Homogeneous Catalysis in the Reactions of Olefinic Substances.[1a] IX. Homogeneous Catalysis of Specific Hydrogenation of Polyolefins by Some Platinum and Palladium Complexes[1b]

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Abstract: Complexes of the type $[MX_2(QPh_n)_2]$ (M = Pt or Pd; X = halide; Q = P or As when $n = 3$ and S or Se when $n = 2$; Ph = phenyl) catalyze the hydrogenation of nonaromatic polyolefins only in the presence of $SnCl_2$. Complexes of the type $[PtX_2(Ol)]$, where Ol = bidentate diene, behave similarly. The product of hydrogenation is the monoene in all cases studied. Over 15 polyolefins are reported to undergo specific hydrogenation in this fashion. The mechanism of the reaction is outlined. Hydrogenation proceeds *via* stepwise migration of the double bonds to conjugation. The conjugated diene is then hydrogenated to the monoene. Treatment of monoenes with these catalytic systems leads only to the isomerization through stepwise migration of the double bonds. Reaction intermediates including complexes in which the platinum atom is bonded simultaneously to a hydride ion, an olefin, and a tin atom are reported. Synthesis of such complexes outside the hydrogenation system is also reported. The effects of solvent, nature of the olefin, nature of the catalyst, and other related effects have been investigated. The kinetics and mechanism of hydrogenation are discussed.

Although metal–hydrogen and metal–hydrocarbon interactions were postulated in the early days of heterogeneous catalysis, metal–olefin π bonding in heterogeneous catalysis was suggested only after such bonding had been recognized in other areas of organometallic chemistry. It has been hoped that the understanding of homogeneous solution catalysis will throw some light on the theory of heterogeneous systems.

Homogeneous catalytic hydrogenation of olefins is a rather new field, and specific hydrogenation has been recognized only in the past few years.[2-4] The term "specific" as used in this article refers to hydrogenation that results in the formation of the monoene as the final product. Although some of the complexes used in the present investigation are stereospecific to some extent, in the sense of enhancing the formation of one geometric isomer of the olefin over the other, such stereospecificity will not concern us here but will be discussed in a later publication.

The term "polyolefin" is used in this series of articles to refer to any organic compound that has more than one carbon–carbon double bond. Correspondingly, a monoolefin or monoene has one carbon–carbon double bond.

It has been reported that transition metal complexes of the type $[MX_2(R_3Q)_2]$ (R = alkyl or aryl; Q = P, As, or Sb; M = Ni, Pd, or Pt; X = a halogen or pseudo-halogen) in the presence of salts of the type $M'X_2$ or $M'X_4$ (M′ = Si, Ge, Sn, or Pb) have the ability to catalyze the hydrogenation of methyl linoleate to the monoene stage, but not further.[5] The questions then arise: Is the catalytic activity of these complexes characteristic of some property of methyl linoleate or is the phenomenon general to all polyolefins? Why should the reaction stop at the monoene stage? What is the function of the added salt? What is the function of the ligand R_3Q? This paper reports attempts to answer such questions. Once these questions are answered, a plausible mechanism for the catalytic hydrogenation may be suggested and a possible parallelism to heterogeneous systems may be pointed out.

Experimental Section

1. **Apparatus.** The infrared spectra, nuclear magnetic resonance data, conductance of the complexes, molecular weight, and gas chromatographic information were obtained using the apparatus described in our previous paper.[1a]

Hydrogenation reactions were carried out in a 300-ml, stainless-steel Magne-Drive autoclave fitted with an air-driven motor, temperature regulator, a valve to allow sampling the reaction mixture while the reaction was in process, and a coiled metal tube through which cooling water could be passed.

Attempts to determine phosphorus by conversion to phosphate by heating the compound with concentrated nitric acid showed that tin interferes with such determination. However, the proton nmr data can be used for the determination of phosphorus, since aromatic protons are associated with phosphorus in the triphenylphosphine ligand.

2. **Chemicals and Syntheses.** *cis*-Dichlorobis(triphenylphosphine)platinum(II), $[PtCl_2(PPh_3)_2]$,[6] *trans*-hydridochlorobis(triphenphosphine)platinum(II), $[PtHCl(PPh_3)_2]$,[7] *cis*-dichlorobis(triphenylarsine)platinum(II), $[PtCl_2(AsPh_3)_2]$,[6a,8] *trans*-hydridotrichlorostannatobis(triphenylphosphine)platinum(II), $[PtH(SnCl_3)(PPh_3)_2]$,[7b] *cis*-dichlorobis(triphenylphosphine)palladium(II), $[PdCl_2(PPh_3)_2]$,[9] and *cis*-dicyanobis(triphenylphosphine)palladium(II), $[Pd(CN)_2(PPh_3)_2]$[9] were prepared by methods reported in the literature. We found that $[PtCl_2(PPh_3)_2]$ and $[PtCl_2(AsPh_3)_2]$, which were reported to be insoluble in most organic solvents, are best purified by precipitation by *n*-hexane from a methylene chloride solution. *cis*-**Dichlorobis-**

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[1] (a) Part VIII: H. A. Tayim and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **89**, 3420 (1967); (b) based partly on a portion of the Ph.D. thesis of H. A. Tayim, University of Illinois, Feb 1967.

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(diphenyl sulfide)platinum(II), $[PtCl_2(SPh_2)_2]$, was prepared by a modification of a method originally applied by Jensen.[10]

A warm (*ca.* 50°) solution of 4.15 g of potassium tetrachloroplatinate(II) in 50 ml of water was treated dropwise and with continuous stirring with a solution of 3.72 g of diphenyl sulfide in 25 ml of ethanol. The mixture was stirred at 50° for 3 hr. Ethanol (25 ml) was added to the mixture and stirring was continued for 2 hr more. The yellowish brown powder which separated was filtered and washed with water and then with alcohol. The product was recrystallized from benzene or a 1:1 alcohol–chloroform solution. The compound is easily soluble in benzene–chloroform mixture and in methylene chloride but difficultly soluble in alcohol, yield 5.0 g (78%), mp 195°.

Anal. Calcd for $C_{24}H_{20}Cl_2S_2Pt$: C, 45.14; H, 3.15; Cl, 11.10. Found: C, 45.37; H, 3.20; Cl, 10.86.

Dichlorobis(diphenyl selenide)platinum(II), $[PtCl_2(SePh_2)_2]$, was prepared by a modification of the method of Fritzman.[11] Diphenyl selenide (2.3 g) in 25 ml of ethanol was added dropwise with continuous stirring to a warm (*ca.* 50°) solution of 2.08 g of K_2PtCl_4 in 50 ml of water. The mixture was stirred for 15 min, and then more $SePh_2$ (*ca.* 0.5 g) was added to effect complete decolorization of the solution. The warm mixture was further stirred for 5 hr. The reddish brown precipitate that separated was washed with water, ethanol, and ether, consecutively. The compound is soluble in chloroform and in methylene chloride, yield 3.0 g (80%), mp 181°.

Anal. Calcd for $C_{24}H_{20}Cl_2Se_2Pt$: C, 39.36; H, 2.75; Cl, 9.68 Found: C, 39.40; H, 2.65; Cl, 9.47.

Diiodo-1,5-cyclooctadieneplatinum(II), $[PtI_2(1,5\text{-COD})]$, was prepared by a modification of the method of Kistner, *et al.*[12] To a suspension of 2.43 g of potassium hexachloroplatinate(IV) in 150 ml of water was added an excess (*ca.* 4.0 g) of 1,5-cyclooctadiene. The mixture was stirred while a solution of 6.64 g of potassium iodide in 30 ml of water was added slowly. The resulting mixture was treated with a 4% aqueous solution of sodium bisulfite (0.5 ml at a time) until the supernatant solution became colorless. The rate of addition of sodium bisulfite was decreased as the reaction approached completion. The crude yellow product was filtered, washed successively with absolute alcohol and ether, and finally recrystallized from methylene chloride, yield 2.0 g (70%), mp 261°.

Anal. Calcd for $C_8H_{12}I_2Pt$: C, 17.24; H, 2.16; I, 45.56. Found: C, 17.41; H, 2.17; I, 45.23.

Dichloro-1,5-cyclooctadieneplatinum(II), $[PtCl_2(1,5\text{-COD})]$, was prepared as previously reported.[1a]

Bis{hydridotrichlorostannatobis(triphenylphosphine)}-μ-(1,5-cyclooctadiene)-diplatinum(II), $[\{PtH(SnCl_3)(PPh_3)_2\}_2(1,5\text{-COD})]$, was prepared by treating 1,5-cyclooctadiene with a mixture of *trans*-$[PtHCl(PPh_3)_2]$ and $SnCl_2 \cdot 2H_2O$ as reported previously.[1a]

Bis{hydridotrichlorostannatobis(triphenylphosphine}-μ-(bicycloheptadiene)-diplatinum(II), $[\{PtH(SnCl_3)(PPh_3)_2\}_2(C_7H_8)]$, was prepared by a similar procedure with bicycloheptadiene substituted for 1,5-cyclooctadiene, mp 161–163°, ν_{Pt-H} 2200 cm^{-1}.

1,4-Cyclooctadiene was prepared by the reduction of cyclooctatetraene by metallic sodium in alcohol.[13]

3. Isolation and Identification of Reaction Intermediates and Products. At the end of each hydrogenation reaction, the reaction mixture is filtered and the filtrate is concentrated to about one-third its volume under reduced pressure. If the boiling points of the olefin and its hydrogenation products differ appreciably from that of the solvent, the olefins are distilled under reduced pressure. Otherwise, the concentrated solution is filtered again and treated with excess low-boiling petroleum ether with continuous stirring until a precipitate is formed. The mixture is left to stand for 15 min and then filtered. The precipitate from this filtrate or the residue from the distillation is purified by dissolution in methylene chloride and precipitation by petroleum ether. The process is repeated until the product gives a constant elemental analysis and a sharp melting (or decomposition) point. The product is either a reaction intermediate, reaction product, or some reactant, depending on the nature and conditions of the reaction. The filtrate from the first precipitation is treated with more petroleum ether until precipitation is complete. The mixture is then filtered. In the residue obtained by the evaporation of this last filtrate some reactants, and occasionally some $[PtHCl(PPh_3)_2]$, are detected. The final filtrate of methylene chloride and petroleum ether is evaporated under reduced pressure to leave a mixture of the hydrogenated products.

Hydrocarbon hydrogenation products were identified by their retention times on the gas chromatographic column and by their infrared spectra through comparison with data obtained from authentic samples.

Reaction intermediates and other compounds recovered from the reaction media were characterized by their elemental analyses, melting points, infrared and nuclear magnetic resonance spectra, molecular weights, and electrical conductance.

Results

1. Generality. Since the first purpose of this investigation was to determine whether the phenomenon of specific hydrogenation of methyl linoleate to the monoene was general, several polyolefins were treated with the catalytic mixture $[PtCl_2(PPh_3)_2] + SnCl_2 \cdot 2H_2O$ under high temperature and pressure of hydrogen. These olefins were chosen so as to represent a wide range of olefin structures. Some of them contained unsaturated functional groups such as carbonyl and nitrile since we wished to see whether hydrogenation of such groups could be effected. The results are shown in Tables I and II.

Table I. Catalytic Hydrogenation of Some Olefins Using $[PtCl_2(PPh_3)_2]$ (0.5 mmole) and $SnCl_2 \cdot 2H_2O$ (5.0 mmoles)[a]

		Composition of product, %		
Olefin	Olefin, mmoles	Satd	Monene	Diene and higher
4-Vinylcyclohexene	10	...	30	70
1,4,9-Decatriene	9	...	24	76
Mesityl oxide	10	67[b]	33	...
1,3,6-Octatriene	20	...	91	9
2,4,6-Octatriene	20	...	90	10
1,7-Octadiene	20	...	89	11
1-Cyclohexen-2-one	20	100[b]	...	...

[a] In 50 ml of 2:3 methanol–benzene solutions under 500 psi of hydrogen, at 90° for 8 hr. [b] Saturated ketone.

2. Practical Considerations. Once the generality of the phenomenon of specific hydrogenation had been established, the various factors affecting the activity of the catalyst were investigated.

Control experiments were carried out whenever a catalyst was used for the first time. In these experiments, hydrogenation was attempted once without the cocatalyst (*e.g.*, $SnCl_2 \cdot 2H_2O$) and again with the cocatalyst only (*i.e.*, in the absence of the catalyst). Hydrogenation was not effected to any degree in either of these sets of experiments except with $[Pd(CN)_2(PPh_3)_2]$, which did effect some hydrogenation in the absence of a cocatalyst.

That the water in $SnCl_2 \cdot 2H_2O$ had no effect on the activity of the catalyst was shown by comparing hydrogenation with the dihydrate and anhydrous $SnCl_2$ as cocatalysts. The results were identical. For convenience, the dihydrate was therefore used throughout this work.

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[10] K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **231**, 365 (1937).

[11] E. Fritzman, *ibid.*, 73, 239 (1912).

[12] C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Starlie, *Inorg. Chem.*, **2**, 1255 (1963).

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Table II. Catalytic Hydrogenation of Some Olefins Using $[PtCl_2(PPh_3)_2]$ (0.5 mmole) and $SnCl_2 \cdot 2H_2O$ (5.0 mmoles)[a]

Olefin	Olefin, mmoles	Pressure, psi	Reaction time, hr	Composition of product, %		
				Satd	Monoene	Diene and higher
3-Ethylidenecyclohexene	24	600	6	...	100	...
1,4,9-Decatriene	18	600	8	...	100	...
Cycloheptatriene	32	600	7	...	2	98
Cyclooctatetraene	30	600	10	...	...	100
1,5-Cyclooctadiene	32	700	8	...	10	90
4-Vinylcyclohexene	35	600	8	...	93	7
1,4-Cyclohexadiene	37	600	8	...	11	89
1,5-Hexadiene	37	500	6	3	70	27
1,5-Heptadiene	33	500	6	...	91	9
1,7-Octadiene	10	500	3	...	26	74
3-Cyclohexenyl cyanide	20	600	8	10[b]	90	...

[a] In 50 ml of methylene chloride at 90°. [b] Cyclohexenyl cyanide.

The effect of varying the ratio of the catalyst to the cocatalyst was investigated. The results of similar studies have been reported in connection with the isomerization of 1,5-cyclooctadiene.[1a] A tin:platinum ratio of 10:1 was used throughout this work.

No hydrogenation could be effected at pressures lower than 400 psi, but varying the pressure above 600 psi had little or no effect on the activity of the catalyst.

Temperature, on the other hand, has a profound effect on the rate of hydrogenation. Thus, at room temperature, only isomerization of 1,5-cyclooctadiene could be catalytically effected, while under the same conditions, but at higher temperatures, hydrogenation was brought about.

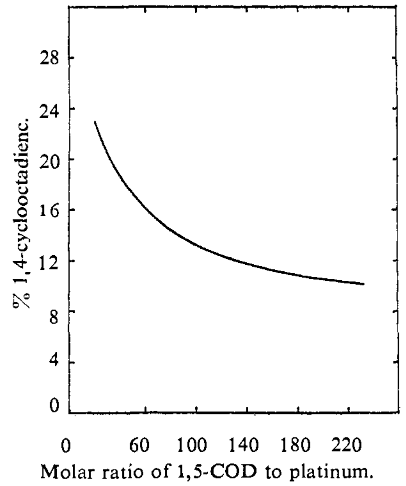

Figure 1. Effect of olefin : catalyst ratio on the catalytic isomerization of 1,5-cyclooctadiene.

The effect of varying the concentration of the olefin at a constant catalyst concentration was examined. Thus, the isomerization of 1,5-cyclooctadiene in various amounts was effected using 0.5 mmole of $[PtCl_2(PPh_3)_2]$ and 5.0 mmoles of $SnCl_2 \cdot 2H_2O$ in 50 ml of methylene chloride under 500 psi of hydrogen at 20° for 2 hr. The results are shown in Figure 1 in terms of olefin:catalyst molar ratio as a function of the yield of 1,4-cyclooctadiene.

The concentration of the catalyst, at constant cocatalyst:catalyst and olefin:catalyst molar ratios, affects the catalytic activity to the extent that at very low concentration (less than 10^{-4} *M*) practically no catalysis is observed. However, at concentrations higher than 10^{-2} *M*, catalytic activity was practically independent of the catalyst concentration. Practical catalyst concentrations were 7 to 10 m*M*.

Considerations of the above effects led to the adoption of the following convenient reaction conditions throughout most of this work: pressure, 500–600 psi; volume of solvent, 50 ml; amount of catalyst, 0.5 mmole; amount of cocatalyst, 5.0 mmoles; amount of olefin, 30 mmoles; temperature of hydrogenation, 50–110°.

3. **Effect of Solvent.** Earlier reports on the use of the system $[PtCl_2(PPh)_2] + SnCl_2 \cdot 2H_2O$ for catalytic hydrogenation recommended a 3:2 benzene–methanol mixture as the most convenient solvent. Variation of the catalytic activity as a function of the nature of the solvent was related to the availability of α-hydrogen atoms in the alcohol which could be utilized in the formation of the metal hydride complex. Our investigation of the isomerization of 1,5-cyclooctadiene has shown that although the solvent can supply the hydrogen for the formation of the metal hydride intermediate, molecular hydrogen supplied by the ambient gas can serve the same purpose, and, under hydrogen pressure, the solvent may be insignificant as a source of hydride ions. Nuclear magnetic resonance data and elemental analyses of crude reaction intermediates from benzene–methanol systems suggested that there was some complex formation between the catalyst and the alcohol. Such interaction may be expected to inhibit catalysis since the solvent will compete with the olefin for a place in the coordination sphere of the catalyst metal atom. Solvents were therefore varied according to their expected ability to combine with the catalyst. Thus, 4-vinylcyclohexene was hydrogenated in 3:2 benzene–methanol solution by 0.5 mmole of $[PtCl_2(PPh_3)_2]$ and 5.0 mmoles of $SnCl_2 \cdot 2H_2O$ under 500 psi of hydrogen at 90° for 8 hr to give 30% monoenes and 70% dienes. The same olefin, when hydrogenated in methylene chloride under the same conditions, gave 93% monoenes and 7% dienes. 1,4,9-Decatriene, when hydrogenated under similar conditions in methylene chloride and in 2:3 methanol–benzene

solutions, yielded 100 and 24% monoenes, respectively. The results of the hydrogenation of 3-ethylidenecyclohexene in various solvents are illustrated in Table III.

Table III. Hydrogenation of 3-Ethylidenecyclohexene in Various Solvents Using [PtCl$_2$(PPh$_3$)$_2$] (0.5 mmole) and SnCl$_2$·2H$_2$O (5.0 mmoles)[a]

Solvent	Composition of product, % Satd	 Monoene	 Diene
Methylene chloride	...	100	...
Acetone	...	83	17
3:2 benzene–methanol	...	77	23
Pyridine	...	...	100

[a] At 90° under 500 psi of hydrogen for 5 hr.

One may expect that if no solvent is used in the hydrogenation, the yield of monoenes will be further improved. This indeed has been observed to be the case, provided, of course, that the platinum–tin catalyst is soluble in the olefin. Thus, when 1.0 g of mesityl oxide was hydrogenated in 2:3 methanol–benzene solution, a yield of 67% of methyl isopropyl ketone was obtained. However, when 40.0 g of mesityl oxide was hydrogenated without a solvent under identical conditions (0.5 mmole of catalyst + 5.0 mmoles of cocatalyst, under 500 psi of hydrogen at 90° for 6 hr), a yield of 70% of the saturated ketone was obtained.

It is interesting that when acetone was used as a solvent, aldol condensation was effected and mesityl oxide was formed and partially hydrogenated to methyl isopropyl ketone. In a typical experiment, in the hydrogenation of 3-ethylidenecyclohexene in acetone solution using the platinum–tin system at 90° for 6 hr, in addition to the hydrogenation products of the hydrocarbon, about 5% of the acetone was converted to a 1:2 mixture of mesityl oxide and methyl isopropyl ketone.

4. **Effects of the Nature of the Cocatalyst and Gas.** These effects were discussed in detail in a previous report.[1a] Suffice it to mention here that SnCl$_2$·2H$_2$O was found to have unique properties that make it the most effective cocatalyst for isomerization and hydrogenation. Either the gas or the solvent may serve as a source of hydrogen in hydrogenation experiments. Thus, the hydrogenation of 1,3,6-octatriene, 2,4,6-octatriene, and 1,7-octadiene was effected in methanol–benzene solution both under hydrogen and under nitrogen. The results were practically the same (90% monoenes) in both cases.

5. **Effect of the Nature of the Catalyst.** Varying the ligands in the catalyst complex, in attempts to learn the function of such ligands, resulted in extending the list of effective catalysts to include [PtCl$_2$(SPh$_2$)$_2$], [PtCl$_2$(SePh$_2$)$_2$], [PtI$_2$(1,5-COD)], and [PtCl$_2$(1,5-COD)].

As in the hydrogenation of soybean oil methyl esters, [PtCl$_2$(AsPh$_3$)$_2$] + SnCl$_2$·2H$_2$O has been found to be a more effective catalyst than [PtCl$_2$(PPh$_3$)$_2$] + SnCl$_2$·2H$_2$O. The relative hydrogenation activity of various catalysts may be appreciated by considering Tables IV and V.

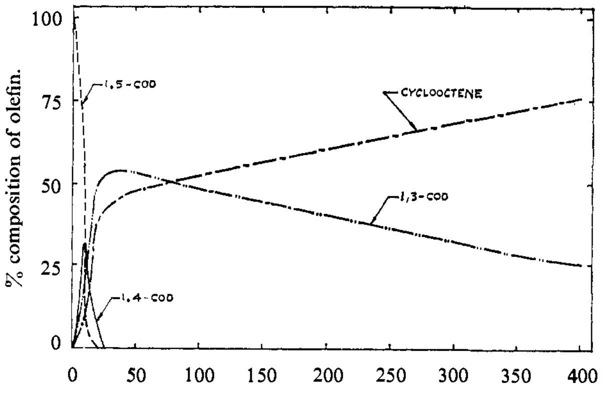

Figure 2. Catalytic hydrogenation of 1,5-cyclooctadiene in methylene chloride under 500 psi of hydrogen at 105°.

No hydrogenation could be effected by the metal–olefin complex [PtCl$_2$(1,5-COD)] or the hydrido complex [PtHCl(PPh$_3$)$_2$] without a cocatalyst.

Table IV. Hydrogenation of 1,3-Cyclooctadiene (2.2 g) in CH$_2$Cl$_2$ (50 ml) Using Various Catalysts (0.5 mmole) and SnCl$_2$·2H$_2$O (5.0 mmoles)[a]

Catalyst	Composition of product, % Monoene	 Diene
[PtCl$_2$(SePh$_2$)$_2$]	17.0	83.0
[PtCl$_2$(SPh$_2$)$_2$]	13.5	86.5
[PtCl$_2$(AsPh$_3$)$_2$]	64.8	35.2
[Pd(CN)$_2$(PPh$_3$)$_2$][b]	3.0	97.0

[a] Under 600 psi of hydrogen at 90° for 8 hr. [b] Without SnCl$_2$.

6. **Kinetics of Hydrogenation.** The hydrogenation of 1,5-cyclooctadiene (3.0 g) in a methylene chloride solution (50 ml) containing 0.5 mmole of [PtCl$_2$(AsPh$_3$)$_2$] and 5.0 mmoles of SnCl$_2$·2H$_2$O under 500 psi of hydrogen at 105° was followed by gas chromatographic analysis. The results are shown in Figure 2. 1,5-Cyclooctadiene isomerizes very rapidly under these conditions to 1,4-cyclooctadiene which in turn isom-

Table V. Hydrogenation of 1,5-Cyclooctadiene (3.0 g)[a]

Catalyst	Composition of product, % Monene	 1,3-COD	 1,4-COD	 1,5-COD
[Pd(CN)$_2$(PPh$_3$)$_2$][b]	4	82	14	...
[PtCl$_2$(PPh$_3$)$_2$]	15	85	...	...
[PtCl$_2$(SePh$_2$)$_2$]	25	75	...	...
[PtCl$_2$(AsPh$_3$)$_2$][c]	100	...	...	...
[PtCl$_2$(AsPh$_3$)$_2$][d]	45	55	...	...
[PtI$_2$(1,5-COD)][d]	40	60	...	...

[a] For 10 hr under the same conditions as in Table IV. [b] Without SnCl$_2$. [c] 105°. [d] 3 hr.

Table VI. Elemental Analysis and Physical Properties of Some Reaction Intermediates

Compound	Color	Mp, °C	Molar conductance,[a] ohm^{-1} cm^2	% C		% H		% Cl		Mol wt[b]	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
A. From 1,5-cyclooctadiene											
I. $[\{PtH(SnCl_3)(PPh_3)_2\}_2(COD)]$	Yellow	140 dec	2.0	48.04	47.93	3.73	3.86	10.64	10.82	2000	1880
II. $[PtH(SnCl_3)(COT)(PPh_3)_2]$[c]	Yellow	187 dec	0.6	50.14	49.27	4.11	4.24	10.08	10.61	1054	1016
III. $[\{PtCl(PPh_3)\}_2(PPh_3)(CO)]Cl_2$	Pink	280		49.04	48.31	3.37	3.88	10.60	11.54		
B. From isoprene											
IV. $[Pt(C_5H_{10})_2(PPh_3)_2][Sn_2Cl_6]$	Red		15.8	42.18	42.57	3.84	4.10	16.23	17.02	1310	1157
C. From 1-octene											
V. $[PtH(SnCl_3)(C_8H_{16})(PPh_3)_2]$	Red	285 dec	0.8	49.98	49.18	4.49	4.77	10.08	9.81	1060	998
D. From bicycloheptadiene											
VI. $[\{PtH(SnCl_3)(PPh_3)_2\}_2(C_7H_8)]$	Green	161–163 dec	2.8	47.83	47.52	3.60	4.01	10.73	10.56		
VII. $[Pt(C_7H_8)(PPh_3)_2]SnCl_4$	Dark brown	95	14.6	48.15	48.50	3.58	4.04	13.23	12.90	1072	1043
E. From 1,4-cyclohexadiene											
VIII. $[PtH(C_6H_8)(PPh_3)_2]SnCl_3 \cdot CH_2Cl_2$	Yellow	95 dec	15.2	46.49	46.88	3.72	4.06	15.59	15.50		

[a] In nitrobenzene at 25°. [b] In methylene chloride. [c] The coordinated olefin is cyclooctene

erizes, very rapidly also, to the conjugated isomer. After 25 min the only diene isomer which could be detected in the reaction mixture was 1,3-cyclooctadiene. The very high rate of isomerization compared to the low rate of hydrogenation prevented a quantitative comparison of the reaction rates of the two reactions under the same conditions.

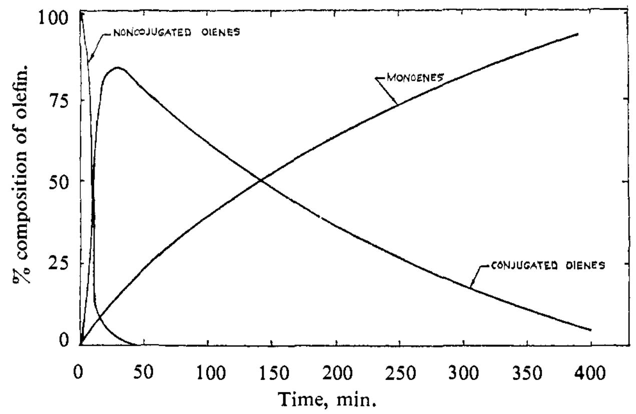

Figure 3. Catalytic hydrogenation of 1,5-heptadiene in ethylene chloride under 500 psi of hydrogen at 90°.

1,5-Heptadiene and 1,5-hexadiene were hydrogenated in CH_2Cl_2 (50 ml) under conditions similar to those applied to the 1,5-cyclooctadiene system, except that the temperature was 90°. The results are shown in Figure 3 (1,5-heptadiene) and Figure 4 (1,5-hexadiene). The rates of isomerization and hydrogenation were determined only semiquantitatively. It is obvious that isomerization proceeds at a very much higher rate than hydrogenation. The curve representing the disappearance of 1,5-heptadiene refers to the total concentration of all the nonconjugated dienes, including the starting material, that were in the system at the time of each measurement.

7. **Analysis of Reaction Intermediates.** In addition to the recovery of the original catalysts from the reaction media, either directly or by decomposition of the crude intermediates, other complexes which were not present in the reaction mixture at the beginning of the reaction were isolated and characterized. Such complexes include the hydrido complex $[PtHCl(PPh_3)_2]$ and the hydridotrichlorostannato complex $[PtH(SnCl_3)(PPh_3)_2]$. A third class of complexes which was isolated from the reaction medium includes platinum–olefin complexes and hydrido–platinum–olefin complexes which are apparently the effective reaction intermediates. Most of these complexes involve platinum–tin bonding.

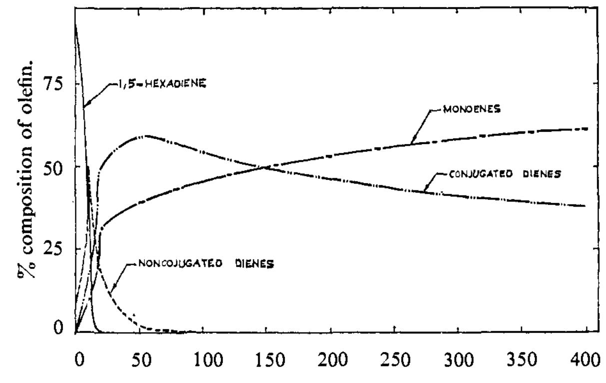

Figure 4. Catalytic hydrogenation of 1,5-hexadiene in ethylene chloride under 500 psi of hydrogen at 90°.

Some of the intermediate platinum–olefin complexes do not lend themselves to isolation. The catalyst $[Pd(CN)_2(PPh_3)_2]$, when used under conditions which did not bring about its reduction to palladium black, was always recovered unchanged from the reaction mixture, but $[PtCl_2(SPh_2)_2]$ and $[PtCl_2(SePh_2)_2]$ did not yield isolable organometallic intermediates. Rather, an unidentified, alcohol-soluble inorganic compound, which may be a platinum–tin–chloride cluster, was isolated. Although a few intermediates from systems

Table VII. Infrared Frequencies (cm^{-1}) of Some Reaction Intermediates[a]

Assignment	Stretching						Deformation			Unassigned
	=CH	C–H in –CH$_2$– and –CH$_3$			Pt–H	C=O	C–H	Pt–H	Sn–Cl, SnCl$_3$	
I	3000 (s)		2925 (s)	2870 (sh)	2200 2100 (m)				350 (m) 300 (s)	
II	3000 (s)		2920 (s)	2842 (s)	2025 (m)		1450 (sh)	810 (m)	320 (s) 300 (s)	1230 (w) 1120 (m) 788 (m) 720 (m)
III						2100 (s)				
IV		2955 (s)	2920 (s)	2860 (sh)					320 (m)	1100 (sh)
V		2960 (s)	2930 (s)	2880 2860 (w)	2220 (m)			805 (w)	370 (s) 300 (s)	970 (m)
VI	3000 (w)	2950 (b)	2860 (m)		2220 (m)			815 (w)	325 (s) 300 (s)	895 (m) 720 (w)
VII		2945 (s)	2900 (sh)	2820 (s)			1445 (sh)			1242 (m) 1100 (sh) 970 (sh) 718 (s)
VIII		2922 (s)	2860 (s)		2030 (s)		1445 (sh)		325 (s) 300 (s)	790 (w) 720 (s)

[a] In KBr disks, excluding frequencies common with those occurring in [PtCl$_2$(PPh$_3$)$_2$].

Table VIII. Proton Nuclear Magnetic Resonance Chemical Shifts of Some Reaction Intermediates and Olefins in CDCl$_3$ Relative to TMS = 10 ppm

Compound	Aromatic protons	Olefinic protons	Aliphatic protons	PPh$_3$: olefin
1,5-Cyclooctadiene		4.45 (4)	7.65 (8)	
1,3-Cyclooctadiene		4.22 (2), 4.32 (2)	7.83 (4), 8.50 (4)	
I	2.60 (15)	4.45 (1)	7.65 (2)	4
II	2.62 (15)	4.05, 4.25, 4.42 (3)	7.85 (2), 8.50 (4)	2
III	2.60			
IV	2.20 (4), 2.55 (7)	4.70 (1)	8.45 (2), 8.85 (3), 9.15 (3)	1
1-Octene		4.90 (1), 5.05 (1), 5.20 (1)	8.00 (3), 8.75 (8), 9.15 (3)	
V	2.55 (30)	4.57 (2)	8.05 (3), 8.40 (2), 8.75 (4), 9.07 (2), 9.15 (3)	2
Bicycloheptadiene		3.27 (4)	6.50 (2), 8.10 (2)	
VI	2.58	4.40, 4.55	6.50, 8.10	
VII	2.25, 2.30, 2.65		7.90, 8.50, 8.80, 9.10	
1,4-Cyclohexadiene	2.75 (benzene impurity?)	4.38 (1)	7.40 (1)	
VIII	2.20, 2.30, 2.47, 2.58	4.80	8.00, 8.55, 8.80, 9.15	

containing [PtCl$_2$(AsPh$_3$)$_2$] could be isolated, complete analysis was not possible. The most that we can say is that they show evidence of platinum–olefin and platinum–hydride bonding.

Tables VI–VIII give the elemental analyses and some physical properties, the infrared spectra, and the proton nuclear magnetic resonance chemical shifts of some of the compounds isolated from the hydrogenation of various olefins using [PtCl$_2$(PPh$_3$)$_2$] and SnCl$_2\cdot$2H$_2$O. Intermediate III was isolated from a system in which carbon monoxide was used as a cocatalyst. Although the melting point of compound III was rather sharp, its elemental analysis may be accounted for by assuming it to be a mixture of the original complex [PtCl$_2$(PPh$_3$)$_2$] and [PtCl$_2$(CO)(PPh$_3$)].

Discussion

Factors enhancing interaction between the olefin and the catalyst would be expected to enhance catalytic activity. However, when the interaction is strong enough to result in the formation of complexes too stable to react further, catalytic activity is inhibited. Factors enhancing olefin–metal interaction may be divided into intrinsic ones, which depend on the electronic and stereochemical properties of both the olefin and the metal, and external ones. The latter include those factors through which interaction sites on the metal or the olefin may be exposed or masked by species not forming an integral part of the reactant molecules. The nature of the solvent and the concentrations of reactants may be included in this group. The results reported in the previous section show the importance of these effects.

1. **Nature of the Olefin.** The structure of the olefin profoundly affects the rate of its hydrogenation. Thus, the ease of hydrogenation of a series of C$_8$ polyolefins decreases in the order: 1,7-octadiene > 1,5-cyclooctadiene > cyclooctatetraene. Similar orders were obtained for C$_6$ and C$_7$ polyolefins. The rate of hy-

drogenation decreases in the order 1,5-heptadiene ~ 1,6-hexadiene >> cycloheptatriene and 1,5-hexadiene > 1,4-cyclohexadiene >> benzene. It is evident that open-chain olefins are more likely to assume the proper arrangement for bonding to the metal than are cyclic olefins. Moreover, the complete unsaturation and conjugation of some cyclic olefins give them an aromatic (*e.g.*, benzene) or a semiaromatic (*e.g.*, cyclooctatetraene) stability that raises the energy of the transition state leading to hydrogenation. It was also observed that while benzene could not be hydrogenated and cyclooctatetraene gave only a trace of hydrogenated products, cycloheptatriene was hydrogenated to a slight but measurable extent. This may be interpreted in terms of the order of aromatic character of the olefins. Little or no difference was observed between the ease of hydrogenation of conjugated and nonconjugated olefins. This is understandable in view of the fact that nonconjugated dienes are hydrogenated to the monoenes *via* the very fast isomerization to the conjugated dienes.

The hydrogenation of bicycloheptadiene, which seems unfavorable from a structural point of view since the two double bonds cannot be forced into conjugation, resulted in a skeletal rearrangement of the olefin. The product was ethylidenecyclopentane and not bicycloheptene. This confirms the finding that hydrogenation of dienes by the catalysts used in this investigation may not be effected directly from a nonconjugated configuration.

2. Nature of the Catalyst. In considering the relationship between the chemistry of the catalyst and its catalytic activity, it should be borne in mind that metal–hydrogen interaction is as important to the catalytic activity as metal–olefin interaction. Catalytic activity of certain transition metals and their complexes has been attributed to the availability of low-lying vacant d orbitals on the metal atom. The activity is further enhanced and, with the choice of the right ligands, selectivity is effected, when only one vacant d orbital is available. This is due to the tendency of the metal atom to acquire the relatively stable closed-shell (or subshell) configuration. Thus, while transition metals of d^6, d^7, and d^8 configurations are known to be effective catalysts, complexes of the d^8 metal ions are the most effective. The tendency of the transition metal atom to acquire a complete d subshell is so important that Halpern[14] suggests a comparison between the reactivity pattern of tetracoordinated d^8 complexes and carbenes. He also considers hydrogen and olefin activation by these complexes as types of insertion reactions comparable to carbene insertions.

With the tendency to acquire a filled shell configuration, there is always the danger of the unfavorable reduction of the metal. If platinum or palladium metal is formed, the system is no longer homogeneous, and the specificity of the reaction is lost. Reduction is not as unfavorable in the case of iridium complexes, since both Ir(I) and Ir(III) are active. Indeed, the reversible oxidation of Ir(I) to Ir(III) has been suggested as a possible mechanism for catalysis by iridium complexes.

The mere availability of a vacant d orbital on the central atom does not make a complex an effective catalyst. The vacant orbital has to have a low enough energy that the electrons of the incoming ligand can occupy it. To construct a catalyst, therefore, it is necessary to make a d^8 metal atom (platinum(II) or palladium(II) in the present work) combine with ligands capable of stabilizing the oxidation state of the central atom under mild reducing conditions, and to lower the energy of the d orbitals. These requirements are fulfilled by ligands which can reduce the electronic density of the metal atom, namely, those with π-accepting capacity. This suggestion is supported by the fact that specific catalysis by platinum(II) complexes was discovered with triphenylphosphine as the ligand. It is further supported by the fact that platinum(II) complexes involving other π-accepting ligands are of comparable activity to triphenylphosphine complexes. Thus, we have found that $[PtCl_2(SPh_2)_2]$, $[PtCl_2(SePh_2)_2]$, and $[PtI_2(1,5\text{-COD})]$ are good catalysts with varying degrees of activity.

Results obtained in the present investigation suggest that triphenylphosphine and related ligands, originally coordinated to the platinum atom, are more important in the stabilization of the valence state of platinum than in the enhancement of coordination of the olefin. Thus, no hydrogenation or metal–olefin complex formation was effected when $[PtCl_2(PPh_3)_2]$ was used as a catalyst without a cocatalyst. However, hydrogenation was effected and metal–olefin complexes were isolated when $SnCl_2 \cdot 2H_2O$ was included in the hydrogenation system. Obviously, $SnCl_2 \cdot 2H_2O$ plays a major role in this reaction. This role was previously discussed in detail.[1a]

A particular advantage conferred by triphenylphosphine and related ligands is the stabilization of the transition metal hydrides which are formed in the course of hydrogenation and isomerization reactions. It is generally accepted now that transition metal hydrides can exist only if they are stabilized by the presence of a π acceptor. Hydrides were formed, in a few cases, when hydrogenation was attempted in the absence of $SnCl_2 \cdot 2H_2O$. This suggests the importance of triphenylphosphine in the enhancement of metal hydride formation, but in reality, this is not significant. The addition of $SnCl_2 \cdot 2H_2O$ to the system enhances catalysis, through the hydride intermediate, whether or not such hydride could be formed in the absence of $SnCl_2 \cdot 2H_2O$. Triphenylphosphine and related ligands play an important role in the stabilization of the hydrides once they are formed. A practical advantage of using triphenylphosphine and related ligands is that they render the otherwise insoluble platinum complexes fairly soluble in some organic solvents.

The catalytic activity among catalysts containing different π-accepting ligands follows the order $[PtCl_2(AsPh_3)_2] + SnCl_2 \cdot 2H_2O > [PtCl_2(PPh_3)_2] + SnCl_2 \cdot 2H_2O$, and $[PtCl_2(SePh_2)_2] + SnCl_2 \cdot 2H_2O > [PtCl_2(SPh_2)_2] + SnCl_2 \cdot 2H_2O$. This suggests a parallel order of π-accepting capacity or a reverse order of σ donation in the ligands. Also, since the arsenic atom is larger than the phosphorus atom, it is expected that the former will push the three phenyl groups farther from the central metal atom than will the latter. Thus, there is a greater chance for the olefin to attack the metal atom in the triphenylarsine complex than in that of triphenylphosphine. The same argument applies to

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(14) J. Halpern, *Chem. Eng. News*, **44** (45), 68 (1966).

the comparison between diphenyl selenide and diphenyl sulfide.

3. Cocatalyst Concentration. Results obtained in the present work indicate that catalytic activity increases with increasing tin:platinum molar ratio to a maximum at a ratio of 10:1, then declines at a much slower rate with increasing ratio of tin to platinum. These results are interesting in view of the fact that no intermediates with a tin:platinum ratio of more than 2:1 were isolated. As previously reported,[5] these observations can be explained by the reversible insertion reaction of $SnCl_2$ in the catalyst molecule between the platinum and chlorine atoms.

4. Solvent Effect. Our results indicate that the significance of the solvent lies mainly in the extent of its tendency to coordinate. Strongly coordinating solvents inhibit the catalytic activity, whereas weakly coordinating ones do not. Results obtained from the hydrogenation of various olefins in different solvents suggest the following increasing order of catalyst–solvent interaction: $CH_2Cl_2 \sim C_2H_4Cl_2 < (CH_3)_2CO < \text{tetrahydrofuran (THF)} \sim CH_3OH < \text{pyridine}$. This roughly parallels the order of increasing coordinating efficiency of the solvent. Monoene yields ranged from 100% in methylene chloride to zero in pyridine. Metal–solvent interaction may range from dipole–dipole interaction or solvent cage formation to actual chemical bonding or coordination, as with pyridine.

The role of the solvent as a possible source of hydrogen is significant only in the absence of any alternative source.

A practical advantage of methylene chloride as a hydrogenation solvent lies in the fact that it is a solvent for almost all of the reaction intermediates. It is also superior to alcohol and benzene in that the decomposition of intermediates in it is much less likely.

5. Reaction Mechanism. A few major observations suggest a plausible mechanism of the hydrogenation reaction.

(1) Hydrogenation of dienes (or polyolefins in general) consists of a very fast isomerization to the conjugated isomer followed by slow reduction to the monoene.

(2) Isomerization or double-bond migration occurs both before hydrogenation, as evidenced by the formation of the conjugated dienes from nonconjugated ones, and after hydrogenation, as evidenced by the isomerization of monoenes under hydrogenation conditions.

(3) Double-bond migration is stepwise, as evidenced by the isomerization of 1,5-cyclooctadiene.

(4) Hydride formation is an essential step in the mechanism of hydrogenation as suggested by the isolation of several hydrido complexes from hydrogenation reaction media. Hydride formation, however, is not the rate-determining step since the rate of hydrogenation is the same with either $[PtCl_2(PPh_3)_2]$ or $[PtHCl(PPh_3)_2]$ as catalysts.

(5) Metal–olefin complex formation is as important as metal–hydride complex formation, but neither is the rate-determining step.

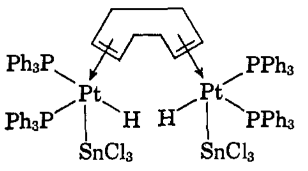
(6) The hydrido–metal–olefin complex may be the actual reaction intermediate, and its formation, or a reaction involving it as a reactant, may be the rate-determining step. Several such complexes have been isolated from the reaction media.

(7) Tin(II) chloride plays a significant role as a cocatalyst, and its presence is essential to hydrogenation with all the catalysts investigated except $[Pd(CN)_2(PPh_3)_2]$ which has intrinsic catalytic activity.

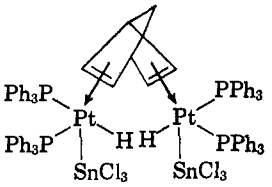
The above observations suggest the following mechanistic steps.

(i) Metal hydride formation involving a platinum–tin complex, as discussed in detail in a previous publication.[1a]

(ii) Hydrido–metal–olefin complex formation. This has also been discussed in our previous paper.[1a] Several such complexes have now been isolated and characterized. Thus, the following complexes were isolated from the hydrogenation or isomerization of the respective olefins.



I



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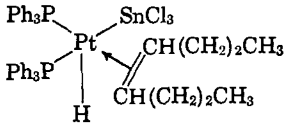
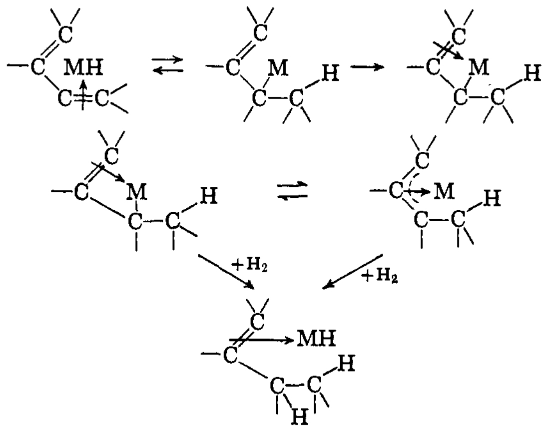


III

These complexes show the infrared stretching frequencies diagnostic of Pt–H bonds. Proton nmr spectra of compounds I and II do not differ much from those of the free olefin, suggesting rather symmetrical arrangements of the olefins in the complex. The possible formation of these complexes in the course of hydrogenation was discussed in detail in our previous report.[1a]

(iii) Stepwise migration of the double bonds by an alkyl–olefin–hydride mechanism as invoked in our previous report on catalytic isomerization.[1a] The conjugated diene is eventually formed.

(iv) Hydrogenation of the conjugated diene to the monoene by the following steps.



One of the conjugated double bonds adds to the metal hydride to form a π complex which rearranges to the σ complex. We are interested in the case where the metal atom is σ-bonded to the carbon atom in a position α to the "free" double bond. The metal atom, being very close to the free double bond, is attacked by it and a σ–π complex is formed. This complex may rearrange to a π-allylic complex. A π-allylic bonding is known to result in a downfield shift of the nmr chemical shift due to the proton on the central allylic carbon atom. Such a shift has not been observed in the nmr spectra of the intermediates isolated by us. It is thus more likely that the intermediate involves one π and one σ bond to the metal atom. The π bond to the metal weakens the metal–carbon σ bond and makes it susceptible to attack by hydrogen (or hydride ion) in a manner similar to the replacement of chloride ion in platinum hydride complex formation. Thus, a π metal–monoene–hydrido complex is obtained.

(v) Exchange of the coordinated monoene with "free" diene.

It should be pointed out that olefin exchange takes place at every stage of the over-all reaction. This is suggested by the fact that isomerized or partly hydrogenated olefins can be isolated at intermediate stages of the reactions. Thus, at one point during the hydrogenation of 1,5-cyclooctadiene, the reaction mixture consists of 1,5-, 1,4-, and 1,3-cyclooctadiene and cyclooctene.

Once the monoene is formed, it may undergo isomerization or double-bond migration to an equilibrium mixture of monoenes. Thus, the positions of the double bonds in the original polyolefins do not determine the position of the double bond in the monoene. 4-Vinylcyclohexene gave a mixture of two monoenes, the major component of which was ethylidenecyclohexane. 1,4,9-Decatriene gave a mixture of decenes. 1,7-Octadiene yielded a mixture of octenes of composition similar to the equilibrium mixture of octenes obtained from the isomerization of 1-octene and 4-octene under hydrogenation conditions.

That hydrogenation to the monoene occurs through coordination of the conjugated diene is reflected in the relative rates of hydrogenation of polyolefins of different steric arrangements. Thus, open-chain dienes such as 1,7-octadiene are hydrogenated much faster than cyclic dienes such as 1,5-cyclooctadiene. It is also reflected in the general observation that the rate of isomerization is much greater than the rate of hydrogenation. This is due to the fact that the isomerization reaction is less stereospecific than the hydrogenation reaction, mainly because a diene has to be conjugated before it can be hydrogenated by the catalyst.

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Activation Parameters for the Aquation of Acidopentaaquochromium(III) Complexes. The Nitratopentaaquochromium(III) Ion[1]

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Abstract: Reduction of aqueous acidic nitratopentaamminecobalt(III) by chromium(II) yields nitratopentaaquochromium(III), in addition to $(H_2O)_5CrNO^{2+}$ and other products; however, the nitratochromium(III) complex is best made by fusion of chromium(III) nitrate nonahydrate at 100°, followed by ion-exchange chromatography. The aquation of nitratopentaaquochromium(III) in aqueous perchloric acid–lithium perchlorate media of ionic strength 1.00 M has been studied. The rate law is of the form $-d[CrNO_3{}^{2+}]/dt = \{k_0 + k_{-1}[H^+]^{-1}\}[CrNO_3{}^{2+}]$ over the acidity range 0.08 to 1.0 M and a temperature range 0 to 43°. The corresponding activation parameters are: $\Delta H_0{}^* = 21.6 \pm 0.1$ kcal mole^{-1}, $\Delta S_0{}^* = -5.1 \pm 0.2$ eu, $\Delta H_{-1}{}^* = 24.9 \pm 1.5$ kcal mole^{-1}, $\Delta S_{-1}{}^* = -2.2 \pm 4.9$ eu. The contribution of the k_{-1} term was very small under the experimental conditions. The value of $\Delta S_0{}^*$ for the aquation of this and other species of the type $(H_2O)_5CrX^{2+}$, where X^- is nonbasic, can be linearly correlated with the entropy of the free aqueous ion X^- if this is corrected for entropy of rotation of X^-.

It has been suggested[2] that, in the aquation of the cations $(H_2O)_5CrX^{2+}$, the entropy $\Delta S_0{}^*$ of activation for the acid-independent reaction pathway may be linearly related to the entropies, $S°$, of the corresponding free aqueous ions X^-, at least when these anions are not basic (in the Brønsted sense) in water. This suggestion was not without precedent[3] and appears to be applicable to the halopentaaquochromium(III) series.[2]

Such a correlation, if generally valid, would be a double-edged sword. On the one hand, it would permit prediction of entropies of activation for reactions

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(1) This work was supported in part by the National Research Council, Ottawa, and by The University of Calgary General Research Fund.

(2) T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 532 (1965).

(3) A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, 47, 25 (1951).