

THE $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ CATALYZED ACETALIZATION OF CROTONALDEHYDE

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(Received in USA 18 April 1974; received in UK for publication 31 May 1974)

The reported acidity of methanolic $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ (1) solutions has led to the conclusion that molecular transformations occurring in this system result from competitive $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ and proton catalyzed processes.¹ Both product differences^{1,2} and relative rates of successive reactions³ have been used to differentiate rhodium(I) and acid catalyzed reactions. We have observed that the acetalization of α,β -unsaturated aldehydes is efficiently catalyzed by $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ in methanolic solution and now wish to present evidence that rhodium(I) species are important in the catalytic process.⁴

A solution of crotonaldehyde (0.125 g, 1.8 mmol) in anhydrous methanol (3 ml) was treated with $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ (10 mg, 1.4 mole %) at room temperature for 60 min. to give crotonaldehyde dimethylacetal (74%) and unconverted aldehyde (26%).⁵ The yield of acetal is equilibrium dependent. A threefold increase of anhydrous methanol led to 89% conversion to acetal.⁶

Acetal production could result from protons produced by $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ in methanol, or by a more complex reaction in which rhodium(I) species are intimately involved. The rates of acetalization of crotonaldehyde and its saturated analog, butanal, in methanolic solutions of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ were monitored by gas chromatography. Plots of $\log[\text{aldehyde}]$ vs. time gave linear initial rates expected for a pseudo-first order rate law.⁷ The rate of acetalization for these two substrates was also measured in methanolic HCl solution of the same pH as that found for $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ in methanol.⁸ The results are given in Table I. The $t_{1/2}$ values obtained show that crotonaldehyde is acetalized 22 times faster than butanal by $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ catalysis but only 3-5 times faster by HCl catalysis. This difference in catalytic activity may result from the complexation of the catalyst with the double bond of crotonaldehyde.

The $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ catalyzed reaction of crotonaldehyde in methanol was allowed to stand at room temperature 24 hrs. Removal of solvent and products under vacuum yielded a brown solid which, when

Table I
Acetalization of Crotonaldehyde and Butanal in Methanol at 25°

Aldehyde	Catalyst ^a	t _{1/2} (min) ^b
Crotonaldehyde	HCl	3 ^c
Crotonaldehyde	Rh ₂ (CO) ₄ Cl ₂	6 ^c
Butanal	HCl	17
Butanal	Rh ₂ (CO) ₄ Cl ₂	130

(a) Catalyst concentration was identical for all runs.⁸ (b) t_{1/2} is the time required to attain one half the equilibrium conversion. Values from duplicate runs agreed to within 20%. (c) These values are less accurate due to the speed of the reaction.

added to a mixture of crotonaldehyde and methanol, catalyzed crotonaldehyde acetalization at a rate about half that of fresh Rh₂(CO)₄Cl₂. Thus significant catalytic activity remains even through the initial rhodium complex is converted to other rhodium(I) species by reaction with solvent. Thus the catalytic specie may be a methoxy containing complex resulting from reaction with solvent rather than Rh₂(CO)₄Cl₂. The partial loss of activity is probably due to reaction with the water produced by acetalization.¹⁰

The addition of sodium bicarbonate (10 mg) or N,N,N',N'-tetramethylnaphthalenediamine (10 mg) led to rapid darkening of the reaction mixture and negligible acetalization. This effect could be due to reduced acidity or more probably due to destruction of Rh₂(CO)₄Cl₂ by nucleophiles.⁹ These observations are consistent with a metal hydride or acidic metal complex as the active agent. However the exact nature of the catalytic event remains unsolved.

We are presently investigating the nature of the acetalization and its potential in synthesis.

Acknowledgment: The author wishes to thank Dr. Brian Walker for helpful comments.

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5. Yields were measured by gas chromatography and the products were identified by comparison with authentic samples.
6. Other unsaturated aldehydes give the corresponding acetals under identical conditions. R. V. Hoffman, unpublished work.
7. The rate law is given by $k[\text{Rh}_2(\text{CO})_4\text{Cl}_2][\text{aldehyde}][\text{CH}_3\text{OH}]^2$ however, since $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ is constant and $[\text{CH}_3\text{OH}]^2$ is constant due to sufficient excess, the rate can be expressed as $k'[\text{aldehyde}]$.
8. Solutions of HCl in methanol (3 ml) were used which had the same conductivity and pH as Rh₂(CO)₄Cl₂ (10 mg) in methanol (3 ml). No decrease in pH was observed upon addition of aldehyde.
9. After 7 hr. in methanol, the carbonyl stretching frequencies of Rh₂(CO)₄Cl₂ disappear due to reaction with solvent.^{2b} Furthermore carbon monoxide is readily displaced by a variety of olefins and nucleophiles. B. R. James, *Coord. Chem. Rev.*, **1**, 505 (1966).
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