

(Isotopic Products) using the procedure of Campbell.³⁰ The trifluoroacetic acid was purchased from the Aldrich Chemical Co. It was distilled before use.

Kinetic Runs.—Procedures have been described previously. Runs were usually on a 5-ml scale but runs with 0.02 *M* allyl ester were on a 25-ml scale. Samples were analyzed by vpc using a 6-ft 20% Carbowax 20M on ABS (70–80 mesh) column programmed from 80° to 200° at 7.5°/min. Helium flow rate was 60 ml/min. Runs not containing CF_3COOH were injected without work-up. The runs containing CF_3COOH were neutralized by a 10% excess of 1 *M* LiOAc in HOAc and diluted to a known volume before injection. Aliquots (1 or 2 ml) of the 25-ml scale runs were worked up by diluting with CH_2Cl_2 and washing with water to remove HOAc, CF_3COOH , and inorganic salts. After drying over MgSO_4 , the organic phase was concentrated to a known volume and analyzed by vpc. In one run, the 2-cyclohexen-1-yl acetate was collected by preparative vpc and positively identified by nmr.

2-Cyclohexen-1-*d*₁-1-yl Acetate-*d*₃ Run.—A 75-ml reaction mixture which was 0.0218 *M* in Pd(II) and 0.4 *M* in CF_3COOH was prepared and the run was started by adding 1.5 g of the deuterated cyclohexenyl acetate. Samples (12 ml) were worked up by extracting in CDCl_3 described above. The samples were

analyzed by nmr and mass spectral analysis. The rate of exchange of deuterated ester (eq 11) was determined by the ratio of the parent peaks of the deuterated (*m/e* 144) and undeuterated (*m/e* 141) esters. Data were plotted as a first-order reaction to give k_{ex} . The isomerization rate (eq 12) was determined by nmr using the relative areas of the proton on the carbon containing the acetate³¹ and the olefinic protons. Initially this ratio is zero. At equilibrium, when a 50:50 mixture of the two allylic isomers are present, it is 0.33. The data was plotted in the usual fashion for reactions approaching equilibrium. Data³² are given in Table III.

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Registry No.—Acetic acid, 64-19-7; 2-cyclohexen-1-yl propionate, 34745-78-3; lithium chloride, 7447-41-8; 2-cyclohexen-1-*d*₁-1-yl acetate-*d*₃, 40893-39-8.

(31) See ref 21 for chemical shifts of two types of protons.

(32) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 86.

(30) P. G. C. Campbell, Ph.D. Thesis, Queen's University, Kingston, Ontario, Canada, 1968, p 256.

Homogeneous Olefin Hydrogenation Catalyzed by Dichlorodicarbonylbis(triphenylphosphine)ruthenium(II)¹

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The relative hydrogenation rates for a variety of alkenes and alkadienes catalyzed by $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ have been measured in the presence of added PPh_3 . Rates decrease in the order conjugated dienes > nonconjugated dienes > terminal alkenes > internal alkenes. In general, polyenes are selectively hydrogenated to monoenes. Double bond isomerization and migration reactions and transannular ring closures (in cyclic dienes) can be important competing reactions. The lower hydrogenation rate for alkenes is attributed to an equilibrium between $\text{RuCl}(\text{alkyl})(\text{CO})_2$ and $\text{RuCl}(\text{alkyl})(\text{CO})_2\text{PPh}_3$ intermediates, which, in the presence of added PPh_3 , favors the sterically crowded PPh_3 complexed intermediate. Sterically congested intermediates suffer rapid RuH elimination, while the uncongested complexes survive long enough to undergo hydrogenolysis. This equilibrium is not so important for dienes, since the fifth coordination site on ruthenium is already occupied by chelation of the alkenyl ligand.

Numerous catalysts are known that are capable of performing selective homogeneous hydrogenations,² but the stabilities and productivities of most of these catalysts have not been well publicized. Thus, despite the alluring appeal many of these catalysts seem to offer in certain applications, their practical value is uncertain. Recently, the selective hydrogenation of 1,5,9-cyclododecatriene to cyclododecene catalyzed by $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ was described.³ In this case, the catalyst is exceptionally stable under the reaction conditions and is highly productive.³ Thus, further elaboration of its behavior seems desirable. Herein are provided relative rate data for a variety of unsaturated hydrocarbons that allow a deeper insight into the hydrogenation process.

Results

Selective Hydrogenation of Polyenes.—The presence of added PPh_3 was previously shown to be necessary in order to achieve selective hydrogenations of 1,5,9-cyclododecatriene.³ Since most of the interest in this catalyst is anticipated to be in its use as a selective hydrogenation catalyst, olefin hydrogenations were routinely performed with added PPh_3 . Under these conditions the $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ catalyzed hydrogenations of several diolefins were carried to greater than 99% conversion to yield the product mixtures given in Table I. The data indicate that the selective hydrogenation of polyunsaturated hydrocarbons to mono-unsaturated hydrocarbons is a fairly general reaction. For 1,5-cyclooctadiene, double bond migration is so rapid that complete isomerization to the 1,3 isomer occurs before significant amounts of cyclooctene appear. Thus, selective hydrogenation of 1,3-cyclooctadiene rather than 1,5-cyclooctadiene was actually observed. Accompanying the double bond migration reaction in 1,5-cyclooctadiene is a cyclization to bicyclo[3.3.0]oct-2-ene. This by-product was formed in 0.4% yield as 1,5-cyclooctadiene was undergoing

(1) Presented in part at the 19th Oklahoma American Chemical Society Tetrareaction Meeting, Bartlesville, Okla., Mar 10, 1973.

(2) For recent comprehensive reviews, see: (a) J. E. Lyons, L. E. Rennie, and J. L. Burmeister, *Ind. Eng. Chem. Prod. Res. Develop.*, **9**, 2 (1970); (b) A. Andreeta, F. Conti, and G. F. Ferrari in "Aspects of Homogeneous Catalysis," Vol. I, R. Ugo, Ed., Carlo Manfredi Editore, Milano, 1970, Chapter 4.

(3) D. R. Fahey, *J. Org. Chem.*, **38**, 80 (1973).

TABLE I
 SELECTIVITY OF POLYENE TO MONOENE HYDROGENATION AT >99% POLYENE CONVERSION^a

Polyene	Registry no.	PPh ₃ , M	RuCl ₂ (CO) ₂ (PPh ₃) ₂ , M	Reaction time, hr	Yield, %			Selectivity ^b
					Polyenes	Alkenes	Alkanes	
1,3-Pentadiene	504-60-9	0.0356	0.00031	0.5	0.0	99.3	0.7	0.99
1,5,9-Cyclododecatriene	4904-61-4	0.0356	0.00247	12.9	0.6	97.3	1.9	0.98
1,5-Cyclooctadiene	111-78-4	0.078	0.00314	3.2	0.8	93.4 ^c	6.1	0.94
Norbornadiene	121-46-0	0.078	0.00314	1.0 ^d	0.4	80.2	19.4 ^e	0.81
3,3-Dimethyl-1,4-pentadiene	1112-35-2	0.078	0.00154	6.0	0.3	37.5	62.3	0.37 ^f

^a Reactions were performed in benzene solutions at ~140° under 150–200 psig. Polyene concentrations were 0.25–0.59 M. ^b Selectivity = [alkene]/([alkene] + [alkane]). ^c Alkenes are cyclooctene (93.0%) and bicyclo[3.3.0]oct-2-ene (0.4%). ^d Nearly all the hydrogen absorption occurred in the first 10 min, but the reaction conditions were maintained for 1.0 hr. ^e Alkanes are norbornane (2.4%) and nortricyclene (17.0%). ^f At 99.0% conversion, the selectivity is estimated to be 0.51 to 0.53.

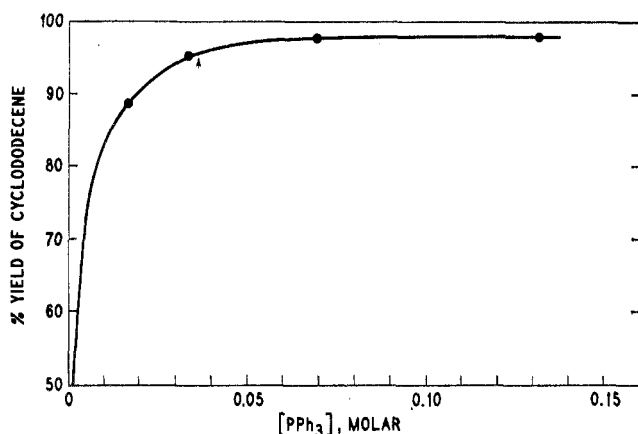


Figure 1.—Effect of added PPh₃ concentration on the maximum yield of cyclododecene attainable in the hydrogenation of 1,5,9-cyclododecatriene (0.55 M) catalyzed by 0.006 M RuCl₂(CO)₂(PPh₃)₂. The arrow is located at 0.0356 M PPh₃. Plotted from data given in ref 3.

isomerization. After 1,5-cyclooctadiene had disappeared, the concentration of the bicyclic compound remained constant. No bicyclo[3.3.0]octane was detected during the hydrogenation. A cyclization also occurred during the hydrogenation of norbornadiene as nortricyclene was formed in 17% yield. If this by-product were neglected, the selectivity value for norbornadiene in Table I would be 0.97 rather than 0.81. For the other olefins, the hydrogenation products were normal. The hydrogenation of 1,3-pentadiene produced pentene with a 1-ene/*cis*-2-ene/*trans*-2-ene isomer ratio of 4:25:70 which remained constant. This same ratio of isomers is rapidly formed from 1-pentene under the hydrogenation conditions.⁴

Rate Studies.—All hydrogenation rates were determined at 140° in benzene with 0.0356 M PPh₃ under a total pressure of 200 psig. This concentration of PPh₃ was somewhat arbitrarily chosen and is approximately the minimum necessary to achieve a highly selective hydrogenation of 1,5,9-cyclododecatriene, as illustrated in Figure 1. Since the pressure in the system is derived from the partial pressures of benzene, the olefin, and hydrogen, the partial pressure of hydrogen was not maintained constant for all olefins studied. If hy-

(4) This ratio is therefore presumed to be the thermodynamic equilibrium ratio at 140°. The experimentally determined equilibrium ratio at 25° is 1.5:17.5:81 [G. C. Bond and M. Hellier, *Chem. Ind. (London)*, 35 (1965)]. Very different ratios (9:41:51 at 140° and 3:32:65 at 25°) are obtained from the free energy of formation values given in F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, p 737.

drogenations are first order in hydrogen (this is believed to be true) and if the solutions obey Raoult's law, the rate constants for the olefins in Table II, except 1,3-pentadiene and the pentenes, are influenced less than 2%. For 1,3-pentadiene and the pentenes, the rate constants in Table II are 7% low. It was

 TABLE II
 SECOND-ORDER RATE CONSTANTS FOR THE HYDROGENATION OF UNSATURATED HYDROCARBONS BY RuCl₂(CO)₂(PPh₃)₂^a

Registry no.	Unsaturated hydrocarbon	K ^b
	1,3-Pentadiene	14,000
	3,3-Dimethyl-1,4-pentadiene	224
	Cyclododecadienes ^c	66
40999-81-3	1,3	
40999-82-4	1,4	
1502-04-1	1,5	
20006-42-2	1,6	
7158-18-1	1,7	
	1,5,9-Cyclododecatriene ^c	43
100-42-5	Styrene	29
3404-73-7	3,3-Dimethyl-1-pentene	27
	Pentenes	7.1
109-67-1	-1-ene	
627-20-3	- <i>cis</i> -2-ene	
646-04-8	- <i>trans</i> -2-ene	
1501-82-2	Cyclododecene ^c	0.6

^a Reaction rates were determined at 140° and 200 psig in benzene solutions containing 0.31–3.1 × 10⁻³ M RuCl₂(CO)₂(PPh₃)₂, 0.0356 M PPh₃, and 0.25–0.59 M olefin. Rate constants presumably contain terms for hydrogen and PPh₃ concentrations. ^b Units of mol⁻¹ l. sec⁻¹ × 10³. ^c Rate constant values were taken from ref 3.

necessary to use varied concentrations of RuCl₂(CO)₂(PPh₃)₂ to ensure conveniently measurable rates or to prevent a diffusion-controlled reaction as dictated by the activity of the olefin. Hydrogenation rates were previously shown to be linearly dependent on the concentration of RuCl₂(CO)₂(PPh₃)₂.³

Rate constants were calculated using the relationship shown in eq 1, where [Ru] is the concentration

$$-d[\text{olefin}]/dt = K[\text{Ru}][\text{olefin}] \quad (1)$$

of RuCl₂(CO)₂(PPh₃)₂ and the apparent rate constant K presumably contains terms for PPh₃ and hydrogen concentrations. For all olefins, plots of ln [olefin]/[olefin]₀ vs. time were linear. For the consecutive hydrogenation of 3,3-dimethyl-1,4-pentadiene to 3,3-dimethyl-1-pentene to 3,3-dimethylpentane, the rate constant for diene hydrogenation was obtained with eq

1, but the rate constant for alkene hydrogenation was determined using eq 2 at the point where the alkene

$$K_{\text{alkene}} = K_{\text{diene}} [\text{diene}] / [\text{alkene}] \text{ at } [\text{alkene}]_{\text{max}} \quad (2)$$

attained its maximum concentration during the hydrogenation. The derivation of eq 2 was given previously.³ Hydrogenation rates for a variety of unsaturated hydrocarbons are listed in Table II.

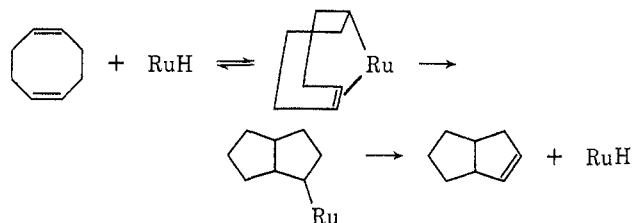
Discussion

From the results of the present work and those from the previous³ study, several general comments can be made about $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ catalyzed hydrogenations.

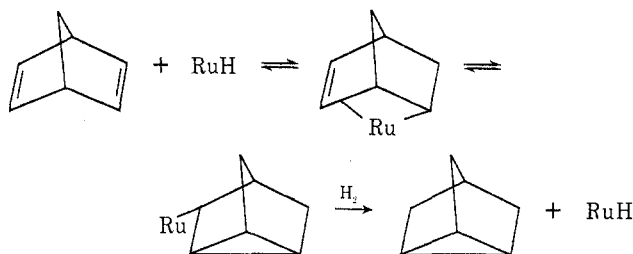
1.—Hydrogenation rates decrease in the order conjugated dienes > nonconjugated terminal dienes > nonconjugated internal dienes > terminal alkenes > internal alkenes. The order of rates parallel the relative stabilities of π -bonded Ru-olefin intermediates towards olefin dissociation and also the predicted relative stabilities of the alkyl-ruthenium intermediates derived from these olefins towards RuH elimination. Ruthenium(II) complexes of dienes are stable,⁵⁻⁷ but no Ru(II) complexes with simple alkenes have been isolated.⁶ The stabilities of the alkyl-ruthenium intermediates would be predicted to decrease in the order π -allyl complexes (formed from conjugated dienes) > σ, π -chelated complexes (from nonconjugated dienes) > n -alkyl complexes (from terminal alkenes) > *sec*-alkyl complexes (from internal alkenes). The hydrogenation of 1,3-pentadiene is extremely rapid, and a π -allyl intermediate is undoubtedly formed. The apparent low hydrogenation rates for the C_{12} polyenes in Table II is attributed to the reluctance of the double bonds to migrate into conjugation. The only positional isomer of cyclododecatriene known is the 1,5,9 isomer.⁸ The most stable cyclododecadiene isomers are also nonconjugated, and the equilibrium isomer mixture at 200° has been found to be 1,3- (10%), 1,4- (6%), 1,5- (57%), 1,6- (16%), and 1,7- (11%).⁹ 3,3-Dimethyl-1,4-pentadiene is a nonconjugated diene but is hydrogenated more rapidly than the C_{12} polyenes since terminal alkenes are hydrogenated faster than internal alkenes. Low rates for the hydrogenation of nonterminal alkenes using $\text{RuClH}(\text{PPh}_3)_3$ and $\text{RuH}(\text{OCOCF}_3)(\text{PPh}_3)_3$ complexes have been attributed to a difficulty in hydride transfer to coordinated alkene as a result of steric interaction with the PPh_3 groups.^{7,10,11} This steric interaction induces a strong preference for anti-Markovnikov addition of RuH to terminal alkenes leading to a less sterically congested primary carbon-ruthenium σ bond.⁷ 3,3-Dimethyl-1,4-pentadiene is hydrogenated seven times faster than 3,3-dimethyl-1-pentene. The rate enhancement over a statistical factor of 2 must result from an ability of the diene to chelate with ruthenium. The

relative order of alkene hydrogenation rates is consistent with the above discussion as terminal alkenes are hydrogenated more rapidly than nonterminal alkenes, and the mixture of pentene isomers is hydrogenated at a sensibly intermediate rate.

2.—Dienes indeed form chelated complexes. Side reactions occurring during the hydrogenations of 1,5-cyclooctadiene and norbornadiene are best explained by the intervention of σ, π -chelated intermediates. The 0.4% yield of bicyclo[3.3.0]oct-2-ene from 1,5-cyclooctadiene thus arises by intramolecular insertion of a coordinated C=C bond into a Ru-C bond as shown.



Likewise, the formation of nortricyclene from norbornadiene undoubtedly results from intermediates of the type shown below. Both norborn- $\pi,5$ -en-2-yl



and nortricyc-3-yl complexes of palladium are known,¹²⁻¹⁴ and, under certain circumstances, the σ, π -chelated complex could be rearranged to the nortricycyl complex.¹² A proposal^{12,15} that the norborn- $\pi,5$ -en-2-yl complex may be more accurately depicted as a π -homoallylic system is also very attractive here, since both norbornene and nortricyclene could be produced from a common intermediate. In addition, the rate of norbornadiene hydrogenation qualitatively compares with that of 1,3-pentadiene.

3.—Isomerization is usually faster than hydrogenation. Cyclododecene is hydrogenated the slowest of all the olefins in Table II; yet its rate of *cis* to *trans* isomerization ($k = 0.54 \text{ mol}^{-1} \text{ l. sec}^{-1}$)⁸ is several hundred times faster than its hydrogenation and is even considerably faster than the hydrogenations of the other olefins in Table II excepting 1,3-pentadiene. Similarly, 1,5-cyclooctadiene is isomerized very rapidly to 1,3-cyclooctadiene which is then more slowly hydrogenated. Thus, for at least the nonconjugated olefins, the rate of RuH addition to the olefin and its reverse are much faster than hydrogenation. For 1,3-pentadiene, the *trans/cis* ratio increased from 2.0 initially to 4.0 at 98% conversion. In this case, isomerization is not sufficiently rapid to maintain the *trans/cis* ratio constant at the equilibrium value.

(5) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

(6) S. D. Robinson and G. Wilkinson, *J. Chem. Soc. A*, 300 (1968).

(7) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *ibid.*, 3143 (1968).

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(9) A. J. Hubert and J. Dale, *J. Chem. Soc.*, 4091 (1963).

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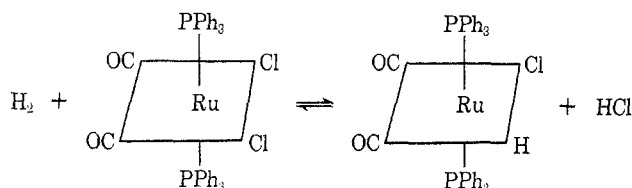
(14) E. Vedejs and M. F. Salomon, *ibid.*, **92**, 6965 (1970).

(15) M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967).

This is in agreement with a high stability of π -allyl complexes towards reversion to RuH and diene. Since the same initial steps are involved in both hydrogenation and isomerization, *i.e.*, formation of an alkyl-ruthenium intermediate, the rate-controlling step for hydrogenation must come after the formation of this intermediate. For conjugated dienes, there is no direct evidence for the validity of this conclusion, but this must certainly be true since RuH addition to 1,3-pentadiene should be very much faster than to *cis*-cyclododecene while hydrogenation of 1,3-pentadiene is only 2.6 times faster than isomerization of *cis*-cyclododecene. In hydrogenations catalyzed by the closely related $\text{RuClH}(\text{PPh}_3)_3$ and $\text{RuH}(\text{OCOCF}_3)(\text{PPh}_3)_3$ complexes, the kinetics agree with the rate-determining step being attack of hydrogen on an alkyl-ruthenium intermediate.¹¹

4.—Added PPh_3 slows hydrogenations. The presence of added PPh_3 (0.0356 *M*) slows cyclododecene hydrogenation by a factor of 74, but cyclododecatriene and cyclododecadiene hydrogenations are slowed only by a factor of 2 to 3.³ The lower sensitivity of polyene hydrogenation rates to added PPh_3 can be accounted for in terms of steric factors, exerted by coordinated PPh_3 , that are more important for alkenes than for dienes. Dienes, unlike alkenes, can occupy an additional site on the catalyst, *via* chelation, which would otherwise be occupied by PPh_3 . Added PPh_3 severely inhibits the hydrogenation activities of $\text{RuClH}(\text{PPh}_3)_3$ and $\text{RuH}(\text{OCOCF}_3)(\text{PPh}_3)_3$, but for a different reason.^{7,10,11} For these complexes PPh_3 dissociation is suppressed.^{7,10,11} This type of phenomenon seems less important in the hydrogenations using $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$.

Nature of Catalyst.—Since the ruthenium complex $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ can be recovered from reaction mixtures after hydrogenations are completed,³ it satisfies the formal definition of a catalyst. However, additional complexes, that are in equilibrium with $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$, may participate in the hydrogenation process. Data presented in the results section of the earlier paper, but not discussed, rules out $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PPh}_3)_2$ as a likely intermediate. This complex was prepared *in situ* by known reactions [$\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2 + \text{LiAlH}_4$ ¹⁶ and $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2 + \text{H}_2$ ¹⁷], and it performed differently in the hydrogenation of 1,5,9-cyclododecatriene than did $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$.³ Another strong possibility for an intermediate could be $\text{RuClH}(\text{CO})(\text{PPh}_3)_3$, since this type of complex can be formed from $\text{RuClH}(\text{CO})_2(\text{PPh}_3)_2$ and PPh_3 at high temperatures.¹⁸ However, the hydrogenation of 1,5,9-cyclododecatriene catalyzed by $\text{RuClH}(\text{CO})(\text{PPh}_3)_3$ (prepared *in situ* from RuCl_3 , CO , H_2 , and PPh_3 and isolated after completion of the hydrogenation) was less selective than with $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$.¹⁹ An intermediate with the composition $\text{RuClH}(\text{CO})_2(\text{PPh}_3)_2$ seems to be most reasonable. Similar to the formation of $\text{RuClH}(\text{PPh}_3)_3$ from $\text{RuCl}_2(\text{PPh}_3)_3$,^{7,11} conversion of $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ to $\text{RuClH}(\text{CO})_2(\text{PPh}_3)_2$, which is shown below, is facilitated by bases such as PPh_3 .³



The first step in hydrogenations catalyzed by $\text{RuClH}(\text{PPh}_3)_3$ and $\text{RuH}(\text{OCOCF}_3)(\text{PPh}_3)_3$ is proposed to be a PPh_3 dissociation from the catalyst.^{7,10,11} This is supported by inhibition by added PPh_3 and by a molecular weight determination of $\text{RuH}(\text{OCOCF}_3)(\text{PPh}_3)_3$. Molecular weight determinations for $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ have however indicated little or no PPh_3 dissociation.^{3,20} Yet dissociation of PPh_3 from the catalyst must be extensive at 140° since diene hydrogenations are retarded only slightly by the mass action effect of added PPh_3 . Likely, PPh_3 dissociation is induced by thermal stimulation. The presence of interligand spin-spin nuclear coupling involving ³¹P nuclei, *e.g.*, **P**-**Ru**-**H** coupling in the ¹H nmr spectrum of $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PET}_3)_2$ ¹⁶ and **P**-**Ru**-**P** coupling in the ¹³C nmr spectrum of $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$,³ has not proved to be a reliable probe in the assessment of PPh_3 dissociation. The $\text{RuH}(\text{OCOCF}_3)(\text{PPh}_3)_3$ complex, which is known to dissociate in solution, still exhibits a quartet hydride resonance in its ¹H nmr spectrum due to **P**-**H** coupling.¹⁰

Origin of Selectivity and Reaction Mechanism.—Any mechanistic proposals must account for the large hydrogenation rate decrease experienced by internal alkenes compared to polyenes when PPh_3 is added; yet alkene isomerization remains rapid. The mechanism of olefin hydrogenations catalyzed by the closely related $\text{RuClH}(\text{PPh}_3)_3$ ^{7,11} and $\text{RuH}(\text{OCOCF}_3)(\text{PPh}_3)_3$ ¹⁰ complexes has previously been elucidated. In its published form,¹¹ the mechanism does not adequately explain the results with the dicarbonyl catalyst. However, it becomes applicable with the incorporation of additional intermediates and equilibria as shown in Scheme I. Initially, the $\text{RuClH}(\text{CO})_2(\text{PPh}_3)_2$ species is formed in step 1 as discussed in the preceding section. Dissociation of PPh_3 from $\text{RuClH}(\text{CO})_2(\text{PPh}_3)_2$ occurs in step 2; so this step should be subject to a mass action effect of added PPh_3 . If the sole function of added PPh_3 in slowing the hydrogenation of 1,5,9-cyclododecatriene (the C_{12} olefin least affected by added PPh_3) is to suppress this dissociation step, then a reasonable estimate for K_2 is 0.03 to 0.04 mol l.⁻¹. Next, the olefin coordinates to the catalyst and is followed by RuH addition to the coordinated olefin *via* steps 3, 8, and 12. These steps must be rapid for all alkenes and more rapid for dienes. The equilibrium constant K_3 is predicted to be large due to the high trans labilizing effect of an alkene in ligand substitution reactions.²¹ The forward direction of step 4 would not be a favorable reaction since the bulky PPh_3 group is expected to hinder hydride transfer to the coordinated alkene.¹¹ Hydrogenation then proceeds through steps 13 and 14, where (13) is presumably the rate-controlling step in the overall scheme.

(16) J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 2162 (1968).

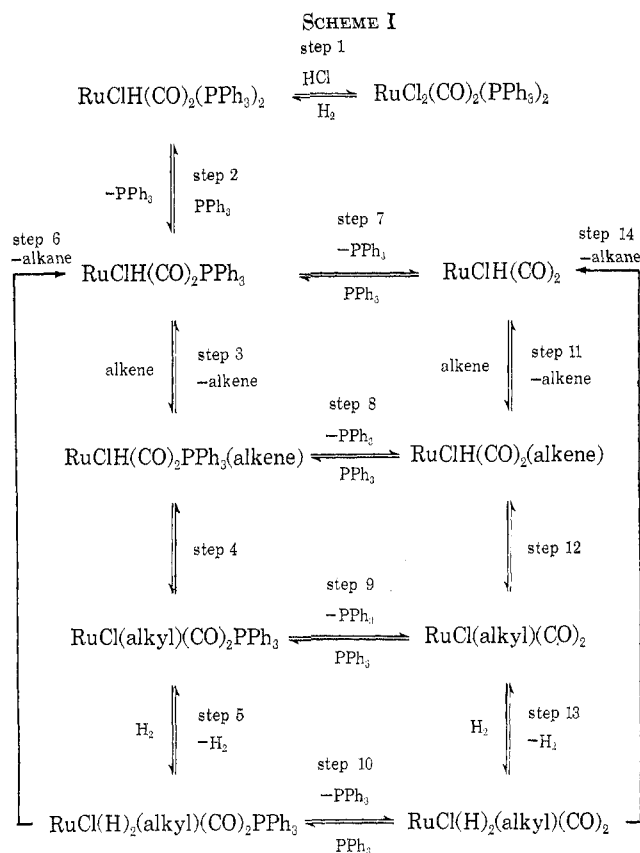
(17) F. L'Éplattenier and F. Calderazzo, *Inorg. Chem.*, **7**, 1290 (1968).

(18) M. S. Lupin and B. L. Shaw, *J. Chem. Soc. A*, 741 (1968).

(19) D. R. Fahey, unpublished studies (1969).

(20) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **23**, 945 (1966).

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Hydrogen activation step 5, like (13) is also rate determining and might be expected to be slower than (13) on steric grounds, since a seven-coordinate intermediate is involved. Rate differences between alkenes and dienes emerge in the sensitivity of equilibrium 9 to PPh_3 concentration. In alkene hydrogenations, added PPh_3 shifts equilibrium 9 in the direction of the $\text{RuCl}(\text{alkyl})(\text{CO})_2\text{PPh}_3$ complex. The complexed PPh_3 group increases the steric congestion about ruthenium, especially for *sec*-alkyl-ruthenium intermediates, and a RuH elimination occurs *via* the reverse direction of step 4. In diene hydrogenations, equilibrium 9 is not so important since the reactive coordination site on ruthenium is already occupied by the pendent $\text{C}=\text{C}$ of the alkenyl ligand.

The four-coordinate ruthenium(II) intermediates in Scheme I appear to violate the 16 and 18 electron rule promulgated by Tolman.²² This objection can be reconciled by allowing other olefins or the benzene solvent to coordinate weakly to these intermediates. In the hydrogenation of 1,5,9-cyclododecatriene, coordination by benzene is indicated by the higher selectivity to cyclododecene in benzene than in either 1-butanol or ethyl acetate.³ Benzene complexes of ruthenium(II) are known.^{23,24} Four-coordinate alkyl-ruthenium(II) complexes are favored by Wilkinson and his coworkers^{7,10} as intermediates in their hydrogenation mechanisms, since they lead to octahedral $\text{Ru}(\text{H})_2(\text{alkyl})\text{X}(\text{PPh}_3)_2$ complexes in the hydrogen activation step. However, there is also precedent

for the addition of hydrogen to five-coordinate ruthenium(II) complexes, as in step 5 of Scheme I, in the reaction of hydrogen with $\text{Ru}(\text{H})_2(\text{PPh}_3)_3$ to form $\text{Ru}(\text{H})_4(\text{PPh}_3)_3$.^{25,26} A number of reaction paths other than those described in Scheme I have been considered but they do not seem to explain adequately the behavior of the catalyst without resorting to seven-coordinate ruthenium(II) intermediates (20-electron complexes).

The relative hydrogenation rates of dienes *vs.* alkenes catalyzed by $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ are opposite to those of hydrogenations catalyzed by $\text{RuClH}(\text{PPh}_3)_3$ ⁷ and $\text{RuH}(\text{OCOCF}_3)(\text{PPh}_3)_3$.¹⁰ These differences can be rationalized by a greater steric hindrance in the addition of hydrogen to five-coordinate $\text{Ru}(\text{alkenyl})\text{X}(\text{PPh}_3)_2$ complexes as compared to four-coordinate $\text{Ru}(\text{alkyl})\text{X}(\text{PPh}_3)_2$ complexes. By replacing the bulky PPh_3 ligands with the smaller CO groups, this steric hindrance is relieved, and the addition of hydrogen to five-coordinate $\text{RuCl}(\text{alkenyl})(\text{CO})_2$ complexes is sterically allowed. An additional consequence of electron-withdrawing CO ligands is that the "promotional energy"²⁷ required in the hydrogen activation steps is increased compared to the other ruthenium catalysts; thus more vigorous conditions are required for the dicarbonyl complex to function as a catalyst.

Experimental Section

Reagents.—Olefins, except 3,3-dimethyl-1,4-pentadiene which was donated by P. W. Solomon, were purchased in high purity from commercial sources. All were passed through activated alumina immediately before use. Benzene was purified by distillation from CaH_2 , and triphenylphosphine was recrystallized from ethanol. *cis*-Dichloro-*cis*-dicarbonyl-*trans*-bis(triphenylphosphine)ruthenium(II)³ was synthesized by the procedure of Stephenson and Wilkinson.²⁰ As in the earlier work,³ the complex was purified by filtering its CH_2Cl_2 solution through activated alumina followed by several recrystallizations from CH_2Cl_2 - CH_3OH solutions. Despite these measures, reaction rates were not always reproducible from one sample preparation to another. Therefore, the relative rates in Table II were all measured using $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ from a single sample preparation.

Hydrogenations.—The apparatus and technique used in the rate studies were described previously.³ Liquids were transferred to the hydrogenation apparatus with a minimum of exposure to air, and the apparatus was immediately flushed with hydrogen to remove air. Although the presence of air or hydroperoxides does influence olefin isomerization reactions catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$ by converting the complex into a carbonyl complex,²⁸ a similar interference is not anticipated here, since, if a tricarbonylruthenium(II) complex were formed, it would be expected to revert to a dicarbonyl complex in the presence of PPh_3 .²⁹ Further, atmospheric oxygen was earlier shown to oxidize PPh_3 to OPPh_3 in the present system.³ A constant 200 psig pressure was maintained in all rate studies, and the bath temperature was $140 \pm 0.4^\circ$.

Product Identification and Analysis.—Reaction samples were analyzed by glpc on a Hewlett-Packard Model 5750 instrument equipped with a 20 ft \times 0.25 in. column packed with 20% tris-1,2,3-(2-cyanoethoxy)propane on 60–80 Chrom P. A flame ionization detector was used. Product identities were determined by comparison of their glpc retention times with those of authentic

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samples, except for 1,4-cyclooctadiene and 3,3-dimethyl-1-pentene. The former was assumed to be the intermediate product in the isomerization of 1,5-cyclooctadiene to 1,3-cyclooctadiene, while the latter was assumed to be the intermediate in the hydrogenation of 3,3-dimethyl-1,4-pentadiene to 3,3-dimethylpentane. Authentic nortricyclene was obtained by treating a

solution of the Grignard reagent of 3-bromonortricyclene³⁰ with anhydrous HCl. Bicyclo[3.3.0]oct-2-ene was a gift from Dr. P. R. Stapp.

Registry No.—RuCl₂(CO)₂(PPh₃)₂, 29079-66-1.

(30) Purchased from Aldrich Chemical Co.

The Role of Hydrate Formation in the Chromium(VI) Oxidation of Aldehydes¹

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Reaction rates for the chromic acid oxidation of a series of aliphatic aldehydes have been determined and correlated with aldehyde hydration equilibria. A value of $\rho^* = -1.1$ for the oxidation of aldehyde hydrates has been obtained. The results support a mechanism consisting of a rate-limiting oxidative decomposition of a chromic acid ester of an aldehyde hydrate. The applicability of the mechanism to the oxidation of aromatic aldehydes is discussed. The deuterium isotope effect for the oxidation of pivaldehyde ($k_H/k_D = 7.9$) shows that even this aldehyde reacts "normally" by carbon-hydrogen rather than by a carbon-carbon cleavage.

We have earlier pointed out that the chromium(VI) oxidation of aldehydes can be better understood and correlated with the oxidation of alcohols if it is regarded as an oxidation of an aldehyde hydrate rather than of the free carbonyl compound.^{2,3}

In the course of the investigation of the chromium(IV) oxidation of aldehydes⁴ we needed to determine the chromium(VI) oxidation of a larger series of aliphatic aldehydes. Since a great deal more information on aldehyde hydration equilibria is now available,⁵⁻¹¹ we were able to analyze the data more completely than could be done at the time of our earlier investigation.²

Table I summarizes the experimental rate constants, k_{obsd} , for the chromic acid oxidation of a series of eight aliphatic aldehydes. Also given are the aldehyde hydrate dissociation constants, K_a , pertaining to the reaction $\text{RCH}(\text{OH})_2 \rightleftharpoons \text{RCHO} + \text{H}_2\text{O}$. From k_{obsd} and K_a , two sets of rate constants referring to the oxidation of the aldehyde in only one of the forms present in solution were computed. The values for k_H were obtained by assuming that only the hydrated form will appear in the rate law

$$v = k_H[\text{Cr(VI)}][\text{RCH}(\text{OH})_2] \quad (1)$$

Conversely, the value for k_A was calculated using only the concentration of the free aldehyde according to the rate law¹²

$$v = k_A[\text{Cr(VI)}][\text{RCHO}] \quad (2)$$

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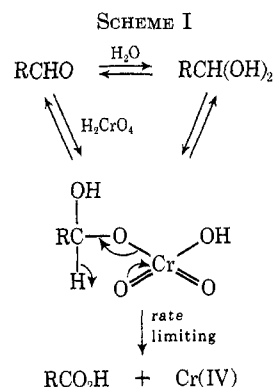
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(12) As all reactions were carried out at constant acidity, the acidity dependence of the oxidation reaction is not explicitly considered. Thus all rate constants used in this paper, k_{obsd} , k_H , and k_A , represent acidity-dependent rate constants.

A plot of $\log k_H$ against Taft's substituent constants σ^* gives a good straight line (Figure 1; correlation coefficient 0.99, standard deviation 0.2) with a slope of $\rho^* = -1.1$.¹³ On the other hand, the correlation of σ^* with k_A is much less satisfactory. The main deviation is observed for formaldehyde, which appears to be almost 1000 times more reactive than would be predicted from the $\sigma^*\rho^*$ plot based on the other aldehydes. When the value for formaldehyde is ignored, a straight line (correlation coefficient 0.97, standard deviation 0.16) giving a value of $\rho^* = 0.53$ may be obtained.

In the above results, the case of formaldehyde is of particular interest. If one assumes that the aldehyde reacts *via* the hydrate (eq 1), a rate constant, k_H , is obtained which compares well with the reactivities of other aldehydes. On the other hand, if only free formaldehyde could be oxidized, then one would have to assume that formaldehyde is about 1000 times more reactive than other aldehydes. This makes a mechanism consisting of a direct hydrogen transfer reaction between the free aldehyde and chromic acid (to yield, *e.g.*, $\text{RC}=\text{O}$ or $\text{RC}^+=\text{O}$) very unlikely.

The results obtained in this study thus agree well with the mechanism in which the rate-limiting step is the oxidative decomposition of a chromic acid ester of an aldehyde hydrate (Scheme I).



(13) This value is in good agreement with the value of $\rho^* = -1.2$ obtained earlier from a much more limited set of experimental data.²