$$\mathrm{Ru^{II}Cl_{\mathit{n}} + HCOOH \overset{\mathit{K}}{\rightleftharpoons} Ru^{II}(HCOOH)Cl_{\mathit{n}-1} + Cl^-} \qquad (9)$$

$$\mathrm{Ru^{II}(HCOOH)Cl_{\mathit{n}-1} \xrightarrow{k_3} Ru^{II}(CO)} \qquad (10)$$

Under the prevailing conditions where [HCOOH] >> $[\mathrm{Ru^{II}}]$ this yields a rate law

$$\frac{\mathrm{d}[\mathrm{Ru^{II}(CO)}]}{\mathrm{d}t} = \frac{k_3K[\mathrm{Ru^{II}}]_0[\mathrm{HCOOH}]}{[\mathrm{Cl^-}] + K[\mathrm{HCOOH}]} \qquad (11)$$

(where $[\mathrm{Ru^{II}}]_0 = [\mathrm{Ru^{II}Cl_{\mathit{n}}}] + [\mathrm{Ru^{II}(HCOOH)Cl_{\mathit{n}-1}}]$), which is the same form as the rate law (6) derived for the earlier mechanism. However, since the spectrum of a ruthenium(II) chloride solution was found to be unaffected by addition of HCOOH up to concentrations (≥ 1 *M*) corresponding to the limiting zero-order region, this interpretation would require that the spectrum of $\mathrm{Ru^{II}(HCOOH)Cl_{\mathit{n}-1}}$ be identical with that of $\mathrm{Ru^{II}Cl_{\mathit{n}}}$, a condition which is considered unlikely. For this reason, as well as the parallel with the reaction between $\mathrm{Ru^{II}}$ and ethylene, the earlier interpretation involving the dissociation mechanism is strongly favored.

Table II. Temperature Dependence of k'

Temp, °C	k',[a] $\mathrm{sec^{-1}}$
50.5	3.06
54.5	4.74
57.5	6.75
60.1	9.18
62.6	11.7
65.2	15.7

[a] Determined for 8.3×10^{-4} *M* $\mathrm{Ru^{II}}$, 0.57 *M* HCOOH, 2.9 *M* HCl.

The detailed mechanism of the decarbonylation step is not revealed by these experiments. In related experiments it was found that under similar conditions to those used in the experiments with formic acid, $\mathrm{Ru^{II}(CO)}$ is also formed by reaction of ruthenium(II) chloride with formaldehyde, *i.e.*

$$\mathrm{Ru^{II} + H_2CO \longrightarrow Ru^{II}(CO) + H_2} \qquad (12)$$

It is of interest that the first-order rate constant of this reaction measured at a high $\mathrm{H_2CO}$ concentration (0.68 *M*) was 1.0×10^{-3} $\mathrm{sec^{-1}}$ (at 60° in 3 *M* HCl), *i.e.*, the same as the limiting rate constant (k_1) of reaction 1 at high HCOOH concentration.

Under the same conditions it was found that ruthenium(II) chloride did not decarbonylate or otherwise react with acetic acid, acetone, acetaldehyde, ethanol, or ethylene glycol. Thus, decarbonylation, at least under acidic conditions, appears to occur readily only when breaking of C–H, but not C–C, bonds is involved. Other workers have reported the decarbonylation of alcohols and aldehydes by chloro(diethylphenylphosphine)ruthenium(II) complexes in the presence of base, to yield $\mathrm{Ru(CO)Cl_2(PEt_2Ph)_3}$ along with alkanes and alkenes, respectively.[3,4] The decarbonylation of various organic compounds including dimethylformamide, aldehydes, and acyl chlorides by rhodium salts with formation of the stable rhodium(I) carbonyl complex, $\mathrm{Rh(CO)Cl(PPh_3)_2}$, has also been reported.[5-7] The detailed mechanisms of these and related decarbonylation reactions remain to be elucidated.

Homogeneous Catalysis of the Hydrogenation of Olefinic Compounds by Ruthenium(II) Chloride[1]

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Abstract: The homogeneous catalytic hydrogenation of maleic and fumaric acids to succinic acid in aqueous solution, using ruthenium(II) chloride as catalyst, is described. The catalytic mechanism apparently involves formation of a ruthenium(II)–olefin complex which reacts homogeneously with hydrogen to form succinic acid. The rate law for the reaction in each case is thus $k[\mathrm{H_2}][\mathrm{Ru^{II}(olefin)}]$. The values of k at 80° in 3 *M* HCl and the corresponding activation parameters are: for maleic acid, $k = 2.3 \pm 0.1$ M^{-1} $\mathrm{sec^{-1}}$, $\Delta H^* = 14$ kcal/mole, $\Delta S^* = -17$ eu; for fumaric acid, $k = 3.6 \pm 0.6$ M^{-1} $\mathrm{sec^{-1}}$, $\Delta H^* = 17$ kcal/mole, $\Delta S^* = -8$ eu. Tracer studies using $\mathrm{D_2}$ and $\mathrm{D_2O}$ reveal that the hydrogen atoms which add to the double bond originate from the solvent rather than the hydrogen gas. The hydrogenation of fumaric acid in $\mathrm{D_2O}$ yields predominantly DL-2,3-dideuteriosuccinic acid indicating that the addition is stereospecifically *cis*. Ruthenium(II) complexes of nonactivated olefins containing isolated double bonds are not reduced by hydrogen but do catalyze the exchange of $\mathrm{D_2}$ with $\mathrm{H_2O}$. A mechanism which accommodates all these observations is proposed. Some equilibrium measurements on the complex formation between ruthenium(II) and olefins also are reported.

The study of the catalytic reactions of transition metal complexes, including homogeneous catalytic hydrogenation, has attracted extensive interest in recent years.[5] Numerous complexes have been found, among them complexes of ruthenium(II),[6] platinum(II),[7]

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[5] For a review see J. Halpern, *Ann. Rev. Phys. Chem.*, **16**, 103 (1965).

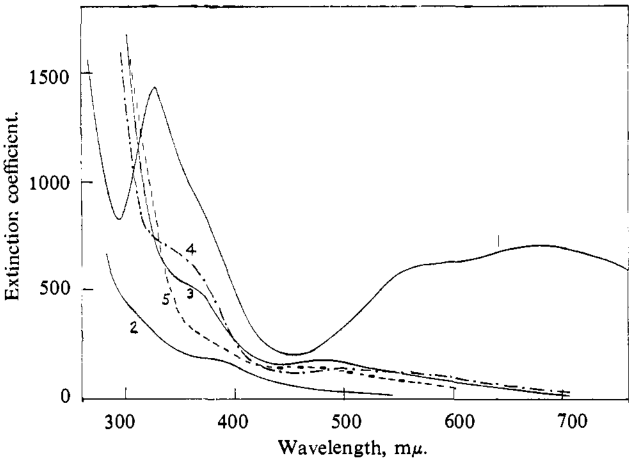

Figure 1. Absorption spectra of ruthenium(II) chloride and various ruthenium(II)-olefin complexes in 3 M HCl: 1, ruthenium(II) chloride; 2, $Ru^{II}(C_2H_4)$; 3, Ru^{II}(maleic acid); 4, Ru^{II}(fumaric acid); 5, Ru^{II}(5-norbornene-2,3-dicarboxylic anhydride).

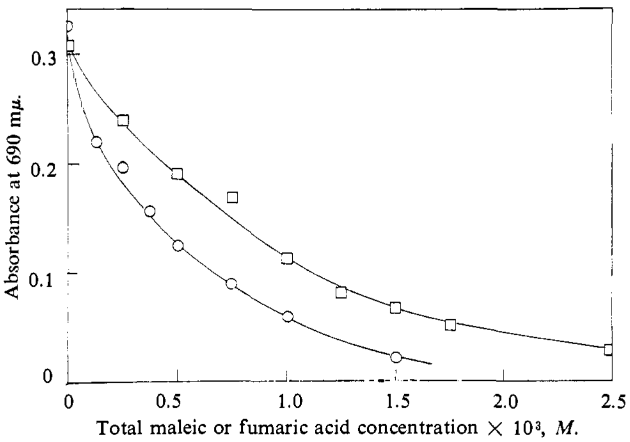

Figure 2. Effect of maleic and fumaric acids on the absorbance at 690 mμ of a 3 M HCl solution containing 5.0×10^{-4} M ruthenium(II) chloride: ○, maleic acid; □, fumaric acid.

cobalt(II),[8] iridium(I),[9] rhodium(I),[10] cobalt(I),[11] and iron(0),[12] which activate molecular hydrogen in solution and which catalyze the hydrogenation of olefins (in some cases only suitably activated, *e.g.*, conjugated, olefins), under homogeneous conditions. One of the first such catalysts to be reported is ruthenium(II) chloride which, in aqueous solution, was found to catalyze homogeneously the hydrogenation of olefinic bonds in compounds such as maleic, fumaric, and acrylic acids in which the double bond is activated by the presence of an adjacent carboxyl group.[6]

In this paper we describe a detailed investigation of this catalyst system. This includes (i) equilibrium measurements of the complex formation between ruthenium(II) and fumaric and maleic acids, and (ii) kinetic measurements and isotopic tracer studies on the catalytic hydrogenation of these acids.

Experimental Section

Ruthenium(II) chloride was generated by reduction of Johnson Matthey Specpure ammonium aquochlororuthenite in aqueous HCl solution (>1 M HCl) with an excess of titanium(III) chloride, as previously described.[13] Such solutions of ruthenium(II) chloride proved stable for periods of up to several days when stored under nitrogen with rigorous exclusion of oxygen. All experiments with ruthenium(II) were performed in an atmosphere of nitrogen or (in the case of the hydrogenation experiments) hydrogen. Injection through serum caps by means of a hypodermic syringe proved to be a satisfactory method of adding or transferring solutions to sealed, nitrogen filled, containers (including spectrophotometer cells) without incurring appreciable contamination by oxygen.

Reagent grade maleic acid, fumaric acid, and 5-norbornene-2,3-dicarboxylic anhydride were recrystallized before use. Hydrogen was purified by passing through a Deoxo catalytic purifier. Hydrochloric acid, lithium chloride, and other chemicals were of reagent grade. Deaerated distilled water was used in the preparation of all solutions.

The kinetics of the hydrogenation reactions were followed by measuring the rate of uptake of hydrogen at constant pressure using the apparatus and procedure previously described.[14] The concentration of H_2 was estimated from the known partial pressure using the solubility data of Seidell.[15] The succinic acid product was recovered from the solution, following hydrogenation, by extraction with ether and was recrystallized from water.

D_2–H_2O exchange measurements were made as previously described.[16]

Visible and ultraviolet spectra were recorded with a Cary 14 spectrophotometer. Infrared spectra of solids (using KBr pellets) were recorded with a Perkin-Elmer 21 spectrophotometer.

Results and Discussion

Formation of Ruthenium(II)–Olefin Complexes. The addition of an excess of any one of a number of olefinic compounds, including ethylene, maleic acid, fumaric acid, and 5-norbornene-2,3-dicarboxylic anhydride, to a solution of ruthenium(II) chloride resulted in the disappearance of the intense blue color of the latter (associated with a broad absorption band in the region 500–800 mμ which has been attributed to $RuCl_4^{2-}$)[17] and the appearance, in each case, of an absorption spectrum characteristic of a new species (Figure 1). In the case of ethylene it was previously shown[13] that the amount of olefin taken up by the solution corresponds to 1 mole per mole of ruthenium(II), apparently due to formation of a 1:1 ruthenium–ethylene π complex. The similarity of the spectral changes suggests that similar complexes are formed with the other olefins.

At sufficiently low concentrations of the added olefin, complex formation with ruthenium(II) attained a measurable equilibrium. As previously found for ethylene, complex formation was relatively slow, several hours generally being required for equilibration. The extent of complex formation, after equilibration, was determined by measuring the decrease in absorbance at 690 mμ, where ruthenium(II) chloride absorbs strongly and the complexes absorb negligibly (Figure 1). The dependence of the extent of complex formation on

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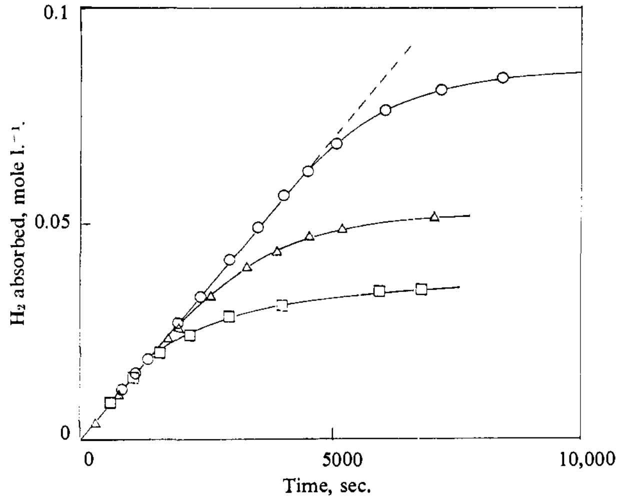

Figure 3. Rate plots for the ruthenium(II) chloride catalyzed hydrogenation of fumaric acid in 3 *M* HCl at 80° (0.012 *M* Ru^{II}; 3.6 × 10^{-4} *M* H_2). Initial fumaric acid concentrations: □, 0.037 *M;* △, 0.061 *M;* ○, 0.097 *M.*

Table I. Kinetic Data for the Hydrogenation of Maleic Acid at 80°[a]

$[Ru^{II}] \times 10^2$, *M*	H_2, mm	$[H_2] \times 10^4$, *M*	Rate of H_2 uptake × 10^5, mole l.$^{-1}$ sec^{-1}	*k*, M^{-1} sec^{-1}
0.244	450	3.6	0.33	3.8
0.61	450	3.6	0.52	2.4
1.22	450	3.6	0.98	2.2[b]
2.44	450	3.6	1.95	2.2
1.22	302	2.4	0.72	2.4
1.22	204	1.6	0.48	2.4
1.22	106	0.86	0.30	2.9
1.22	450	3.6	0.69	1.6[c]
1.22	450	3.6	0.88	2.0[d]
1.22	450	3.6	0.94	4.3[e]
1.22	450	3.6	1.05	4.8[f]
1.22	450	3.6	1.3	3.0[g]
1.22	450	3.6	1.4	3.2[h]
1.22	450	3.6	1.0	2.2[i]
0.85	450	3.6	0.50	1.7[i,j]
1.07	450	3.6	0.59	1.5[j]

[a] Unless otherwise indicated solutions contained 0.061 *M* maleic acid, 0.06 *M* $TiCl_3$, and 3.0 *M* HCl. [b] Unaffected by addition of up to 0.1 *M* $TiCl_4$ or by variation of the maleic acid concentration from 0.03 to 0.1 *M* and of the $TiCl_3$ concentration from 0.03 to 0.1 *M*. Higher $TiCl_3$ concentrations slowed down the reaction. [c] 1.2 *M* HCl; 1.8 *M* LiCl. [d] 2.2 *M* HCl; 0.8 *M* LiCl. [e] 4.2 *M* HCl. [f] 5.4 *M* HCl. [g] 3.0 *M* HCl; 1.2 *M* LiCl. [h] 3.0 *M* HCl; 2.4 *M* LiCl. [i] D_2 in place of H_2. [j] 3 *M* DCl in D_2O.

Table II. Kinetic Data for the Hydrogenation of Fumaric Acid at 80°[a]

$[Ru^{II}] \times 10^2$, *M*	H_2, mm	$[H_2] \times 10^4$, *M*	Rate of H_2 uptake × 10^5, mole l.$^{-1}$ sec^{-1}	*k*, M^{-1} sec^{-1}
0.244	450	3.6	0.36	4.1
0.49	450	3.6	0.72	4.1
0.61	450	3.6	0.91	4.1[b]
0.85	450	3.6	1.04	3.4
1.22	450	3.6	1.32	3.0[c]
1.22	305	2.4	0.94	3.2
1.22	212	1.7	0.71	3.4
1.22	82	0.66	0.34	4.2
0.61	450	3.6	0.78	3.5[d]
0.61	450	3.6	0.82	3.7[e]
0.61	450	3.6	0.84	3.8[f]
1.22	450	3.6	1.37	3.1[g]
0.61	450	3.6	0.65	3.0[g,h]
0.61	450	3.6	0.69	3.0[h]

[a] Unless otherwise indicated solutions contained 0.061 *M* fumaric acid, 0.06 *M* $TiCl_3$, and 3.0 *M* HCl. [b] Unaffected by addition of up to 0.12 *M* $TiCl_4$. [c] Unaffected by variation of the $TiCl_3$ concentration from 0.03 to 0.12 *M* and variation of the fumaric acid concentration from 0.03 to 0.12 *M*. [d] 1.0 *M* HCl; 2.0 *M* LiCl. [e] 0.5 *M* HCl; 2.5 *M* LiCl. [f] 5.2 *M* HCl. [g] D_2 in place of H_2. [h] 3 *M* DCl in D_2O.

the concentrations of maleic and fumaric acids is shown in Figure 2. It was found in each case that this dependence could be fitted by an equilibrium relation derived for the formation of a 1:1 ruthenium(II)–olefin complex, *i.e.*

$$Ru^{II} + \text{olefin} \rightleftharpoons Ru^{II}(\text{olefin}) \qquad (1)$$

with a formation constant *K* (=$[Ru^{II}(\text{olefin})]/[Ru^{II}]\cdot[\text{olefin}]$) of 2 × 10^3 M^{-1} for fumaric acid and 5 × 10^3 M^{-1} for maleic acid (both at 25° in 3 *M* HCl). Similar measurements indicated the formation of a somewhat weaker complex ($K \sim 2 \times 10^2\ M^{-1}$) with 5-norbornene-2,3-dicarboxylic anhydride.

Kinetics of Homogeneous Catalytic Hydrogenation of Maleic and Fumaric Acids. Solutions of ruthenium(II) chloride containing a sufficient excess of maleic or fumaric acid so that complexing of ruthenium(II) was substantially complete took up hydrogen smoothly and apparently under homogeneous conditions at temperatures in the range of 60–90° as shown in Figure 3. In each case the hydrogen taken up was accounted for by the reduction of the unsaturated acid to succinic acid. The rate of reaction was independent of the concentration of fumaric (or maleic) acid provided that the latter was sufficiently high so that complexing of the ruthenium(II) was substantially complete. Only when hydrogenation had proceeded to the point where the concentration was insufficient to complex all the ruthenium(II) (marked by the reappearance of the blue color of ruthenium(II) chloride) did the rate begin to fall off from its initial zero-order value.

Kinetic measurements were confined to the limiting range of sufficiently high maleic or fumaric acid concentrations so that the rate was independent of the latter and the uptake of H_2 (at constant Ru^{II} and H_2 concentrations) exhibited pseudo-zero-order kinetics. The results of the kinetic measurements are summarized in Tables I–III. For both maleic and fumaric acids it was found that an appreciable range of solution compositions existed over which the rate of reaction was approximately first order in hydrogen and in the ruthenium–olefin complex, *i.e.*

$$\text{rate} = k[H_2][Ru^{II}(\text{olefin})] \qquad (2)$$

and substantially independent of the concentrations of excess olefin, of added titanium(III) chloride (provided that the latter was in at least fivefold excess over the initial ruthenium(IV) concentration in order to ensure complete reduction of the latter to ruthenium(II)), and of added titanium(IV) chloride. At 80°, in 3 *M* HCl the approximately constant values of *k* in this region of solution compositions were 2.3 ± 0.1 M^{-1} sec^{-1} for maleic acid and 3.6 ± 0.6 for fumaric acid. The activation parameters determined from the temperature dependence of k over the range 65–90° (Table III) were: $\Delta H^* = 14$ kcal/mole and $\Delta S^* = -17$ eu for maleic acid; $\Delta H^* = 17$ kcal/mole and $\Delta S^* = -8$ eu for fumaric acid.

Table III. Temperature Dependence of Rate Constants

Olefin	Temp, °C	k,[a] M^{-1} sec^{-1}
Maleic acid	65	0.88[b]
	70	1.2[b]
	75	1.8[b]
	80	2.2[b]
	85	3.1[b]
	90	4.3[b]
Fumaric acid	65	1.1[c]
	70	1.8[c]
	75	2.7[c]
	80	4.1[c]
	85	5.3[c]
	90	7.6[c]

[a] All measurements in 3 M HCl. [b] Based on measurements on solutions containing 1.22×10^{-2} M Ru^{II} and 6.1×10^{-2} M maleic acid. [c] Based on measurements on solutions containing 6.1×10^{-3} M Ru^{II} and 6.1×10^{-2} fumaric acid.

The above values of k were found to be relatively insensitive to variations of the H^+ and Cl^- concentrations over the moderate ranges examined, and to substitution of H_2 by D_2. Both values of k decreased by about 30% when D_2O was substituted for H_2O as solvent, this decrease being of the same order as previously observed for a number of other homogeneous catalytic hydrogenation reactions.[18]

It was found that under the conditions of these experiments maleic acid was slowly isomerized to fumaric acid presumably due to catalysis by HCl. At 80°, in 3 M HCl the rate of isomerization was approximately 6% per hour (the duration of a typical kinetic experiment). The effect of this on the measured rates of hydrogenation of maleic acid was negligible, particularly in view of the fact that maleic acid complexes ruthenium(II) more strongly than fumaric acid. This was confirmed by showing that the rate of uptake of H_2 by a 0.33 M solution of maleic acid (containing 0.02 M Ru^{II}) was unaffected by the addition of 0.33 M fumaric acid.

Ruthenium(III) chloride, previously shown to be a homogeneous catalyst for the oxidation of H_2 by Fe^{III},[19] and for the isotopic exchange of D_2 with H_2O,[16] did not appear to complex with olefins nor to catalyze directly their hydrogenation. However, aqueous solutions of maleic or fumaric acid containing ruthenium(III) chloride did take up hydrogen in an autocatalytic manner (Figure 4) reflecting the slow reduction of ruthenium(III) to ruthenium(II) and the resulting catalysis by the latter of the hydrogenation of the maleic or fumaric acid. Addition of iron(III) to reoxidize the ruthenium(II) to ruthenium(III) completely inhibited the hydrogenation reaction.

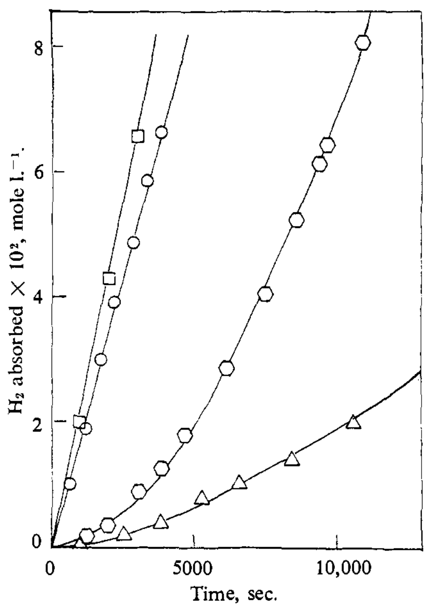

Figure 4. Uptake of hydrogen by solutions of maleic and fumaric acids containing ruthenium(III) chloride or ruthenium(II) chloride (80°, 3.6×10^{-4}, M H_2, 3.0 M HCl, 0.33 M maleic or fumaric acid, 1.9×10^{-2} M Ru^{III} or Ru^{II}): □, Ru^{II} (fumaric acid); ○, Ru^{II} (maleic acid); ○, Ru^{III} (maleic acid); △, Ru^{III} (fumaric acid).

Other Olefins. While the ability to complex with ruthenium(II) under the conditions of the above experiments appeared to be a general characteristic of olefins, including simple olefins such as ethylene and propylene, catalytic hydrogenation was observed only in the case of those olefins in which the double bond was activated by the presence of an adjacent carboxyl group, *e.g.*, maleic, fumaric, acrylic, or crotonic acids. Treatment of a ruthenium(II) chloride solution with a mixture of ethylene (or propylene) and hydrogen failed to result in hydrogenation under homogeneous conditions. Instead reduction to metallic ruthenium took place slowly with the resulting appearance of heterogeneous catalytic activity. Attempted studies on isobutene and butadiene were complicated by the fact that these gases are taken up rapidly by HCl solutions (even in the absence of ruthenium) under the conditions of these experiments, presumably due to acid-catalyzed hydration and/or polymerization. With isobutene no evidence either of complexing with ruthenium(II) (as judged by the persistence of the blue color) or of homogeneous hydrogenation could be found. With butadiene there was evidence of complexing but no clear evidence of hydrogenation. 2,3-Dimethylmaleic anhydride exhibited only a very weak tendency to complex with ruthenium(II) (in line with the generally low stabilities of metal complexes of highly substituted olefins) resulting in some reduction to metallic ruthenium when hydrogen was introduced. As noted earlier, 5-norbornene-2,3-dicarboxylic anhydride (which contains an isolated double bond) formed a moderately stable complex with ruthenium(II) ($K \sim 2 \times 10^2$ M^{-1}), but under the conditions of hydrogenation of maleic or fumaric acid this olefin was not hydrogenated.

D_2–H_2O Exchange Measurements. Using the procedure previously described,[16] it was found that during the hydrogenation of maleic or fumaric acid in H_2O–HCl solution by D_2, no isotopic exchange between D_2 and H_2O occurred, *i.e.*, *there was no appearance of HD or H_2 in the gas phase.* This implies that the up-

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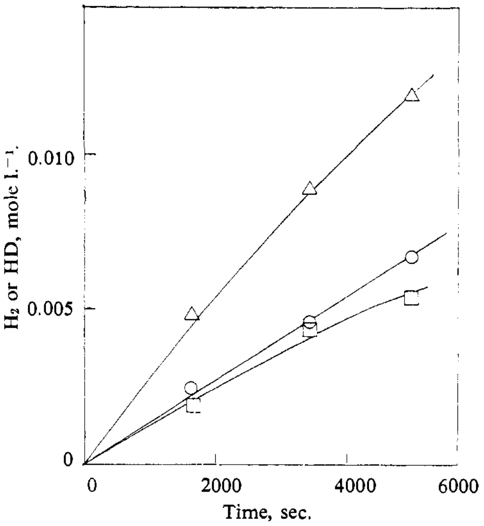

Figure 5. Catalysis of D_2–H_2O exchange by 0.042 M Ru^{II}(5-norbornene-2,3-dicarboxylic anhydride) in 3 M HCl at 80°: □, HD; ○, H_2; △, (HD + H_2).

take of hydrogen by this catalyst system, at least beyond the dissociative stage, is not reversible. On the other hand, the ruthenium(II) complex of an olefin, 5-norbornene-2,3-dicarboxylic anhydride, which does not undergo hydrogenation, did catalyze the exchange of D_2 with H_2O. The rate of exchange of D_2 (450 mm = 3.6×10^{-4} M D_2) with a 3 M HCl solution containing 0.042 M Ru^{II}(5-norbornene-2,3-dicarboxylic anhydride) in the presence of a 0.3 M excess of the olefinic compound at 80° was 2.8×10^{-5} mole of D_2 $l.^{-1}$ sec^{-1} (Figure 5). The products of exchange were H_2 and HD in the approximate ratio 1:1. This rate is of the same order as the observed rates of hydrogenation of maleic and fumaric acids (3.5×10^{-5} and 5.4×10^{-5} M sec^{-1}, respectively) under the same conditions and at the same ruthenium(II) concentration.

Deuterium Tracer Studies. The previous preparation by Childs and Bloch[20] of various deuterated succinic acids (including the 2,2-dideuterio, *meso*- and DL-2,3-dideuterio, and 2,2,3,3-tetradeuterio compounds), and the characterization of their infrared spectra which serve to distinguish between the isomeric compounds, made it possible to conduct certain tracer studies and to determine the stereochemistry of the hydrogenation of maleic and fumaric acids.

Various experiments were made using D_2 in place of H_2 gas, and/or using D_2O–DCl in place of H_2O–HCl as the medium. In each case the succinic acid product was recovered by ether extraction and evaporation and recrystallized from H_2O. This recrystallization served to convert -COOD to -COOH in the case of succinic acids prepared in D_2O solutions. It was further established that neither the recrystallization nor treatment with hydrochloric acid solutions of ruthenium(II) chloride under the conditions of the hydrogenation experiments resulted in any exchange of the hydrogen atoms bonded to the carbon atoms of maleic, fumaric, or succinic acids. The recrystallized succinic acids were incorporated into KBr pellets and their infrared spectra determined and compared with the spectra reported by Childs and Bloch.[20] The results of these experiments are summarized in Table IV and support the following conclusions.

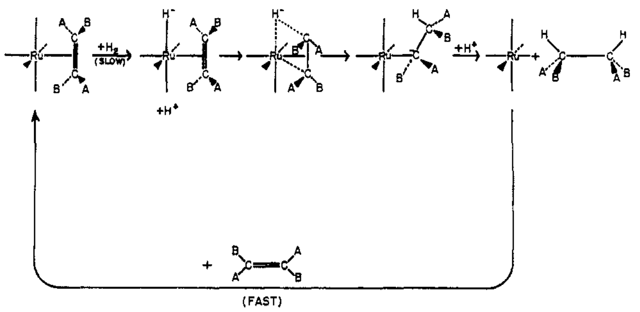

Figure 6. Porposed mechanism for the hydrogenation of fumaric acid.

Table IV. Results of Tracer Experiments[a]

Olefin	Gas	Medium	Succinic acid product[b]
Fumaric acid	D_2	H_2O	Undeuterated
	H_2	D_2O	DL-2,3-Dideuterio[c]
	D_2	D_2O	DL-2,3-Dideuterio[c]
Maleic acid	D_2	H_2O	Undeuterated
	H_2	D_2O	Mixture of *meso*- and DL-2,3-dideuterio
	D_2	D_2O	Mixture of *meso*- and DL-2,3-dideuterio

[a] 0.4 M maleic or fumaric acid reacted at 80° for 18 hr with 450 mm (3.6×10^{-4} M) H_2 (or D_2) in 3 M HCl (DCl) containing 0.07 M ruthenium(II). [b] After recrystallization from H_2O to convert -COOD to -COOH. [c] Product estimated from infrared spectrum to contain at least 85% of this isomer.

1. Hydrogenation of fumaric or maleic acid with D_2 in H_2O solution yields undeuterated succinic acid, whereas hydrogenation with H_2 (or D_2) in D_2O yields predominantly 2,3-dideuteriosuccinic acid. The hydrogen atoms which add to the double bond thus originate from the solvent, whereas the hydrogen atoms originally bonded to the olefinic carbon atoms do not exchange with the solvent.

2. The addition of deuterium to fumaric acid (to give predominantly DL-2,3-dideuteriosuccinic acid) is stereospecifically *cis*. It is difficult to draw any conclusions concerning the stereochemistry of addition to maleic acid since the formation of the observed mixture of *meso*- and DL-2,3-dideuteriosuccinic acids in D_2O could result from the extensive isomerization of maleic to fumaric acid which is known to occur over the 18-hr period of these hydrogenation experiments.

Mechanism of Hydrogenation. To accommodate the above observations in terms which also derive plausibility from investigations on related systems the mechanism depicted in Figure 6 is proposed. This mechanism incorporates the following sequence of steps.

1. Formation of the ruthenium(II)–olefin complex described above. This step is sufficiently rapid compared to the hydrogenation reaction that equilibration is effectively achieved.

2. Rate-determining reaction between the ruthenium(II)-olefin complex and H_2. It is suggested, by analogy with the mechanism of catalytic activation of hydrogen by ruthenium(III) chloride and related complexes,[16,19] that this step involves the heterolytic

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(20) C. R. Childs, Jr., and K. Bloch, *J. Org. Chem.*, **26**, 1630 (1961).

splitting of H_2 with formation of a hydridoruthenium(II) complex. This suggestion also derives support from the observation that the ruthenium(II) complex of an olefin (5-norbornene-2,3-dicarboxylic anhydride) which does not undergo hydrogenation catalyzes the isotopic exchange of D_2 with H_2O at about the same rate as the ruthenium(II)-maleic acid complex catalyzes the hydrogenation of maleic acid. Homogeneous catalysis of D_2–H_2O exchange by a ruthenium(II)–carbonyl chloride complex has also been reported recently.[21]

3. Rearrangement of the hydrido-π-olefin complex to a σ-alkyl complex by "insertion" of the olefin into the metal–hydride bond. There are many known examples of reactions involving the insertion of olefins into transition metal hydride bonds and it has been suggested that coordination of the olefin to the metal as a π-bonded ligand is an intermediate step in such insertion reactions.[22]

4. Electrophilic attack on the metal-bonded carbon atom by a proton to complete the hydrogenation reaction and regenerate the ruthenium(II) chloride catalyst.

The above mechanism accounts readily for the observed stereochemistry of the hydrogenation reaction. Hydrometalation of the olefin (step 3) *via* the depicted four-center transition state is expected to result in *cis* addition. *cis* addition of hydrogen in the over-all reaction, therefore, requires that the final electrophilic displacement of carbon (step 4) occur with retention of configuration. This is consistent with the retention of configuration which is generally observed to accompany the electrophilic displacement of carbon from other metals, *e.g.*, mercury.[23]

The isotopic tracer observation that the hydrogen atoms which add to the double bond originate from the solvent is also consistent with the proposed mechanism although not unequivocally predicted by it. The mechanism does predict that at least one of the hydrogen atoms (that which adds in step 4) originates from the solvent. The implication for the proposed mechanism of the observation that the second hydrogen atom also originates from the solvent is that the hydrido intermediate formed in step 2 exchanges its hydrogen with the solvent before undergoing rearrangement. Such exchange is consistent with the behavior exhibited by analogous hydrido intermediates such as the hydridoruthenium(III) intermediate in the ruthenium(III) chloride catalyzed D_2–H_2O exchange reaction.[16]

Finally, the requirement of an adjacent carboxyl substituent to activate the double bond for hydrogenation calls for some comment. The observation that the ruthenium(II) complex of an olefin (5-norbornene-2,3-dicarboxylic anhydride) in which the double bond, lacking such a substituent and therefore not susceptible to hydrogenation, nevertheless catalyzes the D_2–H_2O exchange reaction, suggests that this requirement is not associated with step 2 of the mechanism, *i.e.*, with the heterolytic splitting of hydrogen. Instead it appears that the requirement of a carboxyl substituent is associated with activation of the olefin for the hydrometalation rearrangement (step 3) which otherwise is too slow to compete with reversal of step 2 (which constitutes the mechanism of D_2–H_2O exchange). A possible explanation of this effect which, however, requires further testing, is that electron-withdrawing substituents increase the rate of hydrometalation by favoring nucleophilic attack of the hydrido ligand on the double bond. This leads to the expectation that less reactive olefins could be hydrogenated with this catalyst system if the rate of the competing back reaction of step 2 could be lowered, *e.g.*, by reducing the acidity of the medium. Unfortunately, it is not feasible to explore this possibility in aqueous solution because of the instability of ruthenium(II) in this medium at low acidities. Somewhat less direct support for these views is derived from observations[24] that in dimethylacetamide and dimethylformamide solutions ruthenium chloride does catalyze the hydrogenation, apparently under homogeneous conditions, of simple olefins such as ethylene and cyclohexene. The relation of the catalytic mechanisms in the two media, however, is not clear and remains to be established.

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

(22) R. F. Heck, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

(23) See for example R. E. Dessy and F. Paulik, *Bull. Soc. Chim. France*, 1373 (1963), and references cited therein.

(24) J. Halpern, A. L. W. Kemp, and F. L. Riley, unpublished results; P. N. Rylander, N. Himelstein, D. R. Steele, and J. Kreidl, *Engelhard Ind. Tech. Bull.*, 3, 61 (1962).