The amount of toluene introduced represents *the maximum* amount of toluene which could be produced in the reaction. This mixture was heated to 65° for one hour and thereafter analyzed. The amount of methane formed was the same as that produced under the same conditions and in the absence of toluene. Hence, the compound responsible for the formation of the additional quantity of methane cannot be toluene.

Bromination of the liquid which was obtained by decomposing the benzene solution of acetyl peroxide, furnished another piece of evidence supporting our mechanism of addition of methyl radicals to an aromatic hydrocarbon. Such a liquid has been shown to contain olefinic compounds. For example, decomposing 0.8 mmole of acetyl peroxide in 10 cc. of benzene (by heating this solution in vacuum to 65° for about 100 hours) produced a liquid which absorbed at 0° 1.5 cc. of 0.1 N solution of bromine. It was proved that neither the pure solvent, nor the unheated solution of acetyl peroxide in benzene, was absorbing bromine. Hence, an olefinic compound was produced by the decomposition of acetyl peroxide.

Investigation of the decomposition taking place in toluene solution shows again that the addition of methyl radicals to toluene occurs to some extent, although the reaction

$$C_6H_5{\cdot}CH_3 + CH_3 \longrightarrow C_6H_5{\cdot}CH_2 + CH_4 \quad (16)$$

competes efficiently with the addition process. Indeed, it will be shown in a later communication that the addition of methyl radicals to aromatic compounds is a quite general phenomenon, and the ability of an aromatic compound to add methyl radical (we propose to call this property the *methyl affinity* of an aromatic molecule) varies enormously. For example, the methyl affinity increases monotonously in a series: benzene, diphenyl, naphthalene, phenanthrene, anthracene and naphthacene, the last compound being about 8000 times as efficient as the first one.

Finally, we report briefly some experiments carried out in solutions of fluorochemicals.[11] Fluorochemicals were chosen as solvents which were expected to be inert toward radicals. The high C–F bond dissociation energy suggests that the reaction

$$C_nF_{2n+2} + R \longrightarrow C_nF_{2n+1} + RF$$

should not occur at the temperature of the experiments. Unfortunately, it appears that the fluorochemicals investigated contain a few extremely reactive C–H bonds, since a considerable amount of methane was produced in the decomposition. The presence of some C–H bonds in the fluorochemicals is evident from the fact that they are peroxidized (see Part II).

In conclusion we would like to thank the National Science Foundation for financial support of this investigation.

[11] The following fluorochemicals were investigated: perfluoromethylcyclohexane (Columbia Organic Chemicals Co.), perfluorodimethylcyclohexane (du Pont Co.), perfluorocyclic ether, probably $CF_3{\cdot}C_5F_9O$ (0-75 Minnesota Mining Co.).

SYRACUSE, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Donor–Acceptor Bonding. V. Studies of Some Molecular Addition Compounds of Stannic Chloride[1,2]

BY A. W. LAUBENGAYER AND WM. C. SMITH

RECEIVED JULY 19, 1954

The reactions of stannic chloride with a number of typical donor molecules have been studied as examples where the coördination of tin may be expected to increase to six. With $(CH_3)_3N$ and C_5H_5N white solid products having the empirical formulas $[(CH_3)_3N]_2{\cdot}SnCl_4$ and $(C_5H_5N)_2{\cdot}SnCl_4$ were obtained. BF_3 reacted with the former to give $(CH_3)_3N{\cdot}BF_3$. Ethyl alcohol and stannic chloride form a solid which upon recrystallization from ethyl alcohol or hot benzene gives well formed crystals having a composition corresponding to the empirical formula $(C_2H_5OH){\cdot}(C_2H_5O)SnCl_3$. The data for this reaction are consistent with the assumption that unstable $(C_2H_5OH)_2{\cdot}SnCl_4$ forms initially but this then loses HCl, as suggested by Rosenheim. The infrared absorption spectrum of $(C_2H_5OH){\cdot}(C_2H_5O)SnCl_3$ has been compared with those for gaseous and liquid ethyl alcohol. The formation of crystalline $[(C_2H_5)_2O]_2{\cdot}SnCl_4$ has been confirmed. This compound was purified by vacuum sublimation and studied in detail. It is reversibly dissociated in benzene. Extended vapor pressure–temperature measurements for the substance have been made and vapor density data indicate virtually complete dissociation of the complex in the vapor phase. Powder X-ray diffraction patterns have been recorded for all the complexes. The possible structures of these complexes of tin are considered.

Introduction

The conditions favoring the formation of molecular addition compounds and the important consequences of the donor–acceptor bond involved have been summarized in the first paper of this series.[3] Those complexes involving donor and acceptor molecules in a 1:1 ratio have been the subject of particularly thorough investigation. Very little is known, however, about reactions in which two donor molecules combine with a given acceptor molecule, and for this reason a study of this type of system was chosen for investigation.

Stannic chloride was selected as the acceptor molecule because of its recognized ability to attain a coördination number of six, as in the chlorostannate ion, $SnCl_6^{=}$. The structural features of such a donor–acceptor molecule offer interesting possibilities because of the opportunity for *cis*–

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[1] Paper IV of this series, A. W. Laubengayer and C. F. Condike, THIS JOURNAL, **70**, 2274 (1948).

[2] Based upon a thesis submitted by Wm. C. Smith to the Faculty of Cornell University in partial fulfillment of the requirements for the M.S. degree, 1951.

[3] A. W. Laubengayer and G. R. Finlay, THIS JOURNAL, **65**, 884 (1943).

trans isomerism to occur. Trimethylamine, pyridine, diethyl ether and ethyl alcohol were chosen as donor molecules as a consequence of their recognized ability to serve in this capacity. Although ethyl alcohol would seem to lend itself readily to hydrogen chloride elimination on reaction with stannic chloride, this system was studied because preliminary studies indicated that the reaction resulted in crystal formation. With the exception of trimethylamine, reaction of each of these molecules with stannic chloride is mentioned in the literature.[4]

Experimental

Stannic chloride and several of the compounds prepared are extremely susceptible to hydrolysis and for this reason a vacuum train and a dry-box were employed for certain phases of the work. The reactions themselves were carried out in an atmosphere of dry nitrogen and precautions were taken throughout the course of the investigation to avoid attack by atmospheric moisture.

Trimethylamine–Stannic Chloride.—Reaction between trimethylamine and stannic chloride in the gas phase at 20° resulted in a finely divided white solid. No suitable solvent could be found for the product and attempts at purification by a vacuum sublimation technique were unsuccessful. Analyses carried out on the unpurified material are in agreement with the empirical formula $[(CH_3)_3N]_2 \cdot SnCl_4$.

Anal. Calcd. for $[(CH_3)_3N]_2 \cdot SnCl_4$: Sn, 32.3; Cl, 37.5; C, 19.0; H, 4.77; N, 7.40. Found: Sn, 31.6, 32.3; Cl, 37.1, 36.9; C, 17.03, 17.09; H, 5.71, 5.68; N, 7.37, 7.33.

The reaction product seemed quite stable to atmospheric moisture but was decomposed when placed in water. It melted with partial decomposition at 171° and gave a well-defined X-ray powder diffraction pattern which is summarized in Table I.

TABLE I

POWDER X-RAY DIFFRACTION PATTERNS

(The "*d*" values given for the principal lines are followed by "S," "M," or "W" denoting strong, medium or weak intensities.)

A. $[(CH_3)_3N]_2 \cdot SnCl_4$: 7.00, S; 5.71, M; 4.89, S; 4.34, M; 2.82, W; 2.34, W; 2.16, W; 1.93, W.

B. $(C_5H_5N)_2 \cdot SnCl_4$: 6.31, S; 5.20, M; 4.15, W; 3.80, S; 3.16, S; 2.56, M; 2.32, W; 1.99, W; 1.85, W.

C. $C_2H_5OH\ (C_2H_5O)SnCl_3$: 6.61, S; 5.75, S; 3.45, S; 2.88, M; 2.21, W; 2.02, W; 1.74, W.

D. $[(C_2H_5)_2O]_2 \cdot SnCl_4$: 6.83, M; 6.15, M; 4.92, S; 4.40, W; 4.00, S; 3.45, S; 2.84, W; 1.64, W; 1.92, S.

A quantitative experiment was performed to study the possible replacement of stannic chloride by boron trifluoride, using a procedure based on that employed by Brown, Schlesinger and Cardon in their study of relative acid and base strengths.[5] Gaseous boron trifluoride and the molecular addition compound were introduced in a mole ratio of 2:1 into the evacuated apparatus. A decrease of 50% in the pressure below that observed immediately after the addition of the BF_3 to the system indicated essentially complete replacement, in agreement with the equation

$$[(CH_3)_3N]_2 \cdot SnCl_4(s) + 2BF_3(g) \longrightarrow 2(CH_3)_3N{:}BF_3(s) + SnCl_4(g)$$

This pressure drop took place in a period of 40 minutes.

Pyridine–Stannic Chloride.—The 2:1 compound, previously reported by Pfeiffer,[4] was prepared by the reaction of pyridine with stannic chloride in carbon tetrachloride.

Anal. Calcd. for $(C_5H_5N)_2 \cdot SnCl_4$: Sn, 28.4; Cl, 33.9; C, 28.7; H, 2.41; N, 6.69. Found: Sn, 28.5, 27.5. Cl, 34.1, 34.6; C, 28.4, 28.5; H, 2.45, 2.55; N, 6.63, 6.68;

The product was attacked very slowly by atmospheric moisture, was insoluble in a wide variety of solvents, and was not susceptible to purification by a vacuum sublimation technique. Although not visibly crystalline it gave a sharp X-ray powder diffraction pattern, the prominent lines of which are listed in Table I.

Ethyl Alcohol–Stannic Chloride.—The reaction at 20° of stannic chloride and absolute ethyl alcohol with petroleum ether as the solvent resulted in a white solid product that was very susceptible to hydrolysis. This material could be crystallized from ethyl alcohol or hot benzene as large monoclinic needles, but decomposed when purification by a vacuum sublimation technique was tried. After having been brought to constant weight at 20° in an Abderhalden dryer, the recrystallized material was subjected to analysis.

Anal. Calcd. for $C_2H_5OH \cdot (C_2H_5O)SnCl_3$: Sn, 37.5; Cl, 33.7; C, 15.2. Found: Sn, 38.2, 38.6; Cl, 33.96, 33.99; C, 15.1, 14.8.

On the basis of these results the simplest formula may be represented as $C_2H_5OH \cdot (C_2H_5O)SnCl_3$. This suggests the initial formation of the compound $(C_2H_5OH)_2 \cdot SnCl_4$, from which one molecule of hydrogen chloride then splits out.

$$(C_2H_5OH)_2 \cdot SnCl_4 = HCl + C_2H_5OH \cdot (C_2H_5O)SnCl_3$$

When a portion of the initially isolated material was placed in the Abderhalden dryer and the latter evacuated, it was found that some chloride ion was taken up by a tube containing solid potassium hydroxide previously placed in the evacuation line. Since there was no tin present in this tube in any form, the postulated formation of an intermediate addition compound from which hydrogen chloride splits off seems to be substantiated. A similar conclusion was reached by Rosenheim and co-workers[6] on the basis of tin and chlorine analyses only, and they reported further that rapid analysis of a solid material formed at 0° indicated the formation of $(C_2H_5OH)_2 \cdot SnCl_4$ compound at that temperature.

The recrystallized condensation product obtained at room temperature in the reaction melted at 187°, apparently with some decomposition. The principal lines for its X-ray powder diffraction pattern are given in Table I. Although the material was quite soluble in hot benzene, it was found during attempted cryoscopic studies not to be sufficiently soluble in this solvent at 25° or below to permit an accurate determination of its molecular weight. The cryoscopic studies did indicate qualitatively, however, that it is polymerized to some extent in benzene solution, perhaps to the dimer $[C_2H_5OH \cdot C_2H_5OSnCl_3]_2$.

The infrared spectrum for solid $C_2H_5OH \cdot (C_2H_5O)SnCl_3$ is given in Fig. 1.[7] A qualitative comparison of the absorption spectrum of the solid compound with those of liquid and gaseous ethyl alcohol indicates shifts in the C–O, C–C and C–H stretching frequencies that would be expected as a consequence of complex formation. Indication of hydrogen bonded OH groups in the chemical compound, as in liquid ethyl alcohol, further supports the concept that association occurs.

Diethyl Ether–Stannic Chloride.—The reaction of diethyl ether and stannic chloride in petroleum ether as solvent resulted in a white, extremely hygroscopic material that fumed on exposure to atmospheric moisture. It could be sublimed readily in the vacuum train by cooling the receiver with liquid nitrogen, and it was purified in this manner. Samples for carbon and hydrogen analyses were prepared in a dry-box, as were the samples for the capillary melting point determination and the X-ray powder diffraction

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(4) The preparation of the pyridine addition compound was studied by Pfeiffer, *et al.*, *Z. anorg. Chem.*, **17**, 82 (1898); **71**, 97 (1911). Studies of the reaction of diethyl ether with stannic chloride have been reported by Levy and Kuhlman, *Ann. chim. phys.*, **16**, 303 (1846); Pfeiffer and Halperin, *Z. anorg. Chem.*, **87**, 335 (1914); Tzionev, *J. Russ. Phys. Chem. Soc.*, **48**, 550 (1916); Sanwei Ai, *J. Soc. Chem. Ind., Japan*, **37**, supplementary binding, 107 (1934); Ulich, Hertch and Nespital, *Z. physik. Chem.*, **B17**, 21 (1932); the stannic chloride-ethyl alcohol reaction has been investigated by Davy, *Phil. Trans.*, **102**, 169 (1912); Meyer and Turnau, *Ber.*, **42**, 1163 (1909); Holmberg, *Z. anorg. Chem.*, **56**, 385 (1908); Thiessen and Koerner, *ibid.*, **195**, 88 (1931); Rosenheim and Schnabel, *Ber.*, **38**, 2778 (1905); Hieber and Reindl, *Z. Elektrochem.*, **46**, 559 (1940).

(5) H. C. Brown, H. I. Schlesinger and S. Z. Cardon, THIS JOURNAL, **64**, 325 (1942).

(6) Rosenheim and Schnabel, *Ber.*, **38**, 2778 (1905).

(7) The authors are greatly indebted to Prof. S. H. Bauer of this Department for his help in connection with this phase of the work.

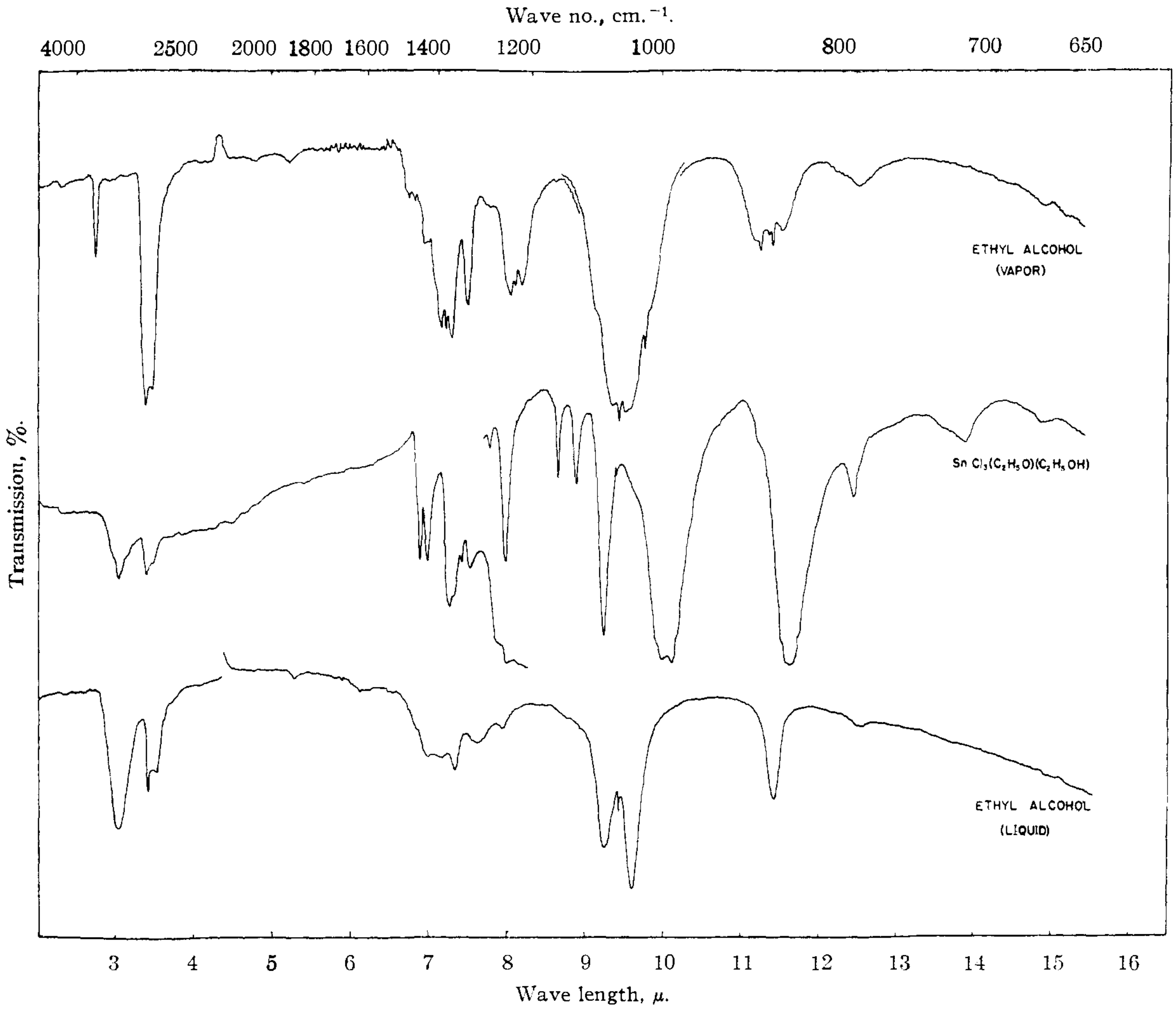

Fig. 1.—Infrared spectra of C_2H_5OH vapor, C_2H_5OH liquid and $C_2H_5OH.(C_2H_5O)SnCl_3$.

pattern. Samples for tin and chlorine analyses were sublimed on the vacuum train into weighed ampoules.

Anal. Calcd. for $[(C_2H_5)_2O]_2{\cdot}SnCl_4$: Sn, 29.04; Cl, 34.70; C, 23.49; H, 4.93. Found: Sn, 27.9, 28.1; Cl, 34.36, 34.39; C, 23.67, 23.57; H, 4.75, 4.81.

The analyses are in good agreement with the empirical formula $[(C_2H_5)_2O]_2{\cdot}SnCl_4$. A sealed capillary melting point value of 80.6° was obtained. In addition to being soluble in ethyl alcohol, water and acetone, in each of which cases reaction with the solvent appeared to occur, it was found to be soluble in benzene. Cryoscopic studies in this latter solvent, using a cell adapted for use on the vacuum train,[8] indicated that the compound is partly dissociated into the reactant molecules. Extrapolation of the apparent molecular weight values as given in Table II indicates essentially complete dissociation at infinite dilution. The principal lines for the X-ray powder diffraction pattern of the molecular addition compound are given in Table I.

TABLE II

CRYOSCOPIC MEASUREMENTS OF $[(C_2H_5)_2O]_2{\cdot}SnCl_4$ IN BENZENE

Concn. (g. solute/1000 g. solvent)	Apparent mol. wt.	Theor. mol. wt. for complex
62.2	268	408
30.2	208	
21.6	190	
17.9	183	

An all-glass "sickle" cell[9] was used in the measurement of vapor pressure and vapor density values for $[(C_2H_5)_2O]_2{\cdot}SnCl_4$. The vapor pressure–temperature curves obtained in three different runs are given in Fig. 2 and the data for the dissociation of the completely vaporized samples are summarized in Table III. The results of this study are as follows.

(1) In run 1, where complete vaporization did not occur, the melting point *D* was shown to be 80.3°, and an extrapolated "boiling point" of 83.7° at 760 mm. was obtained.

(2) In runs 2 and 3, where complete vaporization took place along C_2 and C_1, nearly complete reversible dissociation occurred.

(3) Darkening of the material in run 1, where liquid–vapor saturation vapor pressures were measured, indicated that some thermal decomposition had taken place on melting. This vapor pressure run was not completely reversible, in agreement with this conclusion.

(4) The pressure–temperature relation in the region of solid-vapor equilibrium (region A) may be expressed by the equation

$$\log_{10} P_{\text{mm}} = (-3766/T) + 13.44$$

in the temperature range 28 to 78°. The equation

$$\log_{10} P_{\text{mm}} = (-1706/T) + 7.613$$

for the temperature interval 81–86° represents the region (B) of liquid–vapor equilibrium.

(5) Using the integrated form of the Clausius–Clapeyron

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[8] Billings, Ph.D. Thesis, Cornell University, 1942.

[9] A. W. Laubengayer and F. B. Schirmer, THIS JOURNAL, **62**, 1578 (1940).

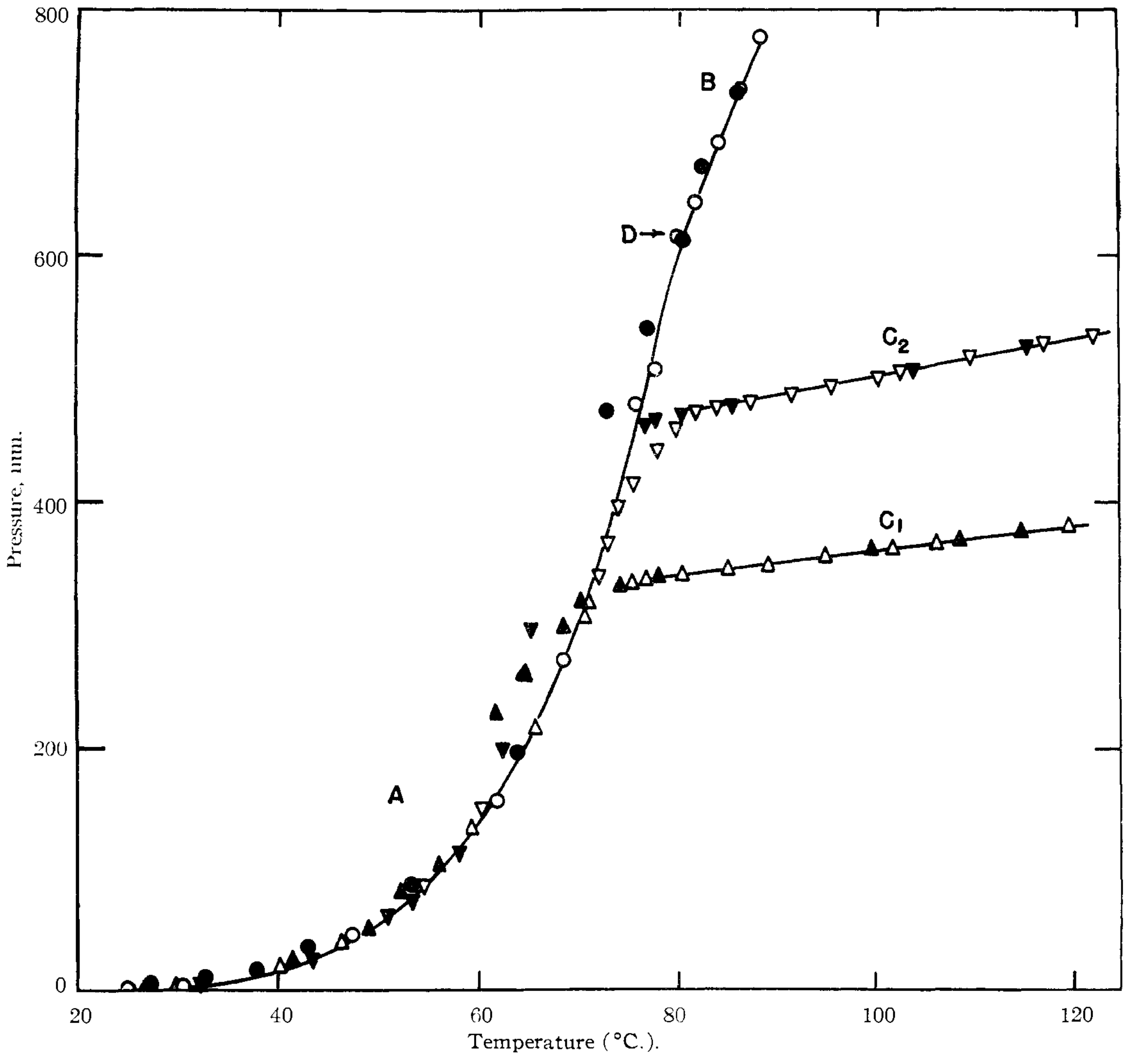

Fig. 2.—Plot of vapor pressure data $[(C_2H_5)_2O]_2 \cdot SnCl_4$; ○, run 1 (heating); ●, run 1 (cooling); ▽, run 2 (heating); ▼, run 2 (cooling); △, run 3 (heating); ▲, run 3 (cooling).

Table III

Dissociation Data for $[(C_2H_5)_2O]_2 \cdot SnCl_4$, Vapor Phase

Run	Cell vol., cc.	Sample, g.	Temp., °C. (±0.1)	Pressure, mm. (±0.1)	Degree of dissocn. (±0.002)
2	669.0	1.4570	80.6	342.4	0.957
			85.1	347.4	.958
			88.9	351.4	.959
			101.5	365.0	.965
			119.3	383.2	.970
			114.2	378.0	.971
			108.0	371.8	.970
			99.6	363.4	.968
			89.8	353.0	.965
			74.2	334.2	.948
3	689.5	2.0899	84.3	477.8	0.964
			87.2	482.2	.966
			95.6	495.2	.970
			116.6	525.6	.977
			121.7	533.4	.979
			115.0	523.6	.977
			103.5	507.6	.976
			85.4	481.0	.969
			77.4	467.0	.958

equation, the apparent heat of sublimation was calculated to be 19.1 kcal. per mole, and the apparent heat of vaporization was calculated as 7.1 kcal. per mole. This latter value corresponds closely to that of 6.7 kcal. per mole found by Hieber and Reindl[10] using a different technique.

(6) The apparent heat of fusion, obtained by difference, was 12.0 kcal. per mole.

Discussion

The properties of the adducts having the empirical formulas $[(CH_3)_3N]_2 \cdot SnCl_4$, $(C_5H_5N)_2 \cdot SnCl_4$ and $(C_2H_5)_2O \cdot SnCl_4$ are consistent with the assumption that these formulas also represent the molecular species formed, although this has not been definitely established. In such 2:1 molecules the tin atoms presumably will have achieved octahedral coördination to the two donor atoms and four chlorine atoms. The interesting possibility of *cis*- and *trans*-isomers arises. Arguments comparing the relative probability of the formation and stability of these alternate forms are highly speculative. Structural analysis of such 2:1 molecular addition compounds is needed and is being undertaken in this Laboratory.

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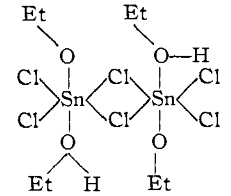
(10) Hieber and Reindl, *Z. Elektrochem.*, **46**, 559 (1940).

The structure of the compound $(C_2H_5OH)\cdot C_2H_5O$-$SnCl_3$ is even more puzzling. If this formula represents the molecular species present, then presumably the tin atom will have a coördination number of five, a condition that has been found for only very few molecular species. However the cryoscopic data for benzene solutions of this substance indicate some association, perhaps to give the dimer $[(C_2H_5OH)\cdot EtOSnCl_3]_2$. Such a dimer could result from the setting up of two chlorine bridges between the two tin atoms, and in the process both of these tin atoms would achieve the stable coördination number of six.



Such dimers could also have *cis*- and *trans*-isomers. Association due to hydrogen bonding is also a strong possibility. Structural analysis is needed to establish the actual situation.

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Catalytic Activity of Metals Produced by the Reduction of Salts in Liquid Ammonia. III. Ruthenium, Rhodium and Palladium[1]

BY GEORGE W. WATT, ARCHIE BROODO, W. A. JENKINS AND S. G. PARKER

RECEIVED JULY 30, 1954

Ruthenium, rhodium and palladium prepared by the reduction of their halides with potassium in liquid ammonia at −33.5° are shown to be exceptionally active catalysts for the hydrogenation of olefins and aromatic nitro compounds at 30° and a hydrogen pressure of 2 atm. These catalysts are compared with the corresponding metals prepared by the reduction of oxides or halides with hydrogen, on the basis of rate of hydrogenation per unit surface area. Ruthenium shows the highest intrinsic catalytic activity; rhodium and palladium substantially the same activity. The interaction of dibromodiammine-palladium(II) and potassium amide in liquid ammonia at −33.5° yields palladium(II) amide. The corresponding reaction with bromopentamminerhodium(III) bromide yields an apparently unstable rhodium(III) amide.

Information relative to the activity of iron,[2] cobalt,[3] nickel,[4] iridium[5] and platinum[6] (prepared by the reduction of suitable salts with solutions of potassium in liquid ammonia at its boiling point) as catalysts for the hydrogenation of simple olefins has been included in earlier publications from this Laboratory. The present paper is concerned with similar data on ruthenium, rhodium and palladium. For the latter two cases there are included also the results of studies on reactions that are potential sources of competition with the reactions employed for catalyst preparation, *i.e.*, the interaction of the rhodium and palladium salts with potassium amide in liquid ammonia.

Experimental

Materials.—With the exceptions recorded below, all chemicals employed in this work were the same as those described earlier.[4]

Ruthenium(III) iodide (calcd.: Ru, 21.1) obtained from the A. D. Mackay Co., New York, was found[7] to contain 19.9% Ru. Lots obtained from the City Chemical Co., New York, had the following ruthenium content at the indicated time intervals: as received, 21.6; after 4 wk., 24.7; after 7 wk., 25.1. The decomposition of this substance was found to be accelerated by both increase in temperature and exposure to light. Most of the ruthenium(III) iodide used in this work was prepared by the method of Gutbier and Trenckner[8]; the product contained 21.3% Ru.

Elemental ruthenium was prepared by converting the commercial reagent grade chloride to a mixture of the oxides of ruthenium(III) and (IV) by the method of Gilchrist.[9] The oxides were reduced with hydrogen at either 170–190 or 300°, cooled to room temperature in an atmosphere of hydrogen and thereafter stored and/or transferred in an atmosphere of oxygen-free nitrogen in a dry box. *Anal.* Found: Ru, 99.0.

Bromopentamminerhodium(III) bromide was prepared by the method of Jorgensen.[10] *Anal.* Calcd. for $[Rh(NH_3)_5Br]Br_2$: Rh, 24.0. Found: Rh,[11] 24.1. Rhodium was prepared from rhodium(III) oxide 5-hydrate as described by Claus.[12] *Anal.* Found: Rh, 99.5.

trans-Dichlorodiamminepalladium(II) was prepared by the method of Gutbier and co-workers.[13] *Anal.* Calcd. for $Pd(NH_3)_2Cl_2$: Pd, 50.5. Found: Pd,[14] 50.3.

trans-Dibromodiamminepalladium(II) was prepared as described by Muller.[15] *Anal.* Calcd. for $Pd(NH_3)_2Br_2$: Pd, 35.5; NH_3, 11.3. Found: Pd, 35.6; NH_3, 11.4. X-Ray diffraction data for this product and for the corresponding chloride are given in Table I. Palladium was prepared by the method of Wichers and co-workers.[16] *Anal.* Found: Pd, 99.8.

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[1] This work was supported in part by the Office of Naval Research, Contract N6onr-26610.

[2] G. W. Watt and W. A. Jenkins, Jr., THIS JOURNAL, **73**, 3275 (1951).

[3] G. W. Watt and C. W. Keenan, *ibid.*, **74**, 2048 (1952).

[4] G. W. Watt, W. F. Roper and S. G. Parker, *ibid.*, **73**, 5791 (1951).

[5] G. W. Watt and P. I. Mayfield, *ibid.*, **75**, 6178 (1953).

[6] G. W. Watt, M. T. Walling, Jr., and P. I. Mayfield, *ibid.*, **75**, 6175 (1953).

[7] (a) Ruthenium was determined either as the metal or by precipitation with thioglycolic-β-aminonaphthalide using procedures described elsewhere[7b]; (b) W. J. Rogers, F. E. Beamish and D. S. Russell, *Ind. Eng. Chem.. Anal. Ed.*, **12**, 561 (1940).

[8] A. Gutbier and C. Trenckner, *Z. anorg. Chem.*, **45**, 166 (1905).

[9] R. Gilchrist, *U. S. Bureau of Standards J. Research*, **12**, 283 (1934).

[10] S. M. Jorgensen, *J. prakt. Chem.*, **27**, 462 (1883).

[11] Rhodium was determined by a modification of the electrodeposition method of Langness [J. Langness, THIS JOURNAL, **29**, 459 (1907)]. In order to achieve satisfactory rates of deposition it was found necessary to increase the voltage to 10–11.5 v. and the current density to 0.17 amp./cm.^{2}.

[12] C. Claus, *J. prakt. Chem.*, [1] **80**, 282 (1860).

[13] A. Gutbier, A. Krell and R. L. Janssen, *Z. anorg. Chem.*, **47**, 23 (1905).

[14] Palladium was determined as described by Langness. See footnote 11.

[15] H. Muller, *Z. anorg. Chem.*, **59**, 29 (1853).

[16] E. Wichers, R. Gilchrist and W. H. Swanger, *Trans. Am. Inst. Min. Eng.*, **76**, 605 (1928).