

k_{-1} by means of the equation $(k_{-1}[\text{OH}^-] + k_2[\text{CN}^-]) = 4.6/$ (induction time in seconds).

Given in Table I are the results of the kinetic investigation along with the rate constants calculated.

The average value obtained for k_2 at 25° was $0.036 \pm 0.0021 \text{ M}^{-1} \text{ sec}^{-1}$ and the average for k_1 at 25° was $0.015 \pm 0.0017 \text{ M}^{-1} \text{ sec}^{-1}$. The uncertainties given are standard deviations. The estimated value of k_{-1} at 25° was $4 \text{ M}^{-1} \text{ sec}^{-1}$. This is only a crude estimate at the best because the determination of the induction time can only be approximated to and within 20 sec, and the calculation of k_{-1} involves the difference of two terms which have about the same magnitude.

Least-squares treatment of the plot of $\log k$ vs. $1/T$ for k_1 and k_2 gave $11.3 \pm 0.5 \text{ kcal mol}^{-1}$ and $14.1 \pm 0.4 \text{ kcal mol}^{-1}$, respectively, as the activation energies and standard deviations of the two rate processes. These activation energies are much larger than that reported for the similar cobalt(II) complex in its reaction with cyanide.⁵ Also, the mechanism of the reaction is totally different since only two cyanides are involved through the slow step in the manganese(III) reaction while three cyanides were found to be involved in the case of the

cobalt(II) reaction. The higher activation energy in the manganese(III) reaction may be because the manganese(III) is in a seven-coordinate hydroxo form and there is only an exchange of cyanide for the hydroxide.

The reactions of EDTA complexes of nickel(II) and cobalt(II) were found to be much faster than the CyDTA complexes.⁵ Simple observation of the rate of reaction of Mn^{III} -EDTA with cyanide showed that at 25° it appeared to have an apparent half-life of less than 10 sec. While this is too fast to make investigation practical by the technique used in this investigation, it is in agreement with the observation that ligand replacement reactions for EDTA complexes are much faster than those for CyDTA complexes.

Registry No. Potassium salt of *trans*-1,2-diaminocyclohexanetetraacetatomanganate(III), 38127-69-4; sodium cyanide, 143-33-9.

Acknowledgment. The authors wish to thank the National Science Foundation for financial support which made the work on this research possible.

Contribution from the Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

Activation of Hydrogen by Bridged Transition Metal Carboxylates. Rhodium(II) Acetate Catalyzed Hydrogenation of Olefins

B. C. Y. HUI, W. K. TEO, and G. L. REMPEL*

Received August 8, 1972

Dimeric rhodium(II) acetate, $\text{Rh}_2(\text{OCOMe})_4$, functions as an efficient and selective catalyst for the hydrogenation of terminal olefins in a variety of solvent media. The detailed kinetics are reported for the hydrogenation of dec-1-ene in *N,N'*-dimethylformamide solution under mild conditions. These studies indicate that the initial step of the hydrogenation mechanism involves activation of hydrogen at only one of the metal centers of the dimer. The hydrogen activation process, which involves heterolytic splitting of hydrogen, leads to the formation of an intermediate metal hydride, $\text{HRh}_2(\text{OCOMe})_3$, which undergoes a subsequent reaction with the olefinic substrate. Insertion of the olefin into the metal-hydride bond followed by proton attack on the intermediate metal alkyl completes the catalytic cycle.

Introduction

The hydrogenation of simple olefins catalyzed by carboxylate complexes of the first-row transition elements scandium(III) to zinc(II) has been extensively studied.¹ The general mechanism proposed for these catalysts involves dimeric catalytic species. A recent series of publications² has reported that dimethylformamide solutions of rhodium(I) complexes with tyrosine, anthranilic acid, or phenylacetic acid are excellent catalysts for the hydrogenation of olefins. Although the structure of these complexes is not clear, they have been represented as $\text{H}[\text{Rh}_2(\text{PhCH}_2\text{COO})_2\text{Cl}]$. The RCOO groups appear to function as bridges or chelates and it has been suggested that the rhodium interacts with the π electrons of the phenyl ring.² The systems using $\text{H}[\text{Rh}_2(\text{PhCH}_2\text{COO})_2\text{Cl}]$ are discussed by Khidekel, *et al.*,² as in-

volving the monomeric catalytic species, $\text{HRh}(\text{PhCH}_2\text{CO}_2)^-$. Protonation of rhodium(II) acetate by noncomplexing, nonoxidizing acids has led to the formation of Rh_2^{4+} which in the presence of triphenylphosphine is an active hydrogenation catalyst.³ The catalytic species in these systems, however, appear to be monomeric Rh(I) complexes. We have noted previously⁴ that certain second-row transition metal acetates, including the dimeric rhodium(II) acetate, $\text{Rh}_2(\text{OCOMe})_4$, function as homogeneous catalysts for the hydrogenation of olefins in a wide variety of solvent media.

The tetrabridged dimeric rhodium(II) acetate, $\text{Rh}_2(\text{OCOMe})_4$, has a Rh-Rh separation of 2.45 Å which suggests a significant Rh-Rh interaction.⁵ A number of adducts of the type $\text{Rh}(\text{OCOMe})_2\text{L}$ have been prepared⁶⁻⁸ and in most cases it is probable that these complexes are also dimeric

(1) V. A. Tulupov, *Russ. J. Phys. Chem.*, **39**, 1251 (1965); **41**, 456 (1967).

(2) N. V. Borunova, L. Kh. Friedlin, M. L. Khidekel, S. S. Danielova, V. A. Avilov, and P. S. Chekrii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 434 (1968); V. A. Avilov, Yu. G. Brod'ko, V. B. Panov, M. L. Khidekel, and P. S. Chekrii, *Kinet. Catal. (USSR)*, **9**, 582 (1968); O. N. Efimov, M. L. Khidekel, V. A. Avilov, P. S. Chekrii, O. N. Eremenko, and A. G. Ovcharenko, *J. Gen. Chem. USSR*, **38**, 2581 (1968).

(3) P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. A*, 3322 (1970).

(4) B. C. Hui and G. L. Rempel, *Chem. Commun.*, 1195 (1970).

(5) L. Dubicki and R. L. Martin, *Inorg. Chem.*, **9**, 673 (1970).

(6) S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, **2**, 960 (1963).

(7) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).

(8) L. A. Nazarova, I. I. Chernyaev, and A. S. Morozova, *Russ. J. Inorg. Chem.*, **11**, 1387 (1966).

with the addends L terminally coordinated to rhodium atoms bridged by the acetate cage. This is consistent with analytical data, diamagnetism, and electronic spectra of the compounds.⁶⁻⁸ Thus, rhodium acetate itself might be expected to have the potential of providing suitable sites at both its terminal positions for the activation of olefins and/or hydrogen.

The results of several important catalytic studies indicate that often complexes emerge as dimers, trimers, etc., in the catalytic reaction.⁹ However, a dimeric structure for the catalytic complex in itself still does not answer the question as to whether both atoms participate in the catalytic process or whether one metal atom functions primarily as a ligand in relation to the other. The latter possibility exists in a number of cases⁹ and is of interest with respect to the effect the nature of the ligand has on the catalytic process. Also it is important to distinguish it from the case where both metals are directly involved in the catalytic complex by way of bond formation with the molecules entering into the reaction. The possibility of the overall catalytic process occurring simultaneously at each metal center also arises.

Kinetic studies with polymetallic complexes under homogeneous conditions may provide further insight into this question as well as information about some of the mechanistic features of their heterogeneous counterparts. This paper reports on the detailed kinetics and mechanism of the homogeneously catalyzed hydrogenation of olefins by $\text{Rh}_2(\text{OCOMe})_4$.

Experimental Section

Rhodium(II) acetate, $\text{Rh}_2(\text{OCOMe})_4$, was prepared from rhodium trichloride trihydrate (Engelhard Industries Ltd.) according to the literature;³ the compound analyzed correctly and the electronic spectra and infrared spectra agreed with that previously reported.⁶ Reagent grade solvents were used throughout. Dimethylformamide and dimethylacetamide were purified by storing over CaH_2 under N_2 for at least 40 hr followed by distillation under reduced pressure; the constant-boiling fraction was collected onto Linde 4A molecular sieve and stored under Linde ultrahigh-purity N_2 . Alkenes and other unsaturated substances were purified¹⁰ before use. Linde ultrahigh-purity H_2 and Matheson CP grade D_2 were passed through an Engelhard Deoxo Purifier before admission to the kinetic apparatus.

IR spectra were recorded on a Perkin-Elmer 337; uv-visible, on a Beckman DK 2. Glc analysis was carried out using a Hewlett-Packard F & M Scientific 700 laboratory chromatograph. For paraffin and isomerized olefin detection a 12-ft column of Union Carbide 10% uc-w 98 at 100° was used.

Kinetic measurements were made by following the consumption of hydrogen at constant pressure using the apparatus and procedure described earlier.¹¹ The solubility of H_2 in dimethylformamide was determined as $2.09 \times 10^{-3} M$ at a total pressure of 750 mm and 50°, Henry's law being obeyed at least up to 1 atm. The solubility was found to vary little over the temperature range 35–60°.

Results

Solutions of 5 mM $\text{Rh}_2(\text{OCOMe})_4$ in a variety of solvents were found to hydrogenate terminal and cyclic monoenes homogeneously at temperatures of 30–80° under 1 atm or less of hydrogen. Comparative rates under standard conditions are given in Table I. No hydrogenation of internal monoenes, dienes, trans olefins, or other functional groups such as ketones was observed. Alkynes reacted very slowly. Molecular oxygen was reduced to water by hydrogen in the presence of $\text{Rh}_2(\text{OCOMe})_4$.

In the absence of olefin no measurable uptake of hydrogen was apparent, even at temperatures as high as 80°, and no

Table I. Relative Rates of Hydrogenation of Substrates by $\text{Rh}_2(\text{OCOMe})_4$ ($[\text{Rh}_2(\text{OCOMe})_4] = 5.0 \text{ mM}$; $[\text{Substrate}] = 1.0 M$; $p'_{\text{H}_2} = 76 \text{ cm} - p'_{\text{vapor}}$; $T = 30^\circ$)

Solvent	Substrate	Initial rate $\times 10^6$, $M \text{ sec}^{-1}$
HCONMe ₂	Dec-1-ene	34.0 ^a
	Hex-1-ene	22.8
	Oct-1-ene	12.9
	Hex-1-en-3-ol	10.8
	Styrene	8.85
	Diethyl Maleate	7.91
	2-Methyl-3-butyn-2-ol	5.40
	Ethylene	4.05 ^b
MeCONMe ₂	Hex-1-ene	1.85
	Cyclooctene	1.75
	Hex-1-ene	5.55 ^a
	Tetrahydrofuran	21.2
	Dioxan	4.78 ^a
	Me ₂ SO	6.70 ^a
	EtOH	5.10
	EtOH	Hex-1-ene

^a $T = 50^\circ$; substrate concentration 0.1 M. ^b $T = 50^\circ$; rate is expressed as $\text{C}_2\text{H}_4 + \text{H}_2$ consumed [$p'_{\text{C}_2\text{H}_4} = 36.5 \text{ cm}$; $p'_{\text{H}_2} = 37.0 \text{ cm}$].

adduct formation of olefin with $\text{Rh}_2(\text{OCOMe})_4$ was apparent. Although ethylene was reduced to ethane by hydrogen in the presence of $\text{Rh}_2(\text{OCOMe})_4$, there did not appear to be any measurable uptake of ethylene in the absence of hydrogen or *vice versa*. The initial visible absorption spectrum of $\text{Rh}_2(\text{OCOMe})_4$ in DMF, λ_{max} (ϵ) 591 nm (137.6), 442.5 nm (51.6), did not change on the addition of olefin and/or hydrogen to the solution and remained unchanged throughout the course of the reaction. Aqueous methanol solutions of $\text{Rh}_2(\text{OCOMe})_4$ were found to be diamagnetic by the nmr method. No esr signal was observed for the $\text{Rh}_2(\text{OCOMe})_4$ catalytic systems in DMF at room temperature or at -20° , thus suggesting that a dimeric Rh^{II} species is the active catalyst. At the completion of a hydrogenation reaction the $\text{Rh}_2(\text{OCOMe})_4$ was easily recovered and could be reused without any appreciable loss in activity.

The reaction kinetics for the hydrogenation reaction appear to be overall first order in olefin at low olefin concentration for the variety of solvent media and olefins used.

Representative uptake plots are shown in Figure 1. In the case of styrene as substrate the total gas consumption and glc analysis of the final reaction solution corresponded to complete conversion to the saturated product. However, when hex-1-ene was used as substrate, the total gas consumption indicated 80% of hex-1-ene had been hydrogenated. This was consistent with the glc analysis which showed 82% of hex-1-ene converted to hexane and 18% to a mixture of *cis*- and *trans*-hex-2-ene which were not hydrogenated by $\text{Rh}_2(\text{OCOMe})_4$ under the reaction conditions used in this investigation. Gas consumption measurements and glc analysis indicated that oct-1-ene and dec-1-ene also were hydrogenated in the presence of $\text{Rh}_2(\text{OCOMe})_4$ to give approximately 85% paraffin and 15% internal olefins. In the absence of hydrogen, $\text{Rh}_2(\text{OCOMe})_4$ in DMF did not cause any isomerization of olefins under the standard conditions used.

In order to study the kinetics of the hydrogenation reaction in detail, dec-1-ene was used as substrate in DMF at temperatures of 36–56.5° under 1 atm or less of hydrogen. The kinetics of the system were obtained by considering the initial linear region of the gas consumption plot. The results obtained, which are shown in Table II, indicate a good first-order dependence on $\text{Rh}_2(\text{OCOMe})_4$ at least up to 0.0057 M and a good first-order dependence on hydrogen over a

(9) A. E. Shilov, *Kinet. Catal. (USSR)*, 11, 256 (1970).

(10) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(11) B. R. James and G. L. Rempel, *Discuss. Faraday Soc.*, 46, 48 (1968).

Table II. Summary of Kinetic Data in DMF at 50°

$10^3[\text{Rh}_2(\text{OCOMe})_4]$, <i>M</i>	$[\text{Dec-1-ene}]$, <i>M</i>	p_{H_2} , mm	$10^3[\text{H}_2]$, <i>M</i>	Initial rate of H_2 consumption $\times 10^5, M \text{ sec}^{-1}$	$k',^a$ $M^{-1} \text{ sec}^{-1}$
0.7	0.10	735	2.09	0.56	3.83
1.2	0.10	735	2.09	0.70	2.79
1.9	0.10	735	2.09	1.28	3.23
2.7	0.10	735	2.09	1.60	2.84
3.8	0.10	735	2.09	2.54	3.19
3.8	0.10	735	2.09	2.72	3.41
5.3	0.10	735	2.09	3.40	3.07
5.6	0.10	735	2.09	3.20	2.74
5.6	0.10	735	2.09	3.50	3.00
5.7	0.10	735	2.09	3.86	3.19
5.6	0.02	735	2.09	0.86	0.74
5.6	0.04	735	2.09	1.42	1.21
5.6	0.06	735	2.09	1.96	1.68
5.6	0.07	735	2.09	2.56	2.19
5.6	0.21	735	2.09	4.00	3.41
5.6	0.42	735	2.09	4.16	3.55
5.6	1.05	735	2.09	5.10	4.35
3.8	0.10	195	0.55	0.69	3.30
3.8	0.10	375	1.06	1.47	3.65
3.8	0.10	629	1.80	2.25	3.29
3.8	0.10	730	2.08	2.72	3.44
5.6	0.10	735	2.09	2.76	2.36 ^b
5.6	0.10	735	2.09	1.39	1.18 ^c
5.6	0.10	735	2.09	3.10	2.65 ^d
5.6	0.10	735	2.09	1.60	1.37 ^e
5.6	0.21	735	2.09	3.08	2.64 ^f

^a $k' = (\text{initial rate})/[\text{Rh}_2(\text{OCOMe})_4][\text{H}_2]$. ^b $[\text{H}_2\text{O}] = 0.9 \times 10^{-2} M$. ^c $[\text{Et}_3\text{N}] = 1.12 \times 10^{-2} M$. ^d $[\text{LiCl}] = 3.0 \times 10^{-2} M$. ^e Using D_2 . ^f Using D_2 at 56.5°.

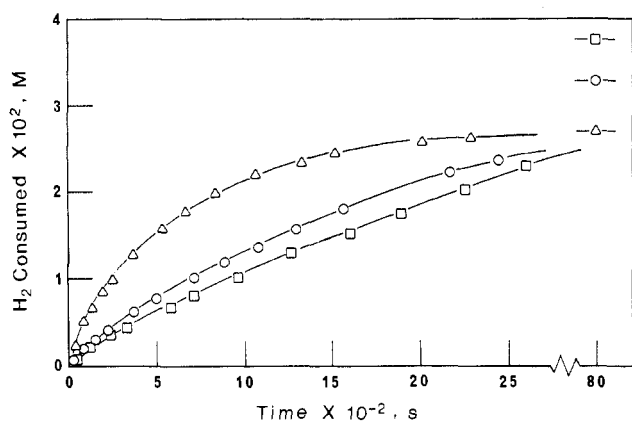


Figure 1. Representative hydrogen consumption plots for the $\text{Rh}_2(\text{OCOMe})_4$ -catalyzed hydrogenation of olefins in DMF, at 1 atm total pressure: Δ , hex-1-ene (0.034 *M*), $[\text{Rh}_2(\text{OCOMe})_4] = 0.0161 M$, 30°; \circ , dec-1-ene (0.040 *M*), $[\text{Rh}_2(\text{OCOMe})_4] = 0.0056 M$, 50°; \square , styrene (0.040 *M*), $[\text{Rh}_2(\text{OCOMe})_4] = 0.0050 M$, 50°.

hydrogen partial pressure range of 195–735 mm. The dependence on dec-1-ene, which is first order at low dec-1-ene concentrations, tends toward zero order at dec-1-ene concentrations above 0.1 *M* as shown in Figure 2 for the reaction conditions specified in Table II.

A marked inverse dependence on acid concentration (HClO_4) was noted over the range of 0–0.005 *M* when the total salt strength was kept constant by addition of LiClO_4 (Table III). Addition of acetic acid (0–4 *M*) also caused an inverse dependence as did *p*-toluenesulfonic acid (0–0.08 *M*) as indicated by the results in Table III. However, in the case of acetic acid and *p*-toluenesulfonic acid, complications due to complexing of acetate or *p*-toluenesulfonate also occur as shown in Table IV. The addition of large quantities of free acid (*i.e.*, $[\text{H}^+ \text{ type species}] > 0.01 M$) causes an added complication to the system in that some protonation of the bridged acetates³ occurs under the reaction conditions used.

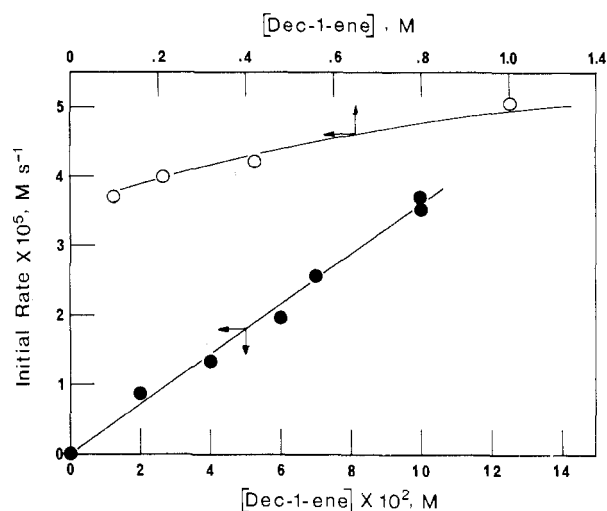


Figure 2. Dependence of the initial rate of hydrogenation on $[\text{dec-1-ene}]$ in DMF at 50°, 0.0056 *M* $\text{Rh}_2(\text{OCOMe})_4$, and 735 mm H_2 .

Addition of small amounts of water (0–0.09 *M*) caused only a slight decrease in the initial rate of hydrogen consumption. Also the addition of a small amount of chloride to the system did not appear to affect the initial rate. The presence of the base, triethylamine (0.0112 *M*), however, did cause a marked inhibition in reaction rate. Rate measurements using deuterium indicated an isotope effect of $k_{\text{H}}'/k_{\text{D}}' \approx 2.6$ at 56.5° (Table II).

Discussion

The results indicate that $\text{Rh}_2(\text{OCOMe})_4$ in a wide variety of solvent media is a fairly efficient and highly selective catalyst for the hydrogenation of terminal olefins and substituted ethylenes, as well as ethylene itself. In the case of terminal olefins a certain amount (~15–20%) of double-bond isomerization takes place during hydrogenation. The

Table III. Effect of Added Acid on the Catalytic Hydrogenation ([Rh₂(OCOMe)₄] = 5.6 mM; [Dec-1-ene] = 0.10 M; [H₂] = 2.09 × 10⁻³ M; 50°)

10 ³ [HClO ₄], M	10 ² [LiClO ₄], M	[HOCOMe], M	k', M ⁻¹ sec ⁻¹
0.00	3.00	0.00	2.60
0.62	3.00	0.00	1.74
1.25	0.00	0.00	1.38
2.50	2.75	0.00	0.68
2.50	0.00	0.00	0.75
5.00	0.00	0.00	0.40
5.00	0.00	0.00	0.43
0.00	0.00	0.17	2.82
0.00	0.00	1.00	1.70
0.00	0.00	1.00	1.76
0.00	0.00	2.00	1.06
0.00	0.00	4.00	0.72
10.0 ^a	20.0 ^b	0.00	1.16
15.0 ^a	15.0 ^b	0.00	1.06
20.0 ^a	10.0 ^b	0.00	0.94
30.0 ^a	0.0	0.00	0.74

^a *p*-Toluenesulfonic acid. ^b Sodium *p*-toluenesulfonate.

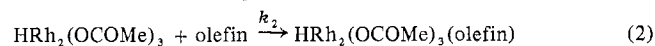
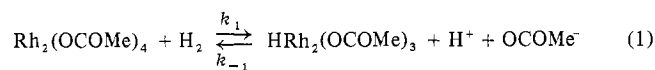
Table IV. Effect of Added Acetate on the Catalytic Hydrogenation ([Rh₂(OCOMe)₄] = 5.6 mM; [Dec-1-ene] = 0.21 M; [H₂] = 2.09 × 10⁻³ M; 50°)

[NaOCOMe·3H ₂ O], M	k', M ⁻¹ sec ⁻¹	[NaOCOMe·3H ₂ O], M	k', M ⁻¹ sec ⁻¹
0.50	3.00	2.00	1.90
1.00	2.52	3.00 ^a	1.50
1.00 ^a	2.45	1.10 ^b	0.28
1.10	2.38		

^a LiOCOMe·2H₂O used in place of NaOCOMe·3H₂O. ^b Sodium *p*-toluenesulfonate.

isomerized product is not hydrogenated under the normal conditions (Table II) employed.

The kinetic data obtained for the hydrogenation system in DMF are consistent with an initial reaction of Rh₂(OCOMe)₄ with hydrogen followed by a subsequent reaction of an intermediate hydride complex with the olefins as shown in eq 1 and 2. The observed inverse dependence on added acid suggests that the hydrogen activation step (eq 1) of the reaction involves a heterolytic splitting of hydrogen.



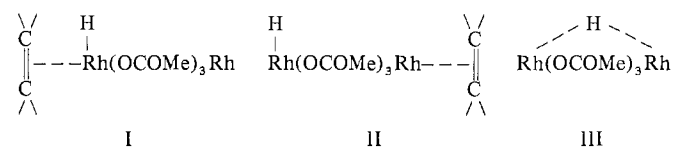
An inverse dependence on acetate suggests that one of the acetate bridges, which may be functioning to some extent as a suitable base for stabilization of the released proton (*i.e.*, H⁺ + OCOMe⁻ ⇌ HOCOMe), is substituted by the newly formed hydride ligand. Such a hydrogen activation mechanism seems very likely in view of the ability of the Rh₂(OCOMe)₄ species to undergo protonation reactions.³ DMF, a moderately high polar solvent (dielectric constant 36.7), has been found to solvate cations readily and act as a proton acceptor^{12,13} and consequently may also be functioning as a suitable base in the present system.

The strict first-order dependences observed for [Rh₂(OCOMe)₄] and [H₂] over the concentration ranges investigated are consistent with an activation of hydrogen at only one of the rhodium atoms of the dimer. However, on the basis of the kinetic results, it is not possible to determine the rhodium atom of the dimer at which olefin activation occurs.

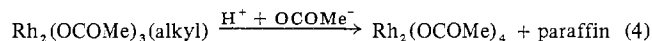
(12) A. J. Parker, *Quart. Rev., Chem. Soc.*, **16**, 163 (1962).

(13) R. S. Kittila, "Dimethyl Formamide Chemical Uses," E. I. du Pont de Nemours and Co., Wilmington, Del., 1967, p 57.

It would appear that the most facile route to hydrogenation would be obtained when the olefin is π bonded to the rhodium hydride as shown in intermediate I, since coordination of the olefin to the nonhydridic rhodium site as shown in intermediate II would probably involve a transfer of the hydride through a considerable distance rather than an olefin insertion into the Rh-H bond. Insertion of the olefin into a metal-hydrogen bond appears to be a general feature of hydrogenation mechanisms which involve an initial heterolytic splitting of hydrogen.^{14,15} A quite likely alternative possibility for the intermediate HRh₂(OCOMe)₃(olefin) species involves the formation of a bridged hydride species as shown for intermediate III in which both rhodium atoms are equivalent with respect to olefin coordination and activation. Bridged hydride structures have been observed for a number of polymeric hydride complexes.¹⁶



The intermediate HRh₂(OCOMe)₃(olefin) complex could undergo a subsequent rapid reaction according to eq 3 and 4 in which an intermediate metal alkyl is formed which subsequently undergoes attack by H⁺ to form the paraffin and Rh₂(OCOMe)₄. Reverse alkyl formation (eq 3) appears to be

$$\text{HRh}_2(\text{OCOMe})_3(\text{olefin}) \rightleftharpoons \text{Rh}_2(\text{OCOMe})_3(\text{alkyl}) \quad (3)$$


likely on the basis of the isomerization which is found to occur. The occurrence of isomerization during hydrogenation is regarded as good evidence for the stepwise addition of hydrogen to the unsaturated substrate.^{15,17}

Application of a steady-state approximation for the HRh₂(OCOMe)₃ species in the hydrogenation mechanism given by eq 1-4 results in the rate law

$$-\frac{d[\text{H}_2]}{dt} = \frac{-d[\text{olefin}]}{dt} = \frac{k_1 k_2 [\text{Rh}_2(\text{OCOMe})_4] [\text{H}_2] [\text{olefin}]}{k_{-1} [\text{H}^+] [\text{OCOMe}^-] + k_2 [\text{olefin}]} \quad (5)$$

At constant [H⁺] and [olefin] eq 5 becomes

$$-\frac{d[\text{H}_2]}{dt} = k' [\text{Rh}_2(\text{OCOMe})_4] [\text{H}_2] \quad (6)$$

where

$$k' = \frac{k_1 k_2 [\text{olefin}]}{k_{-1} [\text{H}^+] [\text{OCOMe}^-] + k_2 [\text{olefin}]} \quad (7)$$

Values of k' are calculated from the initial slopes of the gas consumption plots using eq 6 and these are listed in Table II. The expression for k' given by eq 7 can be rewritten as

$$\frac{1}{k'} = \frac{1}{k_1} + \frac{k_{-1} [\text{H}^+] [\text{OCOMe}^-]}{k_1 k_2 [\text{olefin}]} \quad (8)$$

(14) J. Halpern, *Discuss. Faraday Soc.*, **46**, 7 (1968).

(15) J. Kwiatek in "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., New York, N. Y., 1971, pp 18-21.

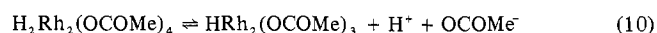
(16) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, pp 60-70.

(17) R. S. Coffey in "Aspects of Homogeneous Catalysis," Vol. I, R. Ugo, Ed., Carlo Manfredi, Milan, 1970, pp 9-10.

Although some uncertainty arises in measuring initial slopes, it is seen that a plot of $1/k'$ vs $1/[\text{olefin}]$, as shown in Figure 3, is reasonably linear and yields the values $k_1 = 4.60 M^{-1} \text{sec}^{-1}$ and $k_{-1}[\text{H}^+][\text{OCOME}^-]/k_2 = 0.095 M$. A plot of $1/k'$ vs. added $[\text{H}^+]$ is shown in Figure 4 and the straight line drawn gives $k_1 = 3.92 M^{-1} \text{sec}^{-1}$ and $k_{-1}[\text{OCOME}^-]/k_2 = 168$. A straight line is also obtained when $1/k'$ is plotted as a function of $[\text{OCOME}^-]$ as shown in Figure 5 and yields a value of $k_1 = 3.85 M^{-1} \text{sec}^{-1}$ and $k_{-1}[\text{H}^+]/k_2 = 113.8$. Consideration of the results of Figures 4 and 5 with the results of the inverse olefin plot (Figure 3) indicates $[\text{H}^+] = 5.65 \times 10^{-4} M$ and a $[\text{OCOME}^-] = 8.3 \times 10^{-4} M$ for a reaction involving a $[\text{Rh}_2(\text{OCOME})_4] = 5.6 \times 10^{-3} M$. Furthermore a value of $k_{-1}/k_2 = 2.05 \times 10^5 M^{-1}$ is obtained from the results of Figures 3-5.

Although it would be expected on the basis of the above results that the addition of a strong base, such as triethylamine, would favor metal hydride formation by accepting the proton generated in eq 1, it is found that the rate of the hydrogenation reaction is greatly decreased on the addition of triethylamine. Spectral studies suggest that this probably results from some degree of complexation of the amine with the $\text{Rh}_2(\text{OCOME})_4$, thus blocking the catalytic sites normally available for activation of hydrogen and the olefinic substrate. A number of nitrogen donors including triethylamine and ammonia have been reported to form adducts with $\text{Rh}_2(\text{OCOME})_4$.⁶ Alternatively the amine may function by decreasing the rate of the reaction given by eq 4 due to a very low concentration of protons. This seems less likely, however, since in the absence of an olefinic substrate no hydrogen uptake is observed even at relatively high $[\text{Rh}_2(\text{OCOME})_4]$ and $[\text{Et}_3\text{N}]$ as might be expected on the basis of the reaction given by eq 1.

At 0.21 M dec-1-ene where k' approximates to k_1 and the rate law given by eq 6 is applicable, the observed kinetic isotope effect, $k_{\text{H}}/k_{\text{D}} \approx 2.6$ at 56.5°, suggests that greater dissociation of the H-H bond by the metal site may be important prior to formation of the activated $\text{HRh}_2(\text{OCOME})_3$ complex (eq 1). In cases where hydrogen reacts with metal complexes by displacing an anionic ligand and forming a metal-hydrogen bond, it has been suggested that the reaction may involve an initial oxidative addition of hydrogen and subsequent loss of $(\text{H}^+ + \text{X}^-)$ from a $\text{H}_2\text{MY}_n\text{X}_m$ intermediate.¹⁸ In the present system this could occur as shown in eq 9 and 10.



In cases where the hydrogen activation process involves solely dihydride formation, as is the case in the addition of hydrogen to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, the small kinetic isotope effect, $k_{\text{H}}/k_{\text{D}} = 1.22$, has been interpreted as suggesting little H-H bond breaking in the activated complex.¹⁹ However, recent detailed studies on the $\text{IrCl}(\text{CO})(\text{PPh}_3)_2\text{-H}_2$ system, with respect to correlations of dynamic and structural data, converge on a mechanism in which the transition state resembles closely the dihydride product, thus implying considerable H-H bond breaking in the activated complex.²⁰ Siegel and Ohrt²¹ have calculated kinetic hydrogen isotope

(18) R. A. Schunn in "Transition Metal Hydrides," E. L. Muettterties, Ed., Marcel Dekker, New York, N. Y., 1971, pp 208-213.

(19) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1968).

(20) L. Vaska and M. F. Werneke, *Trans. N. Y. Acad. Sci.*, **31**, 70 (1971).

(21) S. Siegel and D. W. Ohrt, *Chem. Commun.*, 1529 (1971).

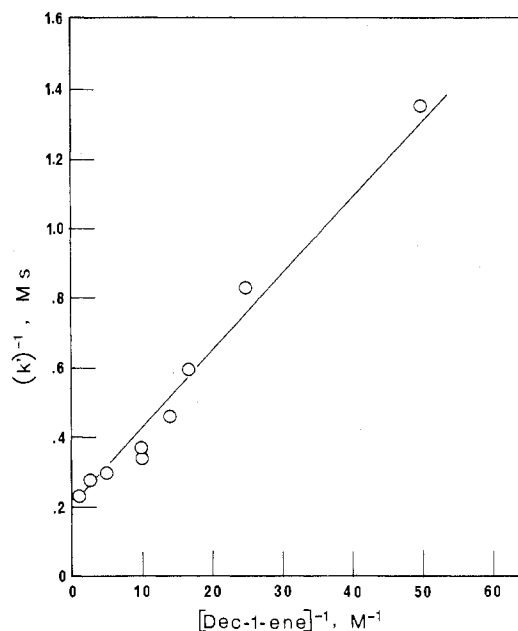


Figure 3. Dependence of initial rate on the olefin concentration plotted in accord with eq 8 ($[\text{Rh}_2(\text{OCOME})_4] = 0.0056 M$, 735 mm H_2 , 50°).

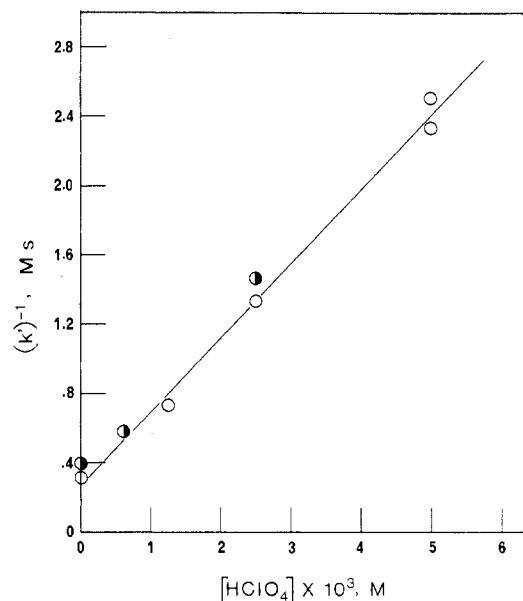


Figure 4. Dependence of initial rate on the proton concentration plotted in accord with eq 8 ($[\text{Rh}_2(\text{OCOME})_4] = 0.0056 M$, 735 mm H_2 , $[\text{dec-1-ene}] = 0.10 M$, 50°): \circ , $[\text{HClO}_4] + [\text{LiClO}_4] = 0.030 M$; \bullet , $[\text{HClO}_4]$.

effects for a number of catalyzed hydrogenations which involve rhodium dihydride species and stated that in cases where the rate-controlling reaction is simply the oxidative addition of hydrogen to a transition metal complex and if the bonding of hydrogen to the metal in the transition state is comparable to that found in the dihydride complex, then the kinetic isotope effect should be the same as that computed for the exchange reaction.

In systems which have been suggested to involve strictly a heterolytic splitting of hydrogen, such as the aqueous chlororuthenate(III) system,²² again very small isotope effects have been observed. This has often been interpreted in terms of a process which involves metal hydride formation and hydro-

(22) J. Halpern and B. R. James, *Can. J. Chem.*, **44**, 671 (1966).

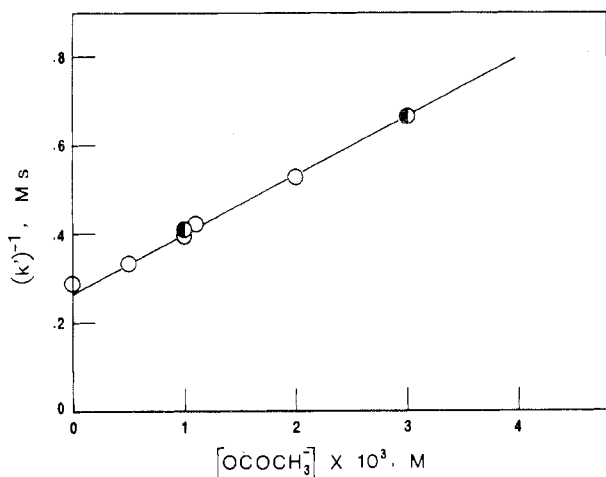
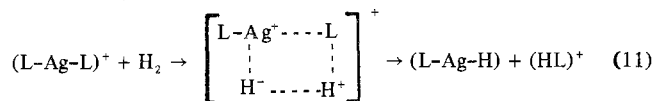


Figure 5. Dependence of initial rate on the acetate concentration plotted in accord with eq 8 ($[\text{Rh}_2(\text{OCOMe})_4] = 0.0056 \text{ M}$, 735 mm H_2 , $[\text{dec-1-ene}] = 0.21 \text{ M}$, 50°): ○, $\text{NaOCOMe} \cdot 3\text{H}_2\text{O}$; ●, $\text{LiOCOMe} \cdot 2\text{H}_2\text{O}$.

gen breaking in a concerted step. In these systems, however, probably only one of the hydrogen atoms of the initial hydrogen molecule is directly involved in binding to the metal center in the activated complex as suggested for the silver-amine systems^{14,23} (eq 11). Consequently, the metal



center itself probably plays only a more limited role in the dissociation of the H-H bond. The small isotope effect observed in the activation of hydrogen by the nonaqueous DMA-trichlorotris(diethyl sulfide)rhodium(III) hydrogenation system also has been interpreted in terms of the breaking of H-H bonds and making of Rh-H bonds in a concerted process.²⁴ Although the detailed mechanism of the hydrogen splitting remains unsubstantiated, it has been suggested²⁴ that the net hydride substitution reaction as shown in eq 12

$$\text{RhCl}_3(\text{Et}_2\text{S})_2 + \text{H}_2 \rightarrow \text{HRhCl}_2(\text{Et}_2\text{S})_2^- + \text{H}^+ + \text{Cl}^- \quad (12)$$

(23) J. Halpern and J. B. Milne, *Proc. Int. Congr. Catal.*, 2nd, 1960, 445 (1960).

(24) B. R. James and F. T. T. Ng, *J. Chem. Soc., Dalton Trans.*, 355 (1972).

Table V. Variation of k' with Temperature ($[\text{Rh}_2(\text{OCOMe})_4] = 5.6 \text{ mM}$; 1 atm Total Pressure)

$T, ^\circ\text{C}$	$[\text{Dec-1-ene}], \text{ M}$	$k', \text{ M}^{-1} \text{ sec}^{-1}$	$T, ^\circ\text{C}$	$[\text{Dec-1-ene}], \text{ M}$	$k', \text{ M}^{-1} \text{ sec}^{-1}$
36.0	0.21	1.02	50.0	0.21	3.42
36.0	1.05	1.32	50.0	1.05	4.35
40.0	0.21	1.51	56.5	0.21	7.05
40.0	1.05	1.92	56.5	0.21	6.84
43.0	1.05	2.41	56.5	1.05	7.96

could involve oxidative addition to give a dihydride with subsequent loss of HCl.

Although it is difficult to draw conclusions from the measured isotope effects, the observed kinetic isotope effect in the present investigation may be the result of an initial interaction of the entire hydrogen molecule with the metal *prior* to the actual splitting process in which the active monohydride rhodium species is generated. It is of interest also that the isotope effect is smaller at lower olefin concentrations (0.10 M), where the more complex rate law (eq 5) is applicable. The activation of molecular hydrogen by ruthenium(II)-chloro complexes in DMA, $k_{\text{H}}/k_{\text{D}} \approx 2.8$,²⁵ again suggests the possibility of an intermediate dihydride complex prior to the heterolytic splitting of hydrogen to generate a $\text{Ru}^{\text{II}}\text{-H}^-$ species.

Measurements on the temperature dependence of k' , defined by eq 7, over the range of 36–56.5° (Table V) yielded good Arrhenius rate plots. At an essentially constant olefin concentration sufficiently high such that $k_2[\text{olefin}] \gg k_{-1}[\text{H}^+][\text{OCOMe}^-]$, the rate constant $k' \approx k_1$. Thus, the activation parameters for the hydrogen activation step (eq 1) are $\Delta H^\ddagger = 17.5 \pm 0.1 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -1.9 \pm 1 \text{ eu}$.

Registry No. $\text{Rh}_2(\text{OCOMe})_4$, 15956-28-2; HCONMe_2 , 68-12-2; MeCONMe_2 , 127-19-5; tetrahydrofuran, 109-99-9; dioxane, 123-91-1; Me_2SO , 67-68-5; EtOH, 64-17-5; dec-1-ene, 872-05-9; hex-1-ene, 592-41-6; oct-1-ene, 111-66-0; hex-1-en-3-ol, 4798-44-1; styrene, 100-42-5; diethyl maleate, 141-05-9; 2-methyl-3-butyn-2-ol, 115-19-5; ethylene, 74-85-1; hex-1-yne, 693-02-7; cyclooctene, 931-88-4; H_2 , 1333-74-0.

Acknowledgment. The authors are grateful to the National Research Council of Canada and the University of Waterloo for financial support of this research.

(25) B. C. Y. Hui, Ph.D. Thesis, University of British Columbia, 1969.