[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF THE CATHOLIC UNIVERSITY OF AMERICA]

The Reduction of Ethylene Platinous Chloride[1]

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The reduction of ethylene platinous chloride with hydrogen and deuterium was investigated. The reaction in toluene solution took place at an appreciable rate at −40°, was autocatalyzed by platinum and inhibited by olefins. Evidence was found for the homogeneous reduction of diethylene platinous chloride in the presence of ethylene below −10° in acetone solution. The reaction had a low activation energy of approximately two kcal. The parallelism of these reactions to the heterogeneous catalytic reduction of olefins by metals suggests that the catalytic activity of metals may be due to the properties of small groups of metal atoms rather than to macroscopic properties peculiar to crystal lattice structure. A mixed ethylene–propylene platinous chloride complex was prepared.

I. Introduction

The first platinum olefin compound was prepared by Zeise[4] in 1827, who found that when platinic chloride was boiled with ethyl alcohol, an acid solution resulted, which, upon treating with potassium chloride, formed "Zeise's Salt," $K(PtCl_2C_2H_4)Cl$. Many other platinum–olefin complexes were later discovered, but not until 1934 was the basic compound of this series of substances—$(PtCl_2C_2H_4)_2$, bis-(ethylene)-dichloro-μ-dichlorodiplatinum(II), "ethylene platinous chloride"—characterized by Anderson.[5]

A comprehensive review by Keller[6] of the literature before 1940 on the platinum olefin compounds has been supplemented by reviews by Chatt.[7,8]

The compound $(PtCl_2C_2H_4)_2$ forms light orange crystals that decompose when heated above 130°, dissolve in many organic solvents, and decompose in water.[5] Molecular weight determinations indicate that the compound exists as a monomer in acetone and methyl ethyl ketone[9] and as dimer in benzene.[5]

Anderson[5] found that solid ethylene platinous chloride is quantitatively reduced by hydrogen at room temperature according to the equation

$$(PtCl_2C_2H_4)_2 + 4H_2 \longrightarrow 2Pt + 4HCl + 2C_2H_6 \quad (1)$$

The investigation of this reaction was undertaken in an attempt to elucidate the role of metal catalysts in the heterogeneous reduction of olefins.

A preliminary investigation of reaction 1 in solution indicated that it occurs at an appreciable rate at about −40° in solvents such as chloroform, acetone and toluene. The platinum formed a mirror on the sides of the glass vessel that was capable of reducing acetone to isopropyl alcohol at room temperature. A kinetic study could not be made in a static system since the ethane formed was soluble in the organic solvents used to dissolve the ethylene platinous chloride.

II. Experimental

Solubilities of Ethylene Platinous Chloride in Organic Solvents.—Dried, distilled solvents were kept in contact with an excess of ethylene platinous chloride for several hours at an elevated temperature and then for several hours at the temperature at which the solubility was to be determined. Five-ml. samples were pipetted into weighing bottles, the solutions slowly evaporated to dryness at reduced pressure and the bottles reweighed.

Preparation of Ethylene Platinous Chloride.—The ethylene platinous chloride used in these experiments was prepared according to the method of Kharasch and Ashford.[10] Platinic chloride powder was suspended in dried, distilled benzene, and ethylene (Matheson Co. C.P.) was bubbled through at 70°. The ethylene platinous chloride obtained was recrystallized four times from hot benzene. Ethylene platinous chloride was also purified in a different manner. Crude $(PtCl_2C_2H_4)_2$ was dissolved in dry acetone and ethylene bubbled through the solution at −78°. Yellow $PtCl_2(C_2H_4)_2$, bis-(ethylene)-dichloroplatinum(II), precipitated out and the acetone was decanted. The precipitate was washed with cold solvent and heated to room temperature whereupon it reverted to the monoölefin complex and ethylene.

Reduction of Ethylene Platinous Chloride.—A weighed sample of ethylene platinous chloride was dissolved in 50 ml. of analytical reagent grade toluene or acetone that had been dried and distilled and placed in the reaction vessel. The vessel was cooled to −78° and flushed with nitrogen. It was then warmed and maintained at the experimental temperature by means of a constant temperature bath consisting of a large Pyrex tube immersed in a Dry Ice–acetone solution. This tube was partially filled with acetone stirred by bubbling nitrogen gas through it, and in it was placed the reaction vessel with gas cooling coil, a Cu–constantan thermocouple with a type S Fisher potentiometer, and an immersion heater with a Cenco bimetallic regulator and a tipping mercury relay.

The system was flushed with nitrogen and then with ethylene or propylene in experiments in which they were used. Hydrogen and the dilutant gas were then passed through drying towers and calibrated flowmeters and bubbled through the reaction vessel. The olefin was removed from the gas stream by two bromine traps, bromine vapor by a sodium bisulfite solution trap, water vapor by a dry ice trap, and HCl gas and the sulfur dioxide given off by the bisulfite solution by an Ascarite tube. The bromine and bisulfite traps were removed from the system during runs in which no dilutant gas was used with the hydrogen or deuterium. The ethane was flushed into a liquid nitrogen trap by a stream of nitrogen gas and transferred to gas sampling bulbs by means of a Töpler pump. The nondeuterated hydrocarbons were analyzed in a Fisher Unitized Gas Analysis Apparatus (Orsat type). The deuterated samples were analyzed by the Mass Spectrometry Section of the National Bureau of Standards.

Determination of Unsaturates in Platinum Olefin Complexes.—Potassium cyanide solution reacts with platinum olefin complexes by replacing the unsaturate with the cyanide ion. A sample of platinum complex was placed in a reaction vessel connected to a high vacuum system. The KCN solution was contained in a bent tube connected to the

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[1] Based on a Dissertation submitted by Joseph H. Flynn to the Faculty of the Catholic University of America in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[4] Zeise, *Pogg. Ann.*, **9**, 632 (1827); *Magaz. Pharm.*, **35**, 105 (1830).

[5] J. S. Anderson, *J. Chem. Soc.*, 971 (1934).

[6] R. N. Keller, *Chem. Revs.*, **28**, 229 (1941).

[7] J. Chatt, *Ann. Repts. on Progr. Chem.* (*Chem. Soc. London*), **43**, 120 (1946).

[8] J. Chatt in "Cationic Polymerization and Related Complexes," Ed. P. H. Plesch, W. Heffer and Sons, Ltd., Cambridge, 1953, pp. 40–56.

[9] J. Chatt, *Nature*, **165**, 859 (1950).

[10] M. S. Kharasch and T. A. Ashford, THIS JOURNAL, **58**, 1733 (1936).

reaction vessel by a standard taper joint. The solution was frozen and pumped out several times to remove any occluded gases. The KCN tube was then inverted to allow the solution to react with the sample. The gases that were not frozen out at Dry Ice temperatures were frozen out in the liquid nitrogen trap, transferred to a gas sampling bulb, and analyzed in the Fisher Gas Analysis Apparatus. Propylene was removed from the mixture with 82.5% sulfuric acid.[11] This reagent was tested with known ethylene-propylene mixtures and found to absorb insignificant amounts of ethylene. The ethylene was removed with fuming sulfuric acid.

III. Results and Discussion

The solubilities of $(PtCl_2C_2H_4)_2$ in mixed xylenes, benzene and toluene at various temperatures are given in Table I. Ethylene platinous chloride is insoluble in carbon tetrachloride and cyclohexane and soluble to the extent of from 0.5 to 5.0 g./100 ml. in chlorobenzene, 1,1′,2,2′-tetrachloroethane, 1,4-dioxane, acetone and chloroform, listed in order of increasing solubility.

TABLE I

SOLUBILITIES OF ETHYLENE PLATINOUS CHLORIDE

Solvent	Temp., °C.	Solubility, g./100 ml.
Mixed	0	0.11
Xylenes	25	.42
Toluene	−78	.54
	0	1.08
	+25	1.21
Benzene	+ 6	0.24
	25	0.45

From the study of the reduction of ethylene platinous chloride in toluene solution by undiluted hydrogen gas at temperatures from −70 to +30°, the following experimental facts were obtained.

(1) As high as 10% ethylene was found in the ethane produced in the reaction.

(2) In quite dilute solutions of complex at room temperatures, an induction period of several minutes might occur before platinum would begin to form. Once begun, the platinum precipitated quite rapidly.

(3) The presence of platinum from a previous run would catalyze the reduction of the complex at temperatures as low as −70°.

(4) At −30°, the platinum formed in the reaction vessel catalyzed the hydrogenation of ethylene with 52% conversion to ethane when a ratio of one part ethylene to 10 parts hydrogen was passed through at a total flow rate of 4.5 ml./sec.

(5) Reduction with deuterium in toluene solution at −23.7° resulted in the formation of ethanes ranging from C_2H_6 to C_2D_6 and ethylenes from C_2H_4 to C_2D_4.

The above results indicate that although the initial reaction may be homogeneous, the reaction becomes heterogeneous, being autocatalyzed by the platinum formed in the reduction.

The deuterium experiments substantiate this conclusion. In the heterogeneous reduction of ethylene with platinum and other metal catalysts many investigators have found that the exchange reaction between ethylene and deuterium takes place at a faster rate than the reduction.[12–14]

Ethane–deuterium exchange in the presence of metal catalysts takes place at appreciably higher temperatures.[15,16] It is necessary, therefore, to assume that either the ethylene in $(PtCl_2C_2H_4)_2$ is capable of exchanging its hydrogens with deuterium molecules or the complex dissociates and ethylene is heterogeneously reduced on the platinum surface.

The reduction of solid ethylene platinous chloride with deuterium will be treated in another paper.[17]

Runs demonstrating the effect of the presence of ethylene and propylene upon the reduction of ethylene platinous chloride in solution are given in Table II. The predominant source of error in these experiments was in the collection and analysis of 1 to 10 ml.-samples of ethane. The analysis was performed on the Orsat apparatus by means of combustion with oxygen. The oxygen consumed, the carbon dioxide formed, and the contraction of gas during the combustion were measured and the calculated values for the volumes of ethane agreed within ±10%.

Comparison of runs E16, E17 and PH1 demonstrates that ethylene or propylene in a 1:1 ratio with hydrogen completely inhibits the formation of platinum at −30°. The presence of nitrogen in the same ratio does not affect the reduction at the same temperature. From runs E3, E4 and E5, one sees that at as high a temperature as +23°, a 10-1 ethylene to hydrogen ratio will prevent the formation of platinum to a considerable extent. This inhibition seems to indicate that the first step of the reduction is a dissociation of the complex with ethylene as one of the products. The platinum formed as a result of the initial dissociation and reduction would catalyze the reduction of the complex. Ethylene, however, still inhibits the reaction markedly in the presence of platinum. This may be due to the preferential adsorption of ethylene on the platinum surface.

Comparison of E13 and E16, for example, indicates that the rate of formation of ethane (net ml. of ethane formed/time of hydrogen flow in minutes) at low temperatures was independent of the rates of flow of hydrogen and ethylene. The minimum value for the ratio of ethylene to hydrogen needed to inhibit effectively the formation of platinum increases rapidly with temperature. At 0° in toluene (E7), a ratio of 2.6 is not great enough. At −4.8° in acetone (E15), an ethylene to hydrogen ratio of 6.4 is sufficient. At −33.5° (E16), a ratio of 0.67 is sufficient.

Comparison of E2 through E6 with E9 through E16 indicates that the rate of ethane formation below −10° is slightly greater in acetone than in toluene. Since the temperature gradient below −10° is quite small, the 2.7-fold increase in rate of E6 over E2 must be due to the increase in the concentration of ethylene platinous chloride.

In runs in which platinum was not formed, the rate of formation of ethane was quite low or zero at temperatures above −10°, but at temperatures below −14°, the rate was larger, falling off slowly with

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[12] A. Farkas, L. Farkas and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **A146**, 630 (1934).

[13] K. Morikawa, N. R. Trenner and H. S. Taylor, THIS JOURNAL, **59**, 1103 (1937).

[14] A. Farkas and L. Farkas, *ibid.*, **60**, 22 (1938).

[15] K. Morikawa, W. S. Benedict and H. S. Taylor, *ibid.*, **57**, 592 (1935).

[16] A. Farkas, *Trans. Faraday Soc.*, **36**, 522 (1940).

[17] J. H. Flynn and H. M. Hulburt, THIS JOURNAL, **76**, 3396 (1954).

TABLE II

EFFECT OF ETHYLENE AND PROPYLENE ON THE REDUCTION OF $(PtCl_2C_2H_4)_2$

No.	Concn.,[a] g./100 ml.	Temp., °C.	Total gas vol., l. H_2	C_2H_4	N_2	Ratio[b] (X)/(H_2)	Net C_2H_6,[c] ml.	Time, min., of H_2 flow	Net C_2H_6 per min.	Platinum formed[d]
E2	0.25	−22.5	0.73	6.62	0.00	9.5	0.9	65	0.014	None
E3	.25[e]	0.0	.50	5.75	.00	9.2	0.0	37	.000	None
E4	.25[e]	+23.0	.47	5.62	.00	11.0	2.9	55	.053	Little
E5	(.25)[e]	+23.0	.35	0.00	2.66	6.4	4.1	25	...	Much[g]
E6	.40	−17.5	1.68	5.71	0.00	2.6	2.1	55	.038	None
E7	.40[f]	0.0	1.32	4.38	.00	2.6	6.3	43	.15	Little
E9	.32	− 7.0	0.61	4.99	.00	6.8	0.4	40	.010	Little
E10	.32	−14.0	.52	4.34	.00	6.4	1.4	34	.041	None
E11	.32	−15.8	.49	4.44	.00	6.4	1.5	32	.047	None
E12	.32	−10.7	.61	5.12	.00	6.4	0.0	40	.000	None
E13	.32	−26.5	.55	4.93	.00	6.4	1.4	36	.039	None
E14	.32	− 8.8	.46	4.73	.00	6.4	0.6	30	.020	None
E15	.32	− 4.8	.43	4.04	.00	6.4	0.1	28	.004	None
E16	.32	−33.5	2.75	3.33	.00	0.67	2.0	60	.033	None
E17	.32	−30.0	2.40	0.00	1.26	.53	9.0	60	...	Much
PH1	.32	−30.0	2.28	3.00[h]	0.00	.77	2.7	61	.044	None

[a] E2 to E7 in toluene; E9 to PH1 in acetone. [b] (X) is av. concn. of dilutant gas. [c] Ethylene contained 0.288 ml. ethane/l.; propylene contained 2.71 ml. ethane and 3.45 ml. propane/l. [d] Small traces of platinum formed a mirror on side of vessel. Presence of platinum also was determined by Tyndall effect and filtration through fritted glass at end of exp. [e] Same sample as E2. [f] Same sample as E6. [g] Mostly in first five minutes. [h] C_3H_6 used instead of C_2H_4.

decreasing temperature. This is illustrated for runs E9 through E16 in Fig. 1.

These results indicate that the formation of ethane without the deposition of platinum in the presence of ethylene at temperatures below −10° occurs by a different mechanism than the ethylene inhibited reduction at higher temperatures. Chatt[9,18] found that $PtCl_2(C_2H_4)_2$ can be formed by bubbling ethylene through an acetone solution of $(PtCl_2C_2H_4)_2$ at low temperatures and that this compound was stable in an atmosphere of ethylene below about −6°. This suggests that the low temperature reduction in the presence of ethylene may consist of the chain given below

$$2PtCl_2(C_2H_4)_2 + 2H_2 \longrightarrow (PtCl_2C_2H_4)_2 + 2C_2H_6 \quad (2)$$

$$(PtCl_2C_2H_4)_2 + 2C_2H_4 \rightleftarrows 2PtCl_2(C_2H_4)_2 \quad (3)$$

$$2C_2H_4 + 2H_2 \longrightarrow 2C_2H_6 \quad (2) \text{ and } (3)$$

An estimate of 2.5 kcal. for the over-all activation energy can be obtained from runs E11, E13 and E16. In run E10, it appears that at −14° the rate of ethane formation has decreased because of a shift to the left of the equilibrium in eq. 3 resulting in a lower concentration of $PtCl_2(C_2H_4)_2$. On this assumption, the apparent activation energy would be ascribed chiefly to eq. 2. Since the amount of ethane formed in these experiments is small and the percentage error is large, this value for the activation energy can be considered to give only the order of magnitude.

The only reported homogeneous catalytic hydrogenation reactions appear to be the reduction of butyraldehyde with cobalt carbonyl catalysts[19] and the hydrogenation of cupric compounds and quinoline in quinoline solution with cuprous acetate and cuprous salicylate catalysts.[20-22]

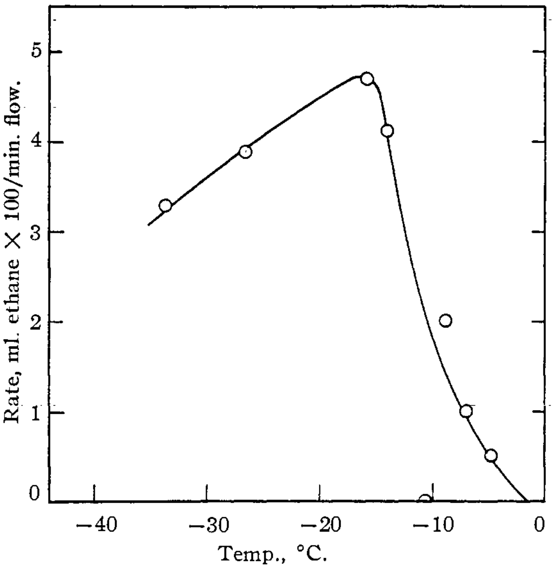

Fig. 1.—Rate of ethane formation *vs.* temperature 3.2 g./l. $(C_2H_4PtCl_2)_2$ in acetone; $(C_2H_4)/(H_2)$ = 6.4; flow rate = 0.11 l./min.

The formation and reduction of the platinum olefin complexes appear to be quite similar to the heterogeneous reduction of olefins by metal catalysts. The hydrogenation of the monoölefin complex is analogous to the high temperature catalytic hydrogenation in which much hydrogen–deuterium exchange takes place. The formation of the diolefin complex at low temperatures has its counterpart in the high adsorption of ethylene at low temperatures. The reduction of the diolefin complex at low temperatures takes place with less H–D exchange and with a low activation energy. This is similar to the metal-catalyzed reduction in which the H–D exchange and activation energy of hydrogenation falls off as the temperature is decreased.[23]

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(18) J. Chatt, *J. Chem. Soc.*, 2622 (1952).

(19) I. Wender, M. Orchin and H. H. Storch, THIS JOURNAL, **72**, 4842 (1950).

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(22) S. Weller and G. A. Mills, *ibid.*, **75**, 769 (1953).

(23) D. D. Eley, *Quart. Rev. (London)*, **3**, 222 (1949).

If the low temperature hydrogenation of the diolefin complex is truly homogeneous, then it appears that this catalytic property of platinum can be accounted for by the properties of the individual atoms rather than some macroscopic property of the metal catalyst.

The Reaction of Propylene with Ethylene Platinous Chloride.—The presence of 2% propanes-*d* from the reduction of ethylene platinous chloride with deuterium suggested that since these samples had been purified by bubbling ethylene through them at −78°, small traces of propylene in the ethylene might react with the ethylene complex to form the propylene complex. However, this conclusion is at variance with that drawn from the observations of Gel'man[24,25] and Anderson,[26] who concluded from replacement studies that $C_3H_6PtCl_2$ would not form in the presence of ethylene. A study was therefore undertaken to find if C_3H_6 would form a diolefin with $(PtCl_2C_2H_4)_2$ at low temperatures.

Dry propylene was bubbled through an acetone solution of ethylene platinous chloride at −78°. The solution turned amber on heating to room temperature and after several hours a brown precipitate formed on the sides of the vessel. The filtered solution was evaporated to dryness and a dark brown oil (I) remained. This oil was soluble in acetone and benzene and formed a red-brown solution in the latter. Upon prolonged evacuation with a high vacuum pump (I) gave off gas and became a brown-black solid (II) which contained platinum.

A sample of (II) was pyrolyzed in vacuum with a sooty gas flame and the gases obtained were analyzed on the Orsat apparatus. The gas sample contained 20% CO_2 or HCl, 6% ethylene, 48% propylene and 26% saturated hydrocarbons with an average carbon content corresponding to C_4H_{10}. This large amount of paraffins is not surprising since platinum is known to polymerize unsaturated hydrocarbons into higher molecular weight alkanes; 6% ethane, 29% butane, and some higher hydrocarbons are reported from the polymerization of ethylene in the presence of platinum at 34°.[13]

(II) was found to contain 86% propylene and 14% ethylene by the KCN method described previously. It appears therefore that $PtCl_2(C_2H_4)(C_3H_6)$ may be formed at low temperatures and that it decomposes mainly into the propylene complex. The inhibitory effect of propylene on platinum formation during the reduction of ethylene platinous chloride at −30° may be due to the formation of the diolefin complex. However, further experimentation with this reaction and upon the reduction of a dipropylene complex, if it exists, is indicated.

Ethylene was bubbled through an acetone solution of (I) and a small amount of tan solid formed. This solid was insoluble in organic solvents, contained platinum, gave off a gas upon heating, and effervesced in the presence of KCN solution. This substance is similar in properties to a solid prepared by Chatt[9,13] which he suggests may be *cis*-$PtCl_2(C_2H_4)_2$ or a polymeric substance.

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[25] A. D. Gel'man, *ibid.*, **20**, 307 (1938).

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF THE CATHOLIC UNIVERSITY OF AMERICA]

The Reduction of Ethylene Platinous Chloride with Deuterium; the Mass Spectra of Deuterated Ethanes[1]

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The 14 *m/e* peak of the mass spectrum of ethane is mainly due to the $C_2H_4^{++}$ ion. This ion appears to be formed by the removal of two hydrogens from the same carbon atom while the $C_2H_4^+$ ion appears to be formed by the removal of one hydrogen from each carbon. The reduction of the solid ethylene platinous chloride with deuterium at −22.0° resulted in the formation of all ethanes from C_2H_6 to C_2D_6 with greater than equilibrium amounts at the tails of the distribution which is similar to the results obtained in heterogeneous catalysis. The results indicated that the deuterium did not add unsymmetrically to the carbon double bond. Bromination of ethylene platinous chloride at room temperature resulted in the formation of $PtCl_2Br_2C_2H_4$ while at 61° symmetrical ethylene dibromide was formed.

I. Introduction

The reduction of solid ethylene platinous chloride by hydrogen takes place rapidly at room temperature, as was found by Anderson,[4] according to eq. 1.

$$PtCl_2C_2H_4 + 2H_2 \longrightarrow Pt + 2HCl + C_2H_6 \quad (1)$$

The reduction of ethylene platinous chloride in toluene and acetone solutions and the reduction of diethylene platinous chloride have been investigated recently.[5] The present investigation of the reduction of solid ethylene platinous chloride with deuterium was undertaken to extend the comparison of this reaction with the heterogeneous hydrogenation of olefins with metal catalysts.

The mode of bonding between the olefin and platinum in these complexes has been a matter of speculation for some time. Chatt[6] had proposed that

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[2] National Bureau of Standards, Washington, D. C.

[3] Chemical Construction Corporation, New York, N. Y.

[4] J. S. Anderson, *J. Chem. Soc.*, 971 (1934).

[5] J. H. Flynn and H. M. Hulburt, THIS JOURNAL, **76**, 3393 (1954).

[6] J. Chatt, *Research (London)*, **4**, 180 (1951).