equation (9) gives a complete description of the difluoroethylene uptake including both the initial and linear region. Initially, the [Ru^{II}Cl_{n-1}(CF₂CH₂)] is zero, and the equation reduces to equation (4). As the reaction proceeds, the [Ru^{II}Cl_{n-1}(CF₂CH₂)] gradually increases; the rate plots show autocatalytic behaviour and hence k₃ must be somewhat greater than k₁. At high olefin concentration, the k₋₁[Cl⁻] becomes small as compared to k₂[CF₂CH₂] (rate independent of [CF₂CH₂]) and hence the concentration of the blue Ru^{II}Cl_n species will also be small. As the [Ru^{II}Cl_{n-1}(CF₂CH₂)] builds up, the rate of uptake will increase and will finally reach a value given by equation 10.

$$\frac{-d}{dt}[\text{CF}_2\text{CH}_2] \sim k_3[\text{Ru}^{\text{II}}\text{Cl}_{n-1}(\text{CF}_2\text{CH}_2)] \quad (10)$$

This relation yields a constant rate and gives rise to the linear region of the uptake plots. The [Ru^{II}Cl_{n-1}(CF₂CH₂)] ~ [Ru^{II}]_{initial} and so the constant rate of olefin uptake will show an approximate first order dependence on [Ru^{II}], as seen in Table I. The value of k₃ obtained from the slope of the plot is ~ 4 × 10⁻⁴ sec⁻¹.

We are thus saying that the mechanism for the linear region of the rate plot at higher olefin concentration can be written as



Using the linear rates from such experiments over the temperature range 55°-70°, approximate values of k₃ were obtained by dividing this linear rate by the [Ru^{II}] (Table III). A good Arrhenius plot yielded the parameters ΔH₃^{*} ~ 21 kcal/mole and ΔS₃^{*} ~ -9 eu. At the lower olefin concentration, the k₋₁[Cl⁻] term becomes more significant indicating that the [Ru^{II}Cl_n] is likely to be higher for these experiments (as observed) and equation 9 should be used for the rate of uptake; this is again consistent with the olefin dependence observed for the linear region (Figure 3).

In all the systems studied the rate gradually falls off after the linear region. A similar effect was observed in the Ru(III) catalyzed hydration of acetylene¹⁰ due to the formation of Ru(II) carbonyl species which are less active catalytically. The infrared of an inorganic residue obtained from an experiment involving difluoroethylene uptake for several days showed strong peaks at 1400 cm⁻¹ (assigned to NH₄⁺), 1620 cm⁻¹ (H₂O), a broad peak at 3100-3500 cm⁻¹ (NH₄⁺ and H₂O) and other sharp peaks at 1940 and 2060 cm⁻¹; these might well arise from the CO stretch in a Ru^{II}(CO) complex and a Ru^{II}(CO)₂ complex respectively,¹⁰ formed probably through the decarbonylation of unstable aldehyde intermediates.¹¹

Hydrogenation Experiments. An experiment was performed to determine whether the Ru^{II}-CF₂CH₂ solution could be hydrogenated or whether the system acted as a catalyst for hydrogenation of the difluoroethylene.

A 10⁻² M solution of Ru^{II} in 3 M HCl was reacted for 2 hours with 630 mm CF₂CH₂ at 60°. The olefin atmosphere was then pumped off and about half an atmosphere of H₂ was introduced into the system; no hydrogen uptake occurred and also no metallic ruthenium was observed. The total gas pressure was then raised to one atmosphere by admitting CF₂CH₂ into the system; the rate of uptake then measured was slightly less than that expected for half an atmosphere of CF₂CH₂ in the absence of hydrogen. Thus Ru^{II} is not a catalyst for the H₂ reduction of the double bond in difluoroethylene.

Vinyl fluoride system. Figure 4 shows uptake plots for the reaction of vinyl fluoride with solutions of chlororuthenate(II) at 50°. The plots are similar to those for the difluoroethylene system but the initial autocatalysis region is more pronounced. The only organic product of the reaction was acetaldehyde, characterized by VPC (Porapak Q column, 100°), NMR and as solid derivatives.

The kinetics of this system have been investigated and analyzed generally in the same manner as described for the very similar difluoroethylene system. Table IV summarizes some of the kinetic data obtained. A good first order dependence on Ru^{II} is observed for both the initial and linear rates, and the same complex dependence of between zero and

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

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

Table IV. Summary of kinetic data for the Ru^{II}-Vinylfluoride system at various temperatures. (3 M HCl, added [Ti^{III}] = 0.06 M).

Temp., °C	[Ru ^{II}] × 10 ³ , M	CH ₂ CHF mm	Rates of uptake × 10 ³ , M sec ⁻¹		k' × 10 ³ , sec ⁻¹ (Initial)
			Initial	linear	
50°	0.48	667	0.2†	0.35	4.45
	0.95	667	0.35	0.78	3.70
	1.90	667	0.73	1.62	3.85
	0.95	320	0.32	0.69	3.37
	0.95	167	0.30	0.67	3.16
55°	0.95	662	0.98	1.48	10.3
	0.95	320	0.79	1.08	8.35
	0.95	167	0.43	0.78	4.55
60°	0.95	630	1.23	2.14	13.0
	0.95	320	0.83	1.41	8.7
	0.95	167	0.45	0.80	4.7

first order in olefin is also observed. The data for the olefin dependence at the three temperatures did not give particularly good linear plots when plotted according to equation (5) and reliable values of k_1 could not be obtained. The k_1 values will however be somewhat greater than the k' values quoted in Table IV for the highest olefin pressures. An Arrhenius plot using these k' values gave considerable scatter, but a value of about 28 ± 5 kcal/mole was estimated for ΔH_1^* . Assuming the solubility of vinyl fluoride to be the same as that of 1,1-difluoroethylene, the value of k_2/k_{-1} at 60° for the vinyl fluoride system is about 4×10^3 . Values of k_3 were estimated as before; these gave a good Arrhenius plot and the parameters $\Delta H_3^* \sim 21$ kcal/mole and $\Delta S_3^* \sim -5$ eu.

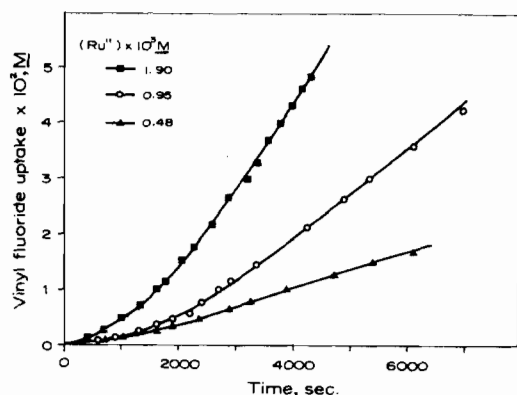


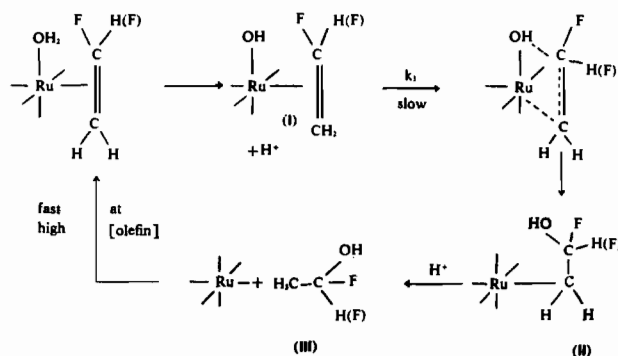
Figure 4. Rate plots for the reaction of Ru^{II} with vinyl fluoride at 50°, 665 mm CH₂CHF, 3 M HCl.

Experiments using hydrogen again showed that (a) Ru^{II} is not a catalyst for the hydrogenation of vinyl fluoride and that (b) the olefin complex is not reduced to the metal by H₂.

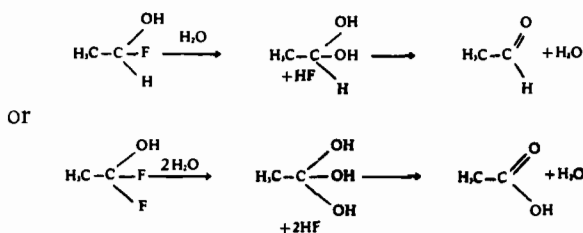
Discussion

Catalytic Properties. The present kinetic studies on the formation of Ru^{II}-fluoroethylene complexes in solution were more complicated than was anticipated because of subsequent decomposition of the complexes. The kinetics of the gas uptake can be

reasonably explained in terms of a catalytic hydration through an intermediate π -complex (the possibility of a doubly σ -bonded complex, which is well known for more highly fluorinated olefins,¹² cannot be ruled out but this is immaterial for the discussion of the hydration process). The following scheme seems plausible:



III would be unstable and be expected to decompose to acetaldehyde or acetic acid with the liberation of HF:



The steps involved in the production of III are of a rather general type that has been postulated for a whole range of catalytic reactions including hydrogenation, polymerization, oxidation and isomerization of olefins and the hydration of acetylenes.¹³⁻¹⁵ The coordinated water ligand will be somewhat acidic and nucleophilic attack by the coordinated OH⁻ at the C atom attached to the fluorine atom(s) yields the σ

(12) G. W. Parshall and F. N. Jones, *J. Am. Chem. Soc.*, **87**, 5356 (1965) and references therein.

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

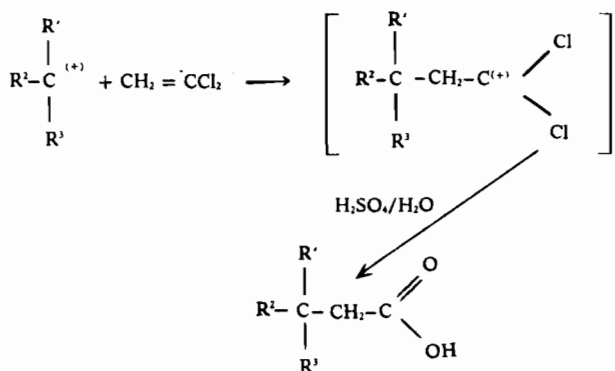
(14) J. Halpern, Proceedings of the 3rd International Congress on Catalysis, North Holland, Amsterdam, 1965, p. 146.

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

complex **II**. This is decomposed by electrophilic attack by a proton at the C atom attached to the metal to regenerate the $RuCl_{n-1}$ catalyst and give the hydration product.

The reaction scheme is similar to that reported for the catalyzed hydration of acetylenes by Ru^{III} ¹⁶ and Rh^{III} ¹⁷ chloride complexes; in these systems the rate determining step involved formation of the π -complex which then rapidly decomposed. In the present system, the initial slower reaction involves π -complex formation but the subsequent decomposition is not rapid; the Ru^{II} π -complex persists in solution and its subsequent decomposition must involve a slow stage determining the rate constant, k_3 . In the Pd^{II} oxidation of ethylene,¹⁸ the initial part of the reaction scheme proposed is similar to that shown here; the rate determining step is thought to be the conversion of a π -ethylene complex to the σ β -hydroxyethyl complex. A similar slow conversion could be involved here; this would require an inverse acid dependence and the limited data in Table II do show this. The activation parameters for the k_3 step for both fluoroethylene systems are very similar to those reported for the Pd^{II} system ($\Delta H^* = 19.8$ kcal/mole; $\Delta S^* = -8.7$ eu).¹⁸

The addition of water to the more reactive olefins, catalyzed by acids through carbonium ion intermediates, is well known. Hydration catalyzed by transition metal complexes has not been reported in any detail although Smidt and coworkers¹⁹ have mentioned that Pd salts catalyze the hydrolysis of vinyl halides, and Kemmitt and Nichols²⁰ have indicated that tetrafluoroethylene coordinated to Rh^I might be hydrolyzed by water. Bott and Kellmann²¹ have described the synthesis of carboxylic acids from 1,1-dichloroethylene by reaction with alcohols which can readily give carbonium ions, and it is of interest to note the similarity of their intermediate with the intermediate **II** in the present ruthenium catalyzed systems.



Complexes of Ru^{II} with ethylene, maleic, fumaric and acrylic acids,¹ and acrylamide²² are not decompo-

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

(17) B. R. James and G. L. Rempel, *J. Am. Chem. Soc.*, **91**, 863 (1969).

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

(19) J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier, and A. Sabel, *Angew. Chem. internat. Edit.*, **1**, 80 (1962).

(20) R. Kemmitt and D. Nichols, *Chem. Commun.*, 919 (1967).

(21) K. Bott and H. Hellmann, *Angew. Chem. internat. Edit.*, **5**, 870 (1966).

(22) B. R. James and J. Louie, unpublished results.

sed in solution to hydration products. The effect is thus far unique for a fluorine substituted ethylene; this could reflect the high electronegativity of the F atom with the resulting nucleophilic attack by OH^- in the π -complex **I**. Studies using vinyl bromide and vinyl chloride were complicated due to very rapid polymerization reactions and no definite conclusions could be drawn.

There was no catalytic hydrogenation of the fluoroethylenes, and the Ru^{II} complexes were not reduced by H_2 to the metal. This may be compared to the behaviour in the ethylene system where reduction to metal occurred¹ and that in the unsaturated acid and acrylamide systems where the olefinic bond is homogeneously reduced.^{1,22} The fluoroolefins thus stabilize the Ru^{II} sufficiently to prevent reduction to the metal. The mechanism postulated for the homogeneous hydrogenation is very similar to that shown above for the hydration but with OH^- replaced by H^- , the π -complex forming an intermediate hydride by heterolytic splitting of a H_2 molecule.¹ The apparent non-activation of the olefinic bond in the fluoroethylenes is probably due to the fact that the hydrogenation rate determining step cannot compete effectively with the hydration process, i.e. the nucleophilic attack by OH^- rather than hydride formation predominates. It is probable that the high electronegativity of fluorine prevents activation of H_2 as well as causing competitive hydration; however, no definite conclusions regarding the activation by fluoro groups of the olefinic bond for catalytic hydrogenation can be drawn.

Formation of the Ru^{II} -Olefin Complexes. The kinetics of formation of the complexes with the fluoroethylenes are similar to those reported for the complexing with ethylene itself² and a common mechanism, as exemplified by equations 1 and 2, presumably operates. The data for these systems are summarized in Table V, together with data for a reaction with formic acid thought to occur by the same mechanism.⁸ On the simple scheme indicated, k_1 should be independent of the type and concentration of the olefins used, while k_2/k_{-1} reflects the relative reactivities of the olefin and Cl^- toward the $Ru^{II}Cl_{n-1}$ intermediate. The difficulty arises as to what is meant exactly by the $RuCl_n$ term; spectral studies show that the Cl^- concentration does affect the distribution of the chlororuthenate(II) species and there is undoubtedly a mixture of such complexes present initially. The blue peak at $680 m\mu$ has been attributed²³ to $RuCl_4^{2-}$ (with unspecified coordina-

Table V. Kinetic data for complex formation of chlororuthenate(II) with olefins, and with formic acid (3 M HCl, 60°)

System	$k_1 \times 10^3$	ΔH_1^* kcal mole ⁻¹	ΔS_1^* eu	k_2/k_{-1}
$CF_2=CH_2$	0.3	29	+13	9.7×10^3
$CH_2=CHF$	~ 13.0	~ 28	—	$\sim 4 \times 10^3$
C_2H_4 ⁽²⁾	3.4	23	-4	6.5×10^3
$HCOOH$ ⁽⁸⁾	1.0	23.5	-5	33.0

(23) C. Jorgensen, *Acta. Chem. Scand.*, **10**, 518 (1956).

tion). Recent work by Adamson²⁴ suggests that a series of interconvertible hexacoordinated chloroaquoruthenium(II) complexes, analogous to the ruthenium(III) series,⁴ exists in HCl solutions; the higher chloro-complexes appear quite labile, and magnetic evidence suggests an equilibrium between low-spin octahedral complexes such as $\text{RuCl}_5\text{H}_2\text{O}^{3-}$ and a high-spin tetrahedral complex such as RuCl_4^{2-} might also be involved. Because of these complications, the observed rate constant k' , and the derived rate constant k_1 , must be considered as composite constants which

(24) M. G. Adamson, *Aust. J. Chem.*, 20, 2517 (1967); *J. Chem. Soc.*, A, 1370 (1968).

may reflect contributions from more than one ruthenium(II) complex.

The complexing in the difluoroethylene system is much slower than in the other olefin systems; the difluoroolefin may complex through two carbon-metal σ bonds, rather than the usual π -bonded complex.¹² The kinetics and mechanism of formation of such systems do not appear to have been reported; it is possible that difluoroethylene requires reaction with an intermediate having two Cl^- ligands displaced.

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