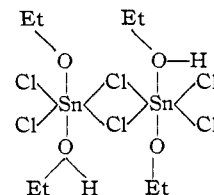


The structure of the compound $(C_2H_5OH) \cdot C_2H_5O-SnCl_3$ is even more puzzling. If this formula represents the molecular species present, then presumably the tin atom will have a coordination number of five, a condition that has been found for only very few molecular species. However the cryoscopic 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 coordination 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 Palladium¹

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 iridium⁵ and platinum⁶ (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 found⁷ 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 Trenckner⁸; 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, 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, 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.

(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).

(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^{6b}; (b) W. J. Rogers, F. E. Beamish and D. S. Russell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 561 (1940).

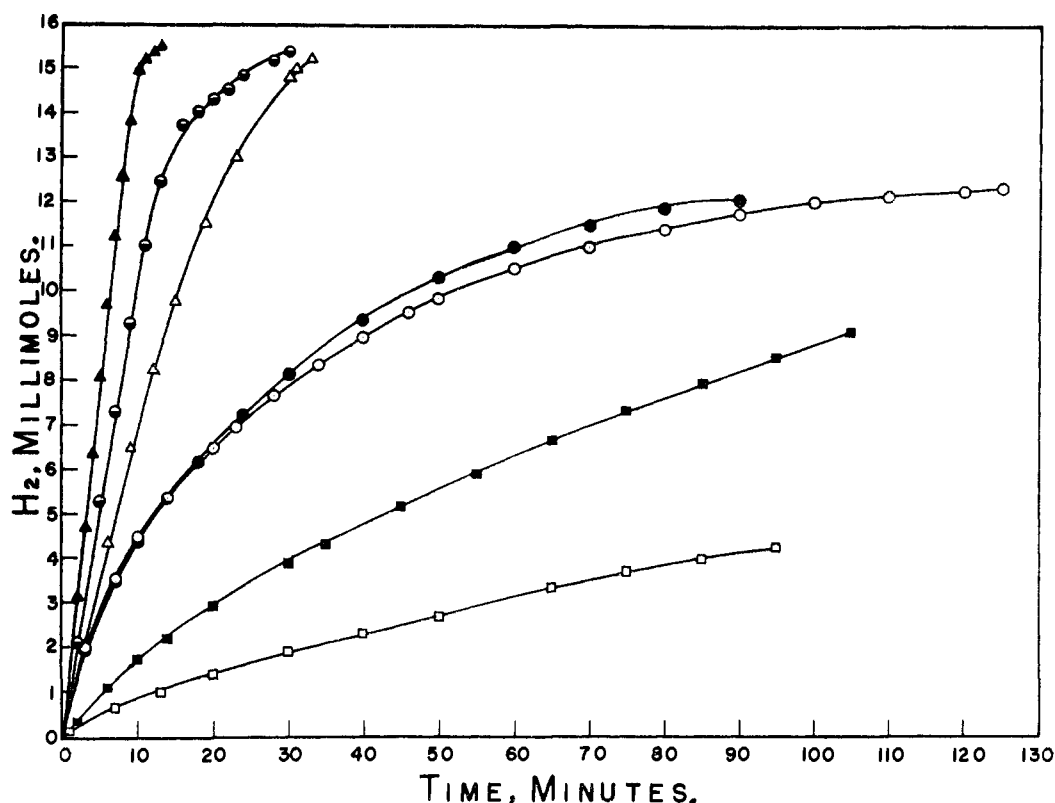


Fig. 1.—Hydrogenation of olefins over ruthenium catalysts: \square , allyl alcohol over 128 mg. Ru from oxides + H_2 at 300° ; \blacksquare , allyl alcohol over 115 mg. Ru from oxides + H_2 at 190° ; \triangle , hexene-1 over 123 mg. Ru from oxides + H_2 at 300° ; \blacktriangle , hexene-1 over 119 mg. Ru from oxides + H_2 at 190° ; \circ , allyl alcohol over 133 mg. Ru from RuI_3 + K in NH_3 ; \bullet , allyl alcohol over 128 mg. ethanol-washed Ru from RuI_3 + K in NH_3 ; \ominus , hexene-1 over 132 mg. ethanol-washed Ru from RuI_3 + K in NH_3 .

Methods.—Reduction reactions in liquid ammonia, hydrogenation rate measurements and surface area determinations were carried out using methods described previously.⁴ Reactions employing ammonia solutions of potassium amide were carried out as described by Watt and Keenan.¹⁷

TABLE I
X-RAY DIFFRACTION DATA FOR *trans*-DIBROMO- AND *trans*-DICHLORODIAMMINEPALLADIUM(II)^a

$Pd(NH_3)_2Br_2$		$Pd(NH_3)_2Cl_2$	
$d, \text{\AA.}$	I/I_1	$d, \text{\AA.}$	I/I_1
4.73	1.00	1.46	0.10
4.00	1.00	1.42	.10
3.39	0.10	1.37	.10
2.97	.70	1.25	.10
2.53	.20	1.23	.10
2.48	.50	1.18	.10
2.43	1.00	1.15	.10
2.10	0.30	1.13	.10
2.01	.20	1.02	.10
1.92	.10	1.01	.10
1.86	.10	1.00	.10
1.67	.10	0.99	.10
1.62	.10	.95	.10
1.58	0.10	.94	.10
1.56	.10	.91	.50

^a Samples were mounted in cellulose acetate capillary tubes; the exposure time was 2.5–3.0 hr., using $Cu K\alpha$ radiation, NiO filter, 30 kv. tube voltage, and 15 ma. filament current.

(17) G. W. Watt and C. W. Keenan, *THIS JOURNAL*, **71**, 3833 (1949).

Reduction Reactions.—In a typical experiment, 1.53 g of ruthenium(III) iodide in 25 ml. of anhydrous liquid ammonia was reduced with 0.416 g. of potassium (added as the solid). The supernatant solution was removed from the resulting black precipitate, and the latter was washed eight times with 25-ml. portions of ammonia. Analysis of the solid residue remaining after evaporation of the solvent from the combined supernatant solution and washings showed the absence of ruthenium and accounted for 99.4% of the iodine used as ruthenium(III) iodide. The volume of hydrogen evolved during the course of the reduction reaction amounted to <10 cc. The ammonia-insoluble product was found to contain 62% Ru; it failed to give a satisfactory X-ray diffraction pattern. However, some 12 such products were formed either in an effort exactly to duplicate all conditions or to study the effect of varying the K/ RuI_3 ratio from 3 to 7, and the ruthenium content of the insoluble products was found to range from 57–80%. The nitrogen content of these products varied in a similarly irregular manner.

In preliminary experiments involving the reduction of chloropentamminerhodium(III) chloride with potassium in liquid ammonia, complete removal of halogen and reduction to elemental rhodium were demonstrated. Owing to the limited solubility of potassium chloride in liquid ammonia at -33.5° , however, purification of the rhodium by washing with liquid ammonia was unsatisfactory. Consequently, the corresponding bromide was used in all subsequent runs. In a typical case, 2.95 g. of the bromide in 25 ml. of ammonia was reduced with 0.839 g. of potassium. During the ensuing rapid reaction, ca. 15 cc. of hydrogen was evolved, and the suspended white bromide was replaced by a dark brown solid, which was washed eight times with 40-ml. portions of ammonia. Upon complete removal of ammonia *in vacuo*, the solid turned black; it was found to contain 80.7% rhodium, qualitative tests for bromide ion were negative. This pyrophoric solid was washed with ethanol, whereupon it lost its pyrophoric character and analysis of the black ethanol-washed product showed it to

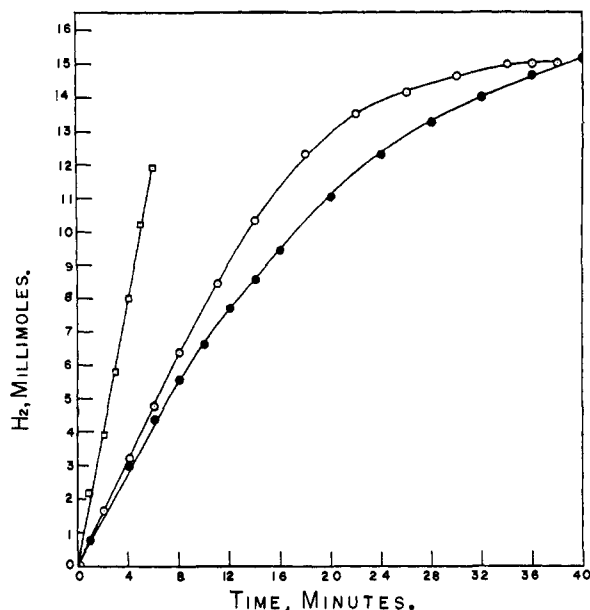


Fig. 2.—Hydrogenation of olefins over rhodium catalysts: O, allyl alcohol over 183 mg. Rh from bromide + K in NH_3 ; ●, allyl alcohol over 102 mg. Rh from oxide + H_2 ; □, hexene-1 over 164 mg. Rh from bromide + K in NH_3 .

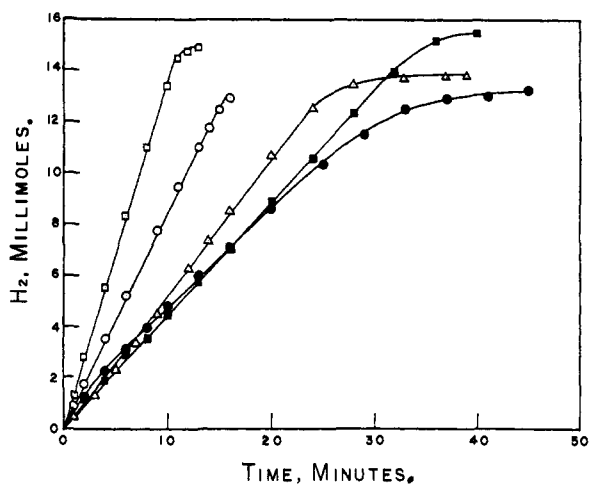


Fig. 3.—Hydrogenation of nitro compounds over rhodium catalysts: O, *o*-nitrotoluene over 145 mg. Rh from bromide + K in NH_3 ; ●, *o*-nitrotoluene over 105 mg. Rh from oxide + H_2 ; □, nitrobenzene over 129 mg. Rh from bromide + K in NH_3 ; ■, nitrobenzene over 104 mg. Rh from oxide + H_2 ; Δ, 1-nitronaphthalene over 145 mg. Rh from bromide + K in NH_3 .

consist of substantially 100% Rh. Subsequent washing with water and exposure to air did not produce any analytically detectable change in composition or alteration in catalytic activity.

Reduction of 2.02 g. of $\text{Pd}(\text{NH}_3)_2\text{Br}_2$ with 0.520 g. of potassium, carried out as described above, yielded a black precipitate and <20 cc. of hydrogen from a strongly exothermal reaction. The mildly pyrophoric black solid after washing with ammonia contained 96.8% Pd and 1.8% NH_3 ; bromide ion was not detected. Following washing with ethanol followed by water and exposure to air, this product was 100% Pd, was non-pyrophoric, and its catalytic activity was essentially the same as that of the initial ammonia-washed product. An X-ray diffraction pattern for this product gave results substantially identical with the values listed for elemental palladium in the A.S.T.M. Index of

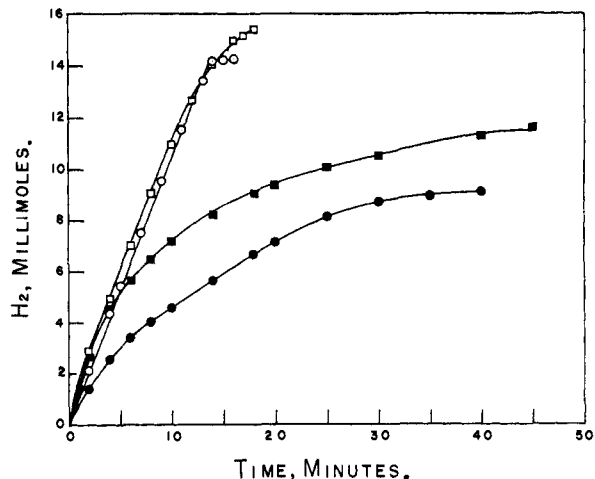


Fig. 4.—Hydrogenation of olefins over palladium catalysts: O, allyl alcohol over 169 mg. Pd from bromide + K in NH_3 ; ●, allyl alcohol over 140 mg. Pd from chloride + H_2 ; □, hexene-1 over 132 mg. Pd from bromide + K in NH_3 ; ■, hexene-1 over 146 mg. Pd from chloride + H_2 .

X-ray Diffraction Patterns; no extraneous diffraction maxima were observed.

Surface Area Measurements.—Surface area data for catalysts prepared in liquid ammonia and by other methods are included in Table II.

Hydrogenation Rate Measurements.—Representative data selected from a very large number of rate measurements that were in good agreement are given in Figs. 1–5.

Reactions with Potassium Amide.—Treatment of a solution and suspension of 2.35 g. of pale yellow $[\text{Rh}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ in 25 ml. of ammonia with the potassium amide equivalent to 0.645 g. of potassium resulted in a rapid reaction in which the suspended bromide was replaced by a somewhat more intensely colored yellow solid. This was washed eight times with 30-ml. portions of ammonia, residual solvent was evaporated, and the sample tube was evacuated at -15° . Analyses of independently prepared samples of this product by complete thermal decomposition showed that bromide ion was absent, but the quantitative data for Rh, NH_3 and N_2 content were not strictly reproducible. The following case is typical. Calcd. for $\text{Rh}(\text{NH}_3)_5$: Rh, 67.8; NH_3 , 22.4; N_2 , 9.8. Found: Rh, 70.0; NH_3 , 22.6; N, 6.7.

In a similar manner, a solution and suspension of 1.97 g. of white $\text{Pd}(\text{NH}_3)_2\text{Br}_2$ in 30 ml. of ammonia was treated with the potassium amide formed from 0.529 g. of potassium. The resulting yellow solid was treated essentially as described above. *Anal.* Calcd. for $\text{Pd}(\text{NH}_3)_2$: Pd, 76.9; NH_3 , 16.4; N_2 , 6.7. Found: Pd, 77.2; NH_3 , 16.0; N_2 , 6.0. Results obtained in independent runs were in good agreement.

Discussion

The reaction between dibromodiamminopalladium(II) and potassium amide in liquid ammonia at -33.5° has been shown to yield palladium(II) amide, a compound that has not been reported previously. For the analogous reaction involving bromopentamminerhodium(III) bromide, earlier work¹⁸ had shown that a reproducible change in potential corresponding to the formation of rhodium(III) amide is observed when the reaction of the bromide with potassium amide is followed potentiometrically. The lack of strict reproducibility of composition of the solid phase isolated in the present studies suggests that rhodium(III) amide is formed initially but, as the temperature is raised from -33.5 to 30° , partial deammonation

(18) G. W. Watt, G. R. Choppin and J. L. Hall, *J. Electrochem. Soc.*, **101**, 235 (1954).

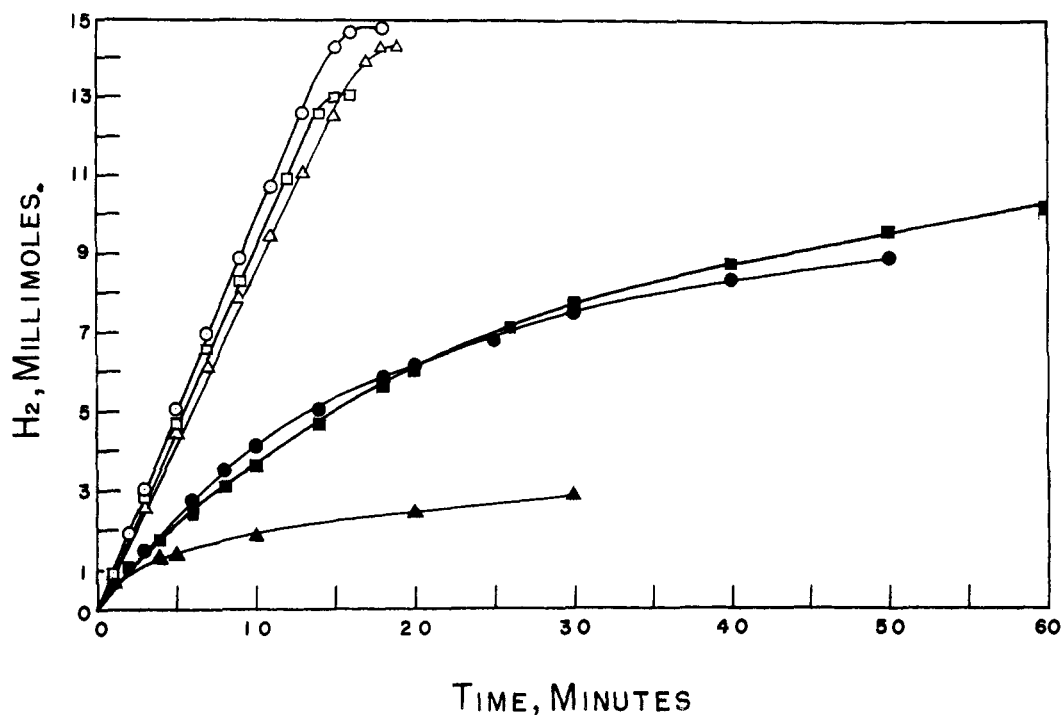


Fig. 5.—Hydrogenation of nitro compounds over palladium catalysts: O, nitrobenzene over 131 mg. Pd from bromide + K in NH_3 ; ●, nitrobenzene over 144 mg. Pd from chloride + H_2 ; □, *o*-nitrotoluene over 132 mg. Pd from bromide + K in NH_3 ; ■, *o*-nitrotoluene over 144 mg. Pd from chloride + H_2 ; Δ, 1-nitronaphthalene over 132 mg. Pd from bromide + K in NH_3 ; ▲, 1-nitronaphthalene over 143 mg. Pd from chloride + H_2 .

occurs. Although the analytical data indicate that the solid product is predominantly rhodium (III) amide, it probably contains variable quantities of deamination products such as imides and/or nitrides. In the cases of both rhodium and palladium, products of side reactions with potassium amide may account for failure to produce the pure metals when the bromides in question are reduced with potassium in ammonia.

In all three cases, reduction of the halide with potassium resulted in complete removal of halogen and precipitation of the impure transitional metals. Except in the case of ruthenium, washing with ethanol and water produced substantially pure metals. In all three cases, however, the activity of the primary ammonia-insoluble reduction products as catalysts for the hydrogenation of olefins was remarkably constant despite considerable variation in composition; this was particularly notable in the case of ruthenium. With but one exception, the catalysts prepared in ammonia were much more effective than the corresponding metals prepared by the reduction of oxides or halides with hydrogen at elevated temperatures. This is shown in Table II, in which rates of hydrogenation of two typical hydrogen acceptors are listed in the column headed *R* which is the rate of utilization of hydrogen (in millimoles/min./unit surface area). Similar data for the other acceptors included in Figs. 1-5 show the same over-all pattern, except that rhodium prepared in ammonia is distinctly superior to that from the reduction of the oxide with hydrogen.

With reference to the catalytic activity per unit surface of ruthenium, rhodium and palladium prepared by the reduction of their halides in liquid

TABLE II
COMPARISON OF ACTIVITY OF RUTHENIUM, RHODIUM AND PALLADIUM CATALYSTS

Catalyst and source	Surface area, $\text{m}^2/\text{g}.$	<i>R</i> (mmoles H_2 used/min./ m^2) Allyl alcohol	Nitrobenzene
Ru from $\text{RuI}_3 + \text{K}$	2	1.18	..
Ru from $(\text{Ru}_2\text{O}_3 + \text{RuO}_2) + \text{H}_2$ (300°)	4	0.11	..
Ru from $(\text{Ru}_2\text{O}_3 + \text{RuO}_2) + \text{H}_2$ (170-190°)	32	.03	..
Rh from $[\text{Rh}(\text{NH}_3)_5\text{Br}]\text{Br}_2 + \text{K}$	16	.26	0.65
Rh from $\text{Rh}_2\text{O}_3 + \text{H}_2$	32	.32	.13
Pd from $\text{Pd}(\text{NH}_3)_2\text{Br}_2 + \text{K}$	21	.25	.31
Pd from $\text{Pd}(\text{NH}_3)_2\text{Cl}_2 + \text{H}_2$	17	.16	.15

ammonia, the decreasing order of activity toward olefinic acceptors is as follows: $\text{Ru} \gg \text{Rh}, \text{Pd}$. For the hydrogenation of three aromatic nitro compounds (Figs. 3 and 5), rhodium was superior to palladium with nitrobenzene and *o*-nitrotoluene but about the same as palladium with 1-nitronaphthalene. With all three of these acceptors, reduction of the nitro compound to the corresponding amine proceeded at extremely high rates; thereafter, ring hydrogenation proceeded extremely slowly if it all.

Attempts to correlate the results obtained in the hydrogenation of olefins with the per cent. *d*-band character of the three transitional metals have been only partially successful. In terms of the views of Pauling,¹⁹ Beeck,²⁰ and Boudart,²¹ it is to be expected that rhodium should have a higher intrinsic

(19) L. Pauling, *Proc. Roy. Soc. (London)*, **A196**, 343 (1949).

(20) O. Beeck, *Record Chem. Progress*, **8**, 109 (1947).

(21) M. Boudart, *THIS JOURNAL*, **72**, 1040 (1952).

catalytic activity than palladium, but this criterion provides no basis for explanation of the consistently higher activity of ruthenium. It is possible, of course, that the relatively impure ruthenium may have contained catalytically active impurities or impurities having promoter properties.

In the course of this work, studies on rates of hydrogenation as a function of ratios of catalyst to acceptor were made. The results of these studies are considered elsewhere.²²

(22) G. W. Watt and M. T. Walling, Jr., *J. Phys. Chem.*, in press. AUSTIN 12, TEXAS

[CONTRIBUTION FROM THE NICHOLS CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

Use of Radioactive Iodine to Determine Equilibrium Constants in Ethylene-Iodine-1,2-Diiodoethane Systems

BY ALBERT ABRAMS AND THOMAS W. DAVIS

RECEIVED JUNE 17, 1954

Radioactive iodine has been used to trace the gas phase equilibrium between ethylene, iodine and 1,2-diiodoethane. The results are consistent with those of Cuthbertson and Kistiakowsky and with the lower temperature results of Mooney and Ludlam. The equilibrium data lead to the following molal values for the dissociation of 1,2-diiodoethane at 25°: $\Delta H^\circ = 11.5$ kcal., $\Delta F^\circ = 2.1$ kcal. and $\Delta S^\circ = 31.2$ cal./deg. The entropy of 1,2-diiodoethane at 25°, therefore, must be near 83.2 cal./deg./mole.

Mooney and Ludlam¹ and Cuthbertson and Kistiakowsky² have studied the gas phase equilibrium between 1,2-diiodoethane and its dissociation products, namely, ethylene and iodine.³ The quantitative results of the two teams of investigators agree rather well at low temperatures but disagree at higher temperatures.

Mooney and Ludlam, whose measurements were all made in systems saturated with respect to both iodine and organic iodo compound, found the heat of formation (ΔH°) of 1,2-diiodoethane to be 13.4 kcal./mole at temperatures below 40–45° and 22.3 kcal./mole at temperatures greater than 40–45°. These ΔH° values were derived from the slopes of logarithmic plots of equilibrium constants against reciprocals of absolute temperatures. The authors considered the figure of 13.4 kcal./mole to be too low because of solid solution formation or because of adsorption of one of the compounds on the surface of the iodine. Cuthbertson and Kistiakowsky studied, at temperatures above 45°, systems in which formation of both solid iodine and solid diiodoethane was avoided. They calculated a heat of formation of diiodo compound of 13.4 kcal./mole and they suggested that Mooney and Ludlam's higher figure of 22.4 kcal./mole was probably in error as a result of some distortion introduced perhaps by solid-solution formation. In an effort to discover which set of equilibrium values and which ΔH° is correct, we have measured equilibrium constants in 1,2-diiodoethane systems using radioactive iodine to indicate the equilibrium concentrations of both iodine and organic iodo compound.

Experimental

Method.—Radioactive iodine placed in tubes made of 5-mm. glass tubing was cooled and sealed in vacuum. The weight of iodine was determined to the nearest 0.2 mg. The selected procedure does not demand an exact knowledge of this weight. An ampoule containing the active iodine was

nicked with a file and was placed in a reaction vessel of capacity in the range 30 to 600 ml. The reaction vessel was evacuated and ethylene was introduced to a pressure judged sufficient to transform half the iodine at equilibrium to diiodoethane. The ethylene was condensed by liquid air and the reaction vessel sealed by means of a flame. Estimates of the change in volume resulting from the presence of the ampoule and from the sealing were applied later as corrections. After allowing the vessel to warm up, the ampoule was broken by shaking the vessel. The amount of iodine was selected so as to avoid saturation with respect to both iodine and iodo compound. Despite these precautions, solids appeared on the vessel surfaces in two experiments. The measurements from these saturated systems were discarded.

After the iodine was released within a reaction vessel, the vessel was thermostated for a period of 12 hours or more, a period of time considerably in excess of what both Cuthbertson and Kistiakowsky and we found necessary to achieve equilibrium. Temperatures were kept within 0.05° of the recorded values in all but a few of the earlier runs in which the range was 0.2°. The preparations thermostated at 9 and 25° were allowed to stand for several days.

Following the thermostating, the reaction vessels were plunged into a large container of liquid air in order to freeze the system at the composition attained at equilibrium. Active bubbling around the vessels stopped in 10 to 30 seconds depending on the surface to volume ratio. Experiments in which the reaction materials reached equilibrium at the same temperature but in vessels of different sizes and shapes gave results that agreed with each other as well as did duplicate results from experiments in which the vessels were identical. It was concluded that the equilibria were effectively frozen by the treatment described.

The reaction vessels were opened at liquid nitrogen temperatures and 20 ml. of carbon tetrachloride added. Thereafter the temperature was allowed to rise to 0° and the solution of iodine and diiodoethane was acidified with acetic acid and titrated with 0.005 *N* thiosulfate until the free iodine color was completely discharged. The two layers were separated. To improve the efficiency of the separation, the carbon tetrachloride was washed with two further portions of water and the water layer with two portions of carbon tetrachloride. The water layer containing radioactive iodide ions, together with the washings, was brought to 100 ml. in a volumetric flask. In the same way the carbon tetrachloride layer containing radioactive diiodoethane, together with the appropriate washings, was diluted to 100 ml. The liquids were counted separately.

Counting Procedure.—A special Geiger-Müller counter was prepared with walls about 0.1 to 0.15 mm. thick. The counter fitted into a double-walled jacket designed to contain the radioactive solution (34 ml.) to be counted. The inner wall of the jacket was of the same thickness as the walls of the counter. The jacket carried two arms, one at

(1) R. B. Mooney and E. B. Ludlam, *Proc. Roy. Soc. Edinburgh*, **49**, 160 (1929).

(2) G. R. Cuthbertson and G. B. Kistiakowsky, *J. Chem. Phys.*, **3**, 631 (1935).

(3) A. Sator, *J. Chem. Soc.*, **85**, 1697 (1904).