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.

Acknowledgments.—The authors wish to acknowledge their appreciation to Dr. Leo A. Wall and Dr. Fred L. Mohler of the National Bureau of Standards for their assistance in obtaining the mass spectrometric analysis of gas samples in the experiments in which deuterium was used.

WASHINGTON, D. C.

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[24] A. D. Gel'man, *Compt. rend. acad. sci. U.R.S.S.*, **32**, 347 (1941).

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

[26] J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).

[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]

BY JOSEPH H. FLYNN[2] AND HUGH M. HULBURT[3]

RECEIVED FEBRUARY 12, 1954

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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[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.

[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).

the C_2H_4 in ethylene platinous complexes was present as the ethylidene (CH_3—CH=) group with carbon to platinum bonding similar to that in metal carbonyls. However, he[7] has later found that the infrared spectra of these complexes indicate that the carbon to carbon double bond is still present, which is consistent with the symmetrical structure proposed by Dewar.[8] The absence of isomerization of the olefin in the formation of *cis*- and *trans*-2-pentene complexes[9] also renders the ethylidene structure improbable. The presence of a preponderance of CH_3–CHD_2 rather than CH_2D–CH_2D among the products of the reduction of $(PtCl_2C_2H_4)_2$ with deuterium would be expected if the ethylidene structure were valid.

II. Experimental

Reduction of Solid Ethylene Platinous Chloride with Deuterium.—The ethylene platinous chloride was prepared by the method of Kharasch and Ashford[10] and purified by the formation of the diolefin complex as described in the previous paper.[5] The deuterium gas, obtained from the Stuart Oxygen Company, assayed 99.5% purity and was dried with liquid air.

The reduction was studied in a vacuum apparatus consisting of a mercury manometer and a manifold containing a reaction vessel connected to a deuterium tank and three gas bulbs, A, B and C. The reaction vessel was maintained at a constant temperature by means of a constant temperature acetone-bath cooled by a surrounding bath of Dry Ice and acetone. Deuterium was introduced into the evacuated reaction vessel containing solid ethylene platinous chloride. Hydrogen chloride was removed from the product gases by sodium hydroxide and the hydrocarbons frozen out in bulb A with liquid nitrogen. Part of the hydrocarbons was distilled into bulb C which contained bromine. This bulb was heated to room temperature to remove any unsaturates that might be present. The bromine was frozen out with Dry Ice and the paraffins were distilled from bulb C to bulb B. The gases in bulbs A and B were analyzed by the Mass Spectrometry Section of the National Bureau of Standards.

Bromination of Ethylene Platinous Chloride.—One gram of ethylene platinous chloride was dissolved in 30 ml. of dry distilled chloroform. A solution of bromine in chloroform was added and the resulting solution was refluxed on a water-bath for 30 minutes. The chloroform solution was washed with sodium bisulfite solution to remove the excess bromine and with several portions of water. The solution was dried with anhydrous calcium sulfate and the chloroform evaporated off. The ethylene bromide was identified by means of its boiling point and refractive index.

III. Results and Discussions

Discussion of the Mass Spectra of Deuterated Ethanes.—The reduction of ethylene platinous chloride with deuterium resulted in the formation of all ethanes from C_2H_6 to C_2D_6. Therefore, before any quantitative treatment of the results can be attempted, a discussion of the calculation of the mass spectra of the deuterated ethanes is in order.

The mass spectra of C_2H_5D, CH_3CHD_2, CH_3CD_3 and C_2D_6 have been reported,[11] but the spectra of the remaining deuterated ethanes are not available. Approximate spectra of deuterated ethanes have been calculated from the spectra of C_2H_6 by assuming that hydrogen and deuterium are removed with equal ease in the formation of ion fragments.[12] Use of this method depends upon the ability to assign ions to the m/e peaks in the spectrum of C_2H_6.

In the 12–15 m/e region of the ethane spectrum, ambiguities arise upon attempting to assign positive ions to the integral value peaks. The 13.5 and 14.5 peaks are caused by the $C_2H_3^{++}$ and $C_2H_5^{++}$ ions, respectively, but the 14 peak, for example, could be caused by the CH_2^+ and/or $C_2H_4^{++}$ ions. By a comparison of the experimental spectrum of C_2H_5D with spectra for C_2H_5D calculated by the method mentioned in the previous paragraph, the portion of the ion current carried by CH_2^+ ions and the portion carried by $C_2H_4^{++}$ ions that will give the best agreement can be obtained. Table I contains the experimental mass spectrum of C_2H_5D and the spectra of C_2H_5D calculated making various assumptions about the formation of double and single ions.

TABLE I

MASS SPECTRA OF C_2H_5D (12–16 m/e)

A, calcd. assuming 14 m/e peak in C_2H_6 due to CH_2^+; B, calcd. assuming 14 m/e peak in C_2H_6 due to $C_2H_4^{++}$; C, calcd. assuming 14 m/e peak in C_2H_6 2.34 CH_2^+; 6.15 $C_2H_4^{++}$; D, same as C except a = 1.09, b = 0.60 (ref. 11).

m/e	Expt. (ref. 11)	A	B	C	D
16	5.87	5.22	5.22	5.22	5.22
15	9.17	10.89	8.06	8.84	9.43
14.5	4.67	0.57	6.23	4.67	4.67
14	3.40	5.94	3.09	3.87	3.47
13.5	0.12	0.12	0.12	0.12	0.12
13	1.13	0.98	0.98	0.98	0.92
12	0.71	0.56	0.56	0.56	0.56
Total dev.:		9.34	3.93	1.75	1.35

The parameters "a" and "b" are introduced[11] to take into account the fact that hydrogen and deuterium are not removable with equal ease. When a hydrogen is removed to form an ion fragment, the calculated value is multiplied by "a," and the calculated value for the ion current is multiplied by "b" for each deuterium removed. The parameters "a" and "b" were evaluated for the 24 to 31 m/e range of C_2H_5D so that the deviation of the ion currents of the peaks in the calculated spectrum from those of the experimental spectrum would be a minimum. Use of these parameters (column D in Table I) results in good agreement between the calculated and experimental spectra.

Table II contains the distribution of ion current between single and double ions calculated for the 12–15 m/e region of C_2H_6 from the data in ref. 11.

TABLE II

DISTRIBUTION OF SINGLY AND DOUBLY CHARGED IONS IN THE MASS SPECTRUM OF ETHANE

m/e	Total ion current	Singly charged ion	Singly charged ion current	Doubly charged ion	Doubly charged ion current
15	10.44	CH_3^+	10.44	$C_2H_6^{++}$	0.00
14.5	3.43	...	...	$C_2H_5^{++}$	3.43
14	8.49	CH_2^+	2.34	$C_2H_4^{++}$	6.15
13.5	0.17	...	...	$C_2H_3^{++}$	0.17
13	1.19	CH^+	1.07	$C_2H_2^{++}$	0.12
12	0.56		C^+ or C_2^{++}		

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[7] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[8] M. J. S. Dewar, *Bull. soc. chim.*, **18**, C79 (1951).

[9] A. Oppegard, Ph.D. Thesis, University of Illinois, 1946—see B. E. Douglas, THIS JOURNAL, **75**, 4839 (1953).

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

[11] D. O. Schissler, S. O. Thompson and John Turkevich, *Disc. Faraday Soc.*, **10**, 46 (1951).

[12] John Turkevich, D. O. Schissler and P. Irsa, *J. Phys. Colloid Chem.*, **55**, 1078 (1951).

The calculation of the spectra of ethane-*d* containing two, three or four deuterium atoms presupposes a knowledge of the mode of formation of the ion fragments. For example, in calculating the ion current carried by $C_2X_4^+$ (X = H or D) in the spectrum of $CH_3\text{–}CD_3$, two different spectra would be obtained depending upon whether the ion was formed by reaction 2 or 3.

$$CH_3\text{—}CD_3 + e \longrightarrow CH_2\text{—}CD_2^+ + 2e + H + D \quad (2)$$

$$CH_3\text{—}CD_3 + e \longrightarrow \begin{array}{c} CH_3\text{—}CD^+ \\ \text{or} \\ CH\text{—}CD_3^+ \end{array} + 2e + 2\begin{array}{c} H \\ \text{or} \\ D \end{array} \quad (3)$$

If 2 occurred, there would be a large peak at 30 *m/e*, while if 3 took place, the spectrum would contain large peaks at 29 and 31 *m/e*.

Schissler, Thompson and Turkevich[11] obtained the pure methyl ion spectra of the deuterated ethanes which they analyzed by lowering the bombarding potential to 17.5 volts. If it is assumed that no intramolecular rearrangement occurred, then their spectrum of $C_2H_3D_3$ resulted from a mixture of 75.7% $CH_3\text{–}CD_3$ and 24.3% $CH_2D\text{–}CHD_2$. These percentages were used in calculating the spectra for $C_2H_3D_3$.

Table III contains the experimental[11] and calculated spectra for $C_2H_3D_3$ for the 14.5, 15, 15.5 and 16 *m/e* peaks. Best agreement was obtained assuming that the $C_2H_4^{++}$ ion was formed by the reaction

$$CH_3\text{—}CH_3 + e \longrightarrow CH_3\text{—}CH^{++} + 3e + 2H \quad (4)$$

TABLE III

CALCULATED MASS SPECTRA FOR $C_2H_3D_3$ FROM 14.5 TO 16 *m/e*

A, calcd. assuming random hydrogen removal in the formation of $C_2H_4^{++}$; B, calcd. assuming one hydrogen removed from each carbon atom in the formation of $C_2H_4^{++}$; C, calcd. assuming two hydrogens removed from one carbon atom in the formation of $C_2H_4^{++}$.

m/e	Expt. (ref. 11)	A	B	C
16	4.77	4.77	4.77	4.77
15.5	3.14	2.63	2.00	3.58
15	6.19	7.24	8.51	5.34
14.5	1.62	0.95	0.32	1.90
Total dev.:		2.23	4.76	1.47

Slight improvements in agreement were obtained by assuming that three hydrogens are removed from the same carbon atom in the formation of $C_2H_3^{++}$ and three removed from one carbon and one from the other in the formation of $C_2H_2^{++}$, but these improvements are quite inconclusive as the ion currents are small.

Table IV contains the experimental and calculated spectra for the 29–33 *m/e* region for $C_2H_3D_3$. It appears that the $C_2H_4^+$ ion is formed by reaction 2.

Since the total ion current of the calculated spectra is considerably less than the total ion current of the experimental spectrum, one could not reasonably speculate upon the mode of formation of the other ion fragments in the 24–33 *m/e* range of $C_2H_3D_3$.

The calculated spectra for $C_2H_4D_2$ are not so sensitive to change in mode of ion formation. However, excellent agreement is obtained in the 12–17 *m/e* range between the experimental spectrum and the calculated spectrum assuming 5.30 $C_2H_4^{++}$ and 3.17 CH_2^+.

TABLE IV

CALCULATED MASS SPECTRA OF $C_2H_3D_3$ FROM 29 TO 33 *m/e*

A, calcd. from the C_2H_6 spectrum assuming that one hydrogen is removed from each carbon atom in the formation of $C_2H_4^+$; B, calcd. from the C_2H_6 spectrum assuming that two hydrogens are removed from one carbon atom in the formation of $C_2H_4^+$; C, calcd. assuming that $C_2H_4^+$ is formed by random hydrogen removal.

m/e	Exp. (ref. 11)	A	B	C
33	100	100	100	100
32	43.9	35.4	35.4	35.4
31	59.6	52.7	169.5	196.8
30	285.9	290.2	56.7	196.8
29	131.8	60.3	177.1	107.0
Total dev.:		91.2	392.9	360.6

In all these calculations, it should be remembered that the assumption that hydrogen and deuterium are equally removable is at best a crude approximation. Also, in applying these results calculated from the data in ref. 11 to the present work, it should be further noted that spectra vary considerably among different mass spectrometers.

Reduction of Ethylene Platinous Chloride with Deuterium.—The residual peaks obtained by subtracting the mass spectrum of the bromine-treated samples from the spectrum of samples not treated with bromine resulted in a spectrum that was quite well explained if it were assumed that all propanes from C_3H_8 to C_3D_8 were present to the extent of 2% of the total gas volume. The presence of a smaller percentage of propanes-*d* in the bromine-treated samples was due to the partial separation of the ethanes from the propanes during distillation of the sample into the bromine bulb. The propylene was introduced into the sample of platinum complex during the purification by the formation of $PtCl_2(C_2H_4)(C_3H_6)$ described in a previous paper.[5] The deuterated propane spectra were calculated from the C_3H_8 spectrum assuming random hydrogen removal. The percentages of various propanes obtained are given in Table V. Since the spectra are consecutively subtracted off beginning with the C_3D_8 spectrum, the errors are cumulative and the percentages of less highly deuterated propanes are probably greatly in error.

TABLE V

DEUTERATED PROPANES FORMED IN THE REDUCTION OF ETHYLENE PLATINOUS CHLORIDE

d-Propane	Total propane-*d* %	*d*-Propane	Total propane-*d*, %
C_3D_8	4.1	$C_3D_3H_5$	13.9
C_3D_7H	8.2	$C_3D_2H_6$	14.9
$C_3D_6H_2$	12.7	C_3DH_7	9.2
$C_3D_5H_3$	12.9	C_3H_8	13.1
$C_3D_4H_4$	11.0		

No unsaturates were found among the products. An excess of deuterium was used so that the platinum formed in the reaction would catalyze the hydrogenation of any olefins present.

The spectra of the deuterated ethanes were calculated assuming equally probable hydrogen or deuterium removal. In the 12–18 *m/e* region, all the isomers were calculated assuming the portions of ion current given in Table II. These spectra were used to calculate the percentages of the ethane isomers. These percentages are plotted in Fig. 1.

The distribution of deuterated ethanes calculated assuming a random distribution from a pool of hydrogen and deuterium according to formula 5

$$\%\ C_2H_{6-x}D_x = \frac{6}{x(6-x)}\left(\frac{n}{n+m}\right)^{6-x}\left(\frac{m}{n+m}\right)^{x} \times 100 \qquad (5)$$

is also plotted in Fig. 1. The factor $n/(n + m)$ is the fraction of H in the ethanes and $m/(n + m)$ is the fraction of D in the ethanes wherein "n" and "m" are obtained by assuming the experimental distribution of ethanes.

If it is assumed that the reaction goes 12.5% by a mechanism that produces only $C_2H_4D_2$, the remaining experimental distribution is symmetrical. A calculated distribution assuming that the reaction goes 87.5% by a mechanism according to formula 5 where $n = m = 0.5$, and 12.5% by a mechanism that produces $C_2H_4D_2$ is also plotted in Fig. 1.

The high percentages at the tails of the distribution indicate that the reaction did not take place in a random manner. It appears that much exchange took place initially on the surface of the solid $(PtCl_2C_2H_4)_2$, thus accounting for the large amount of C_2D_6, while not all of the hydrogen formed by the exchange reaction escaped to mingle with the large excess of D_2, but caused reduction in the interior of the solid resulting in the formation of C_2H_6 and C_2H_5D. The rate constant for the reduction of ethylene by hydrogen on metals has been found to be twice as great as those for the reduction of ethylene by deuterium.[13-15]

The comparison of the distribution of deuterated ethanes formed in the reduction of ethylene by deuterium over a nickel catalyst at 90° obtained by Turkevich, *et al.*,[12] with the distribution calculated from formula 5 also exhibits a low kurtosis for the experimental distribution. Wilson, Otvos, Stevenson and Wagner[16] have investigated the reduction of *cis*-2-butene over a commercial nickel catalyst and have obtained a broadening of the distribution of deuterated butanes with increasing temperature. Bond and Turkevich[17] have found from the investigation of the reduction of propylene with deuterium over a platinum catalyst that the yields of propanes with more than four deuterium atoms rose with increasing temperature. These deviations from the random distribution found in heterogeneous catalysis were much less than those found with the platinum olefin complex.

An analysis of the 12–18 m/e region of the experimental spectrum was undertaken to attempt to determine whether the addition of deuterium occurred, in the main, symmetrically (one deuterium on each carbon atom) or unsymmetrically (both deuteriums on the same carbon atoms). If the additions were symmetrical, then the $C_2H_4D_2$ would be 100% CH_2D-CH_2D; the $C_2H_3D_3$, 100% CH_2D-CHD_2; and the $C_2H_2D_4$, 67% CHD_2-CHD_2 and 33% CH_2D-CD_3. If the addition were unsymmetrical, the $C_2H_4D_2$ would be 100% CH_3-CHD_2; the $C_2H_3D_3$, 75% CH_2D-CHD_2 and 25% CH_3-CD_3; and the $C_2H_2D_4$, 50% CH_2D-CD_3 and 50% CHD_2-CHD_2.

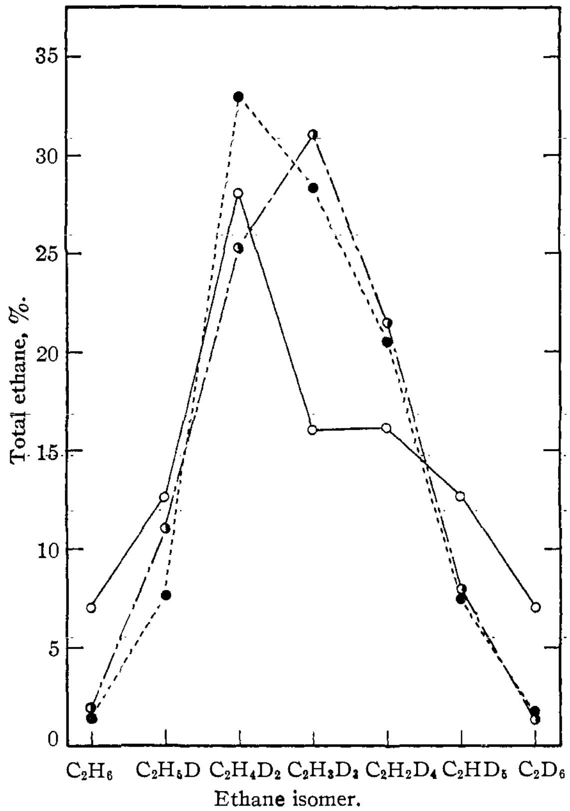

Fig. 1.—Distribution of ethane isomers from D_2 + $(PtCl_2C_2H_4)_2$ at −22°: ○—○, expt.; ◑——◑, from formula 5; ●----●, from formula 5 + 12.5% $C_2H_4D_2$.

The calculated non-integer m/e peaks were much larger than the experimental ones in all cases. This suggests that a much higher ratio of double to single ions was obtained by Turkevich, *et al.*,[11] than was obtained in this work from the National Bureau of Standards mass spectrometer. However, total deviations of the calculated integer peaks from the experimental ones are 39.6 for the symmetrical case, 59.2 for the random case and 114.5 for the unsymmetrical case, so it appears unlikely that the addition occurs unsymmetrically.

The complexity of the analysis of the mass spectrometric results demonstrates the importance of using smaller bombarding potentials than the conventional 70 volts in the analysis of deuterated hydrocarbon isomers. The production of fewer varieties of ion fragments simplifies the analysis of the spectra.

Bromination of Ethylene Platinous Chloride.—The refluxing of $(PtCl_2C_2H_4)_2$ and bromine in chloroform solution resulted in the formation of the symmetrical ethylene dibromide. At room temperature, a deep red crystalline solid, soluble in benzene and containing ethylene and 44.2% plati-

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[13] G. Joris, H. S. Taylor and J. C. Jungers, THIS JOURNAL, **60**, 1982 (1938).

[14] R. N. Pease and A. Wheeler, *ibid.*, **57**, 1144 (1935).

[15] A. Wheeler and R. N. Pease, *ibid.*, **58**, 1165 (1936).

[16] J. N. Wilson, J. W. Otvos, D. P. Stevenson and C. D. Wagner, "Symposium on Catalysis in Hydrocarbon Chemistry," No. 24, Atlantic City, 1952, p. 105.

[17] G. C. Bond and John Turkevich, *Trans. Faraday Soc.*, **49**, 281 (1953).

num, was formed. It appears to be $PtCl_2Br_2C_2H_4$ (%Pt = 43.00) formed by reaction 6

$$PtCl_2C_2H_4 + Br_2 \longrightarrow PtCl_2Br_2C_2H_4 \qquad (6)$$

Chatt[6] obtained $PtCl_4C_2H_4$ in the chlorination of $(PtCl_2C_2H_4)_2$ at room temperature and the symmetrical ethylene dichloride at higher temperatures. Kharasch and Ashford[10] brominated $[PtCl_2(Styrene)]_2$ and obtained the symmetrical dibromide and a red solid. In light of the above experiments with the ethylene complex, it appears that this red solid was probably $PtCl_2Br_2(CH_2CHC_6H_5)$.

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WASHINGTON, D. C.

[CONTRIBUTION FROM THE ISTITUTO DI CHIMICA FISICA DELL'UNIVERSITÀ DI FIRENZE]

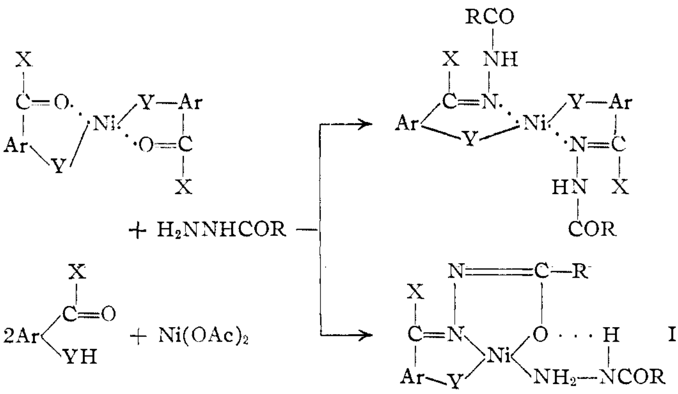
Chemical Reactions of Complexes. VII. Reaction of Hydrazides and Aromatic *o*-Oxy- and *o*-Aminoaldehydes and Ketones with Nickel Acetate

BY LUIGI SACCONI

RECEIVED JANUARY 4, 1954

The formation of complexes by competitive reactions between aromatic *o*-oxy- and *o*-aminoaldehydes and ketones, acylhydrazines and nickel acetate has been studied, and the influence of the ligand molecules has been investigated. In the case of salicylaldehyde, the tendency to yield bicyclic planar complexes parallels the aromaticity of the acyl group and hence with the presence of an extra negative charge on the enolate oxygen atom of the carbonyl group.

Our study[1] of the reaction of hydrazides with nickel disalicylaldehyde or with nickel acetate and salicylaldehyde demonstrated the occurrence of the following competitive reactions.



I

II

Ar = C_6H_4; X = H; Y = O; R = alkyl, phenyl, phenylalkyl

According to the nature of the R group, symmetrical paramagnetic ionic complexes I or diamagnetic bicyclic planar complexes II are formed.

In the present work we have studied the behavior of the same nickel salt in aqueous alcoholic solution with hydrazides and aldehydes or ketones of the above general formula and where Ar = C_6H_4, $C_{10}H_6$; X = H, CH_3; Y = O, NH; R = alkyl, phenylalkyl, phenyl, hexahydrophenyl, naphthyl, diphenyl, 2-furyl, 3-methyl-5-isoxazolyl.

(1) Complexes of type I are formed when Ar = C_6H_4; X = H; Y = O (salicylaldehyde); and R = furylhydrazide or 3-methyl-5-isoxazolylhydrazide. When R = C_6H_{11} (hexahydrobenzhydrazide), the reaction proceeds in the direction of complex I. When R = C_6H_5–C_6H_4 (*p*-phenylbenzhydrazide), complex II is first formed; if treated with salicylaldehyde, this compound gives complex I. When R = $C_{10}H_7$ (α- and β-naphthydrazide), the reaction proceeds in the direction of complex II. In the case of α-naphthydrazide treatment with salicylaldehyde yields the corresponding complex I; this treatment has no effect on the complex from β-naphthydrazide.

From our present and published results,[1] we can list the R groups in order of their increasing tendency to yield bicyclic planar complexes as follows

A. alkyl
arylalkyl
hexahydrophenyl
furyl
3-methyl-5-isoxazolyl

B. phenyl
substituted phenyl
diphenyl
α-naphthyl

C. β-naphthyl

The R groups in series A give only green paramagnetic complexes (I) with sp^3 ionic structures; those in B first yield complexes of type II which, when treated with excess salicylaldehydes, are transformed to complexes of type I; β-naphthyl yields only an orange diamagnetic complex (II) with a square-planar dsp^2 covalent structure. Roughly speaking, the tendency to form bicyclic complexes of type II increases with the aromaticity of the R group. Indeed, the increase in aromatic character of some of the R groups, from furyl to α- and β-naphthyl, parallels the resonance energy of the corresponding molecules, which increases in the following order[2]

Substance	Resonance energy, kcal./mole
Furan	23
Benzene	39
Diphenyl	47
Naphthalene	75

On the other hand the aromaticity of the R groups is paralleled with the tendency toward

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[1] L. Sacconi, THIS JOURNAL, **74**, 4503 (1952).

[2] L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933); *cf.* A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 157.