assumption inasmuch as the small corrections obtained with the use of activity coefficients would not affect our discussion on the probable structures of the chelates.

Preliminary experiments have been done on copper(II)–oxidized glutathione complex. The indication is that again only one complex of the MA type is formed and that the copper chelate is much more stable than the corresponding zinc chelate. These are as expected. More work on the copper(II) chelate is being continued at this Laboratory.

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PITTSBURGH, PA.

[CONTRIBUTION NO. 123 FROM THE UNIVERSITY OF TENNESSEE, DEPARTMENT OF CHEMISTRY]

Platinum Oxide Catalysts

BY C. W. KEENAN, BETTY W. GIESEMANN AND HILTON A. SMITH

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The sodium present in Adams platinum catalyst fusion product has been shown to be associated with a strong proton acceptor. The sodium can be largely removed by washing with acid, even quite dilute acid. The sodium found in the fusion mass is probably a reaction product whose precursor is sodium oxide formed by the thermal decomposition of the sodium nitrate melt. This study indicates that in the case of the hydrogenation of benzene, in the presence of Adams catalyst the need for additives or solvents is due to the effect such substances have in reacting with or removing the sodium component from the catalyst. A platinum oxide catalyst free of sodium has been prepared. It will catalyze the hydrogenation of benzene in the absence of additives or solvents.

Introduction

Experimental studies of the hydrogenation of benzene at room temperature and hydrogen pressures up to three or four atmospheres have indicated that this compound is not hydrogenated in the presence of Adams platinum catalyst alone. The use of methanol as a solvent is ineffective; however, when acids such as acetic acid are employed as solvent, the benzene readily accepts hydrogen.[1,2] It has been found in this Laboratory that certain organic additives of the quaternary ammonium salt type will promote the hydrogenation of benzene in the presence of platinum.[3] Moreover, if Adams platinum oxide is prereduced in acetic acid or methanol and subsequently thoroughly rinsed, the catalyst thus prepared will enable the hydrogenation of benzene either alone or in methanol.[4]

A comparison of the rates of hydrogenation and of deuteration of benzene cannot be made in the presence of a solvent such as acetic acid since the acidic proton of the solvent undergoes rapid exchange with gaseous deuterium in the presence of platinum.[5] Therefore it was of interest both to find out what prevented the hydrogenation of benzene in the absence of additives or pre-treatment of the catalyst, and also to prepare a platinum catalyst which by itself would be effective in causing the hydrogenation of benzene at ordinary temperatures and pressures.

Experimental

Adams Platinum Oxide.—Unless otherwise noted the fusion products were prepared according to the standard procedure[6] except that the temperature cycles followed were based on those described in an earlier paper.[7] For comparison, preparations of fusion products were also made according to a recent modification of the Adams procedure.[8]

Platinic Acid.—Platinic acid was prepared according to the directions of Wohler.[9,10] The several preparations were purified until they gave negative or questionable flame tests for sodium.

Anal. Calcd. for $H_2Pt(OH)_6$: Pt, 65.2; H_2O, 24.1. Found: Pt, 64.5; H_2O, 24.3.

Partially Dehydrated Platinic Acid.—A material with the approximate composition of the monohydrate of platinic oxide was prepared by the careful dehydration of platinic acid at 95° for one week.

Anal. Calcd. for $PtO_2 \cdot H_2O$: Pt, 79.6; H_2O, 7.3. Found: Pt, 77.0; H_2O, 9.6.

Sodium Nitrate.—The sodium nitrate was J. T. Baker C.P. Samples of this substance were heated for 10-minute intervals and then tested for basicity. Temperatures up to about 450° did not result in enough decomposition to cause distilled water solutions of the salt to be basic to litmus or phenolphthalein. However, the aqueous solutions of fusions above 500° appeared strongly basic. Duplicate fusions at 600° of 5-g. samples of sodium nitrate resulted in a basicity of 0.0052 meq. per gram. At 700° the basicity found was 0.233 meq. per gram.

Chloroplatinic Acid.—The chloroplatinic acid was obtained from the American Platinum Company.

Acetic Acid, Methanol, Benzene.—Commercial samples of high quality were fractionated at atmospheric pressure as needed in a 6-foot column packed with glass helices (equivalent to approximately 30 theoretical plates). Middle fractions of constant boiling points were collected for use.

Hydrogen Gas.—The gas was obtained from the National Cylinder Gas Company.

Analyses.—Platinum was determined by the electrolytic precipitation of the metal on a tared platinum electrode.[11] All samples were first dissolved in aqua regia. It was found that the sodium nitrate–chloroplatinic acid fusion

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[1] R. Adams and J. R. Marshall, THIS JOURNAL, **50**, 1970 (1928).

[2] H. A. Smith, D. M. Alderman and F. W. Nadig, *ibid.*, **67**, 272 (1945).

[3] H. A. Smith and W. H. King, unpublished work.

[4] J. Young and H. A. Smith, unpublished work.

[5] Lloyd E. Line, Jr., Betty Wyatt and Hilton A. Smith, THIS JOURNAL, **74**, 1808 (1952).

[6] R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses," Col. Vol. I, John Wiley and Sons, Inc., New York, N. Y. 1932, p. 452.

[7] R. Adams and R. L. Shriner, THIS JOURNAL, **45**, 2171 (1923).

[8] V. L. Frampton, J. D. Edwards, Jr., and H. R. Henze, *ibid.*, **73**, 4432 (1951).

[9] L. Wohler, *Z. anorg. Chem.*, **40**, 434 (1904).

[10] For the purpose of qualitative analysis an X-ray pattern of platinic acid was obtained. The data may be of interest to others since they have not been reported previously. X-Ray diffraction pattern of $H_2Pt(OH)_6$: 4.47 (s), 4.19 (s), 3.66 (m), 3.54 (m), 2.69 (m), 2.39 (m), 2.27 (m), 2.18 (m). There were over a dozen other weak lines visible.

[11] A. Schleicher, "Die Chemische Analyse," W. Bottger, Editor, "Electroanalytische Schnellmethoden," IV/V, Ferdinand Enke, Stuttgart, 1947, p. 86.

products could be reduced by suspending them in a little methanol and then slowly evaporating to dryness on the steam-bath. Thus treated they dissolved readily in aqua regia.

Total water was determined by the Brush–Penfield method.[12]

Analyses for sodium were made in portions of the samples as dissolved for platinum analysis. The amount of sodium present was determined with a Perkin–Elmer flame photometer, using lithium as the internal standard. The instrument was always recalibrated with standard solutions just prior to use.

Qualitative tests were utilized in testing for traces of certain anions in the catalysts. Silver nitrate was used to indicate chloride ion, the diaminophenol hydrochloride test was used to indicate nitrate[13] ion, and nitrite[13] ion was tested for by means of pyrocatechol and sodium hydroxide.

X-Ray Diffraction Patterns.—Powder diffraction photographs were made by exposures in a Picker–Waite diffraction unit at about 45 kv. The samples were enclosed in thin-walled Pyrex capillaries and exposed in a 70-mm. camera to radiation from a standard copper tube (λ, 1.541 A.), filtered through nickel. Exposure times were usually 2 hours.

Kinetic Studies.—The hydrogenation and deuteration reactions were carried out in a modified Parr apparatus. The hydrogen storage tank was replaced by a brass fitting. This made possible a system which had a total volume of but 0.390 l. The initial pressure was commonly between 50 and 60 p.s.i.g. The rate data are expressed in terms of $k_{1.0}$ liters sec.$^{-1}$ gram^{-1}.[14] In order to establish a comparative standard and to check on poisoning, calibration runs with benzene in acetic acid were made periodically.

Results

Analyses of Catalysts.—In Table I are recorded representative analyses of several of the catalysts prepared and, for comparison, the range of composition for original Adams preparations.

TABLE I

ANALYSES OF CATALYSTS

	Pt	H_2O	Na	Alkali salts
Adams original	78.00–79.80	7.13–9.16		1.72–4.80
Preparation A	82.1	8.1	1.8	
Preparation B	80.4	4.6	2.3	
Commercial preparation[15]	77.7	7.1	2.2	
Dehydrated platinic acid	77.0	9.6	Trace	

Because of the attention given to washing of the preparation it was felt that the modified recipe[8] recently reported might result in a fusion product of very low sodium content. However, analyses of five preparations showed 1.1, 1.2, 1.4, 1.8 and 2.0% sodium, respectively.

Removal of most of the sodium from the standard fusion preparations was accomplished in several ways. Results of several different methods as applied to representative Adams preparations are given in Table II.

Samples of Adams fusion preparation weighing approximately 0.1 g. were exposed for one hour to 10 ml. of 0.0565 N H_2SO_4 at 70°, then filtered and washed. After titration of the filtrate and washings with 0.0500 N NaOH it was found that 0.75 meq. of H_2SO_4 had been neutralized per gram of catalyst. Calculated as sodium this is equivalent to 1.7% sodium in this particular fusion product, which contained 1.82% sodium according to a flame photometer analysis.

TABLE II

Treatment	Sodium, % Before	Sodium, % After
Washed with water[16]; 25 ml. H_2O with 0.71 g. solid	0.85	0.70
Dialysis through cellophane, three months with changing of water every 2–3 days	1.20	.40
Leached with 1 N HNO_3	1.31	.13
Leached with 0.056 N H_2SO_4	1.82	.04
Reduced with hydrogen under methanol	1.20	.18
Reduced under methanol, washed, used in catalytic reduction of benzene with hydrogen, then washed with methanol	1.20	.05

Qualitative analyses made on various preparations of Adams catalyst and on solutions containing hydrogenation products revealed no chloride ion and no nitrite ion. Usually the tests for nitrate ion were negative also, although some weak positive tests were obtained.

X-Ray Data.—The X-ray powder diffraction photographs of Adams fusion product showed several distinct lines. These lines duplicated those reported for PtO_2 by Busch[17] and confirmed by Waser,[18] as shown in Table III. The patterns obtained in this research were the same for the fusion product before and after leaching with aqua regia to remove sodium. The diffraction pattern of a sample prepared according to the modified procedure[8] was not significantly different from these.

TABLE III

X-RAY DIFFRACTION DATA

PtO_2 (Busch)	PtO_2 (Waser)	Adams (this study)
	4.26 (s)	4.34 (b)
2.66	2.67 (s)	2.70 (s)
1.55	1.55 (m)	1.57 (m)
1.45	1.46 (w)	1.48 (w)
1.34	1.34 (m)	1.35 (w)
1.02	1.01	

No powder diffraction pattern was given by the dehydrated platinic acid corresponding to $PtO_2 \cdot H_2O$. However, when this material was heated to 350° for 16 hours, as suggested by a report of a previous investigation,[19] two fuzzy areas in the regions of 4.18 and 2.68 Å. appeared. When heated to 600° for 16 hours the oxide decomposed to yield platinum.[20]

Kinetic Data.—Specific rate constants were determined for each catalyst prepared. The hydrogenation of benzene in acetic acid was chosen for calibration and control and all other hydrogenations were made under conditions precisely similar. In Table IV the several catalysts are listed by letter, as follows: A-1, Adams standard preparation

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(12) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., Inc., New York, N. Y., 1936, p. 714.

(13) I. Mellan, "Organic Reagents in Inorganic Analysis," Blakiston Co., Philadelphia, Penna., 1941, pp. 476, 490.

(14) H. A. Smith and W. C. Bedoit, *J. Phys. Colloid Chem.*, **55**, 1090 (1951).

(15) American Platinum Works.

(16) J. M. Googin, Student Research Project, University of Tennessee, 1951.

(17) R. H. Busch, *Z. Naturforschung*, **5a**, 130 (1950).

(18) Jurg Waser, Abstracts of Southwest Regional Meeting of ACS, Austin, Texas, October, 1951.

(19) E. E. Galloni and R. H. Busch, *J. Chem. Phys.*, **20**, 198 (1952).

(20) The authors are indebted to Mr. R. D. Ellison of the Oak Ridge National Laboratory for several diffraction photographs and for aid in interpreting them.

as prepared in this Laboratory; A-2, commercial Adams catalyst[15]; B, Adams catalyst prereduced in methanol, washed, dried *in vacuo;* C, Adams catalyst prereduced in acetic acid, washed, dried *in vacuo;* D, Adams preparation as modified[8]; E, Adams fusion product leached with 1 *N* HNO_3, washed, dried *in vacuo;* F, partially dehydrated platinic acid.

TABLE IV

SPECIFIC RATE CONSTANTS FOR CATALYSTS

Catalyst	Liquid components	$k_{1.0} \times 10^3$ l. g.$^{-1}$ min.$^{-1}$	Remarks
A-1	1 ml. benzene plus 50 ml. acetic acid	139–200	Seven runs. So-called standard "check run"
A-1	1 ml. benzene plus 10 ml. acetic acid	160–184	4 runs
A-1	10 ml. benzene	0	
A-2	1 ml. benzene plus 50 ml. acetic acid	171	
A-2	10 ml. benzene	0	
B	10 ml. benzene	44–55	4 runs
C	10 ml. benzene	71–79	4 runs
D	1 ml. benzene plus 10 ml. acetic acid	48–72	2 runs
D	10 ml. benzene	0–51	5 runs (two negative); particularly erratic
E	1 ml. benzene plus 50 ml. acetic acid	201	
E	10 ml. benzene	0	
F	1 ml. benzene plus 10 ml. acetic acid	37–41	3 runs
F	10 ml. benzene	29–50	4 runs

Discussion

During the work which gave the first indication that benzene could be hydrogenated over Adams catalyst without the use of a solvent[4] both acetic acid and methanol were used in prereduction of the fusion product. Upon evaporation of the washings and rinsings from either of these prereductions minute quantities of white solids were found. The appearance of the solids was different for acetic acid and methanol washings but the following characteristics were common: melting point or decomposition point above 300°; intense sodium flame qualitative test; negative nitrate or nitrite ion test; soluble in water, sodium hydroxide and acetic acid; very slightly soluble, if at all, in benzene. Approximately 0.1 g. of solid obtained from methanol reductions and dissolved in 3 ml. of water had a *p*H of 10. A sample of the solid obtained by evaporation of the methanol under nitrogen was analyzed by a commercial analyst; found: H, 3.55; C, 19.50; Na, 22.93. (These values have relative worth only since the white solid was visibly contaminated with finely divided catalyst.)

It is indicated then that the standard preparation of Adams platinum oxide catalyst contains sodium in some form which reacts with methanol to form some metallo-organic compound. (Attempts have been made and are being made to identify this compound.) It is indicated further that the sodium component will also react with acetic acid. When acetic acid is present the sodium does not prevent the hydrogenation of benzene even though the sodium compound is not removed from the system.

In Adams' original report[7] the sodium present was referred to as "alkali salts." It is emphasized that this investigation showed that neither of the probable anions of such hypothetical salts, chloride or nitrate, is present, except in trace amounts.

Since it is shown in this study that the sodium equivalence of the fusion product is essentially equal to the basic equivalence it may be concluded that the sodium is associated with a strong proton acceptor. Probably the sodium is present as sodium hydroxide or as an amorphous sodium platinate, the latter formed during the fusion following the decomposition of some of the sodium nitrate. The equivalent amount of sodium present is of the same order of magnitude as the amount of basic sodium formed when sodium nitrate is heated alone. (Exhaustive determinations of the variation of basicity of sodium nitrate with temperature were not made since it was not felt that the heating of the sodium nitrate melt would reproduce the thermal conditions of the Adams fusion.) One reason for not immediately concluding that sodium hydroxide is present is that the fusion product cannot be easily washed free of sodium with distilled water. This procedure has been studied with the results given in Table II. A previous report[16] noted the possibility that "the sodium is present as a salt of one of the hydroxyplatinic acids, and that the acid is strong as compared to water, but weak as compared to nitric acid." It may be pointed out that partially dehydrated sodium platinates[21] could not on the basis of per cent. composition be distinguished from Adams fusion product.

Recent calculations and interpretations have been reported for the structure of PtO_2. From X-ray and neutron diffraction data Jurg Waser[18] concludes that the oxide is made up of sheets consisting of two layers of closely packed oxygen atoms with the platinum atoms sitting in octahedral holes formed by these layers. The shapes and widths of the various diffraction lines indicate a large amount of stacking disorder between adjoining sheets as well as small particle size. The PtO_2 preparations of Waser were fusion products similar to those prepared during this investigation.[6,8,15] His work indicates, then, that the fusion product is not $PtO_2 \cdot H_2O$ as suggested by Adams and Shriner.[7] Further, the sodium is not a part of the compound which gives the characteristic X-ray diffraction lines listed in Table III, since the pattern is not changed when the sodium is removed by aqua regia.[22]

Kinetic studies were made with fusion products of different sodium content but no correlation of the specific activity with per cent. sodium appeared possible. Qualitatively it can be stated that it is the sodium component which appears to interfere with the hydrogenation of benzene. When there are present certain substances which react with or

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(21) J. W. Mellor, "Treatise on Inorganic Chemistry," Vol. XVI, Longmans, Green and Co., New York, N. Y., 1937, pp. 246–247.

(22) In a private conversation with one of the authors Dr. Waser expressed the opinion that the water and the sodium found in the fusion product samples were external to the PtO_2 lattice, probably being adsorbed or occluded.

largely remove the sodium component from the fusion product the hydrogenation of benzene will proceed. A noteworthy exception to this generalization is the 1 *N* HNO_3 leach described in Tables II and IV.

It was found that some of the modified[8] preparations would effect the hydrogenation of benzene alone, but the results were erratic and could not be correlated with sodium content.

One aim of this work was realized in the preparation of Catalyst F, Table IV. All preparations of this sodium-free, partially dehydrated platinic acid, stoichiometrically $PtO_2 \cdot H_2O$, effected the hydrogenation of benzene alone. (Platinic acid, stoichiometrically $PtO_2 \cdot 4H_2O$, was not active as a catalyst for the hydrogenation of benzene alone or in the presence of acetic acid.) The object of preparing $PtO_2 \cdot H_2O$ by the method of Wohler was to obtain a sodium-free material similar to Adams fusion product by an independent method. Unfortunately the $PtO_2 \cdot H_2O$ prepared in this way cannot be said to be structurally similar to the fusion product because repeated X-ray powder diffraction studies of the former failed to yield any pattern indicative of crystallinity. However the $PtO_2 \cdot H_2O$ can be considered a precursor of a product similar to the fusion product (*i.e.*, PtO_2) since its diffraction pattern indicates that it slowly assumes a like structure on heating at 350°. The fact that two substances of possibly very different structure effect hydrogenation similarly is not surprising since the oxides undergo a partial reduction and an evident change in physical appearance as they are reduced by the hydrogen prior to the hydrogenation of the acceptor. For example, analyses of one batch of fusion product before and after reduction in methanol showed the following platinum contents: fusion product, 78.5%; after reduction and washing in methanol, 94.4%. Commonly the catalysts after use are pyrophoric whereas the fusion product and the dehydrated platinic acid are unreactive toward the atmosphere.

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KNOXVILLE, TENNESSEE

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Magnesium–Cadmium Alloys. V. Low Temperature Heat Capacities and a Test of the Third Law of Thermodynamics for the MgCd Superlattice[1,2]

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The heat capacities of an alloy containing 50.52 atomic per cent. cadmium between 12 and 300°K. are presented. From these data the entropy increase between 0°K. and 25°C. is computed and an estimate of the residual entropy for the superlattice (intermetallic compound) MgCd made. The alloy deviates negatively from the Kopp–Neumann rule below 200°K., where the configuration is frozen-in. At temperatures of 230°K. and above a transformation is observed. This has been established as the beginning of the order–disorder transition, which culminates in destruction of the superlattice at 528°K. In the temperature range where the configuration is changing, positive deviations from the Kopp–Neumann rule are observed. Debye characteristic temperatures are presented for the alloy, the equivalent mixture and the pure component metals.

Introduction

In the preceding papers of this series results of determinations of (1) the densities and atomic volumes at 25°,[3] (2) heats, free energies and entropies of formation between 270 and 300°,[4] (3) heats of formation at 25°[5] and (4) certain crystallographic data[6] for the binary system magnesium–cadmium have been presented. The present paper contains results of measurements of the heat capacity of an alloy having a composition near to MgCd (actually 50.52 atomic per cent. cadmium) from 12 to 300°K. From these data and the entropy of MgCd obtained earlier in this Laboratory using the electrochemical cell the residual entropy of the MgCd superlattice can be calculated. The heat capacities have also been used together with data in the following paper for the pure metals (1) to ascertain the degree of conformity with the Kopp–Neumann rule for additivity of heat capacities at temperatures so low that the configuration is frozen-in and (2) to study the effect of temperature and composition on the Debye characteristic temperature.

Experimental

General Aspects of the Calorimetric Assembly.—The calorimeter used was similar in principle to that employed by Southard and Brickwedde.[7] It was arranged so that it could be mounted either in a conventional cryostat using liquid nitrogen or solid carbon dioxide as a refrigerant for experiments at 80°K. or above or in the Collins Helium Cryostat for experiments below 80°K.

The design of the calorimeter differed appreciably from the conventional type of adiabatic calorimeter in only three respects: (1) the arrangement of certain components, especially the "thermal trap" and "floating ring," was altered so as to permit use of the Collins machine, (2) the customary sample container was replaced by a solid cylinder of the metallic sample in the center of which was a "core" containing the thermometer and heater and (3) the electric timer was operated by current generated by a calibrated tuning fork

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(1) From a thesis submitted by Mr. C. B. Satterthwaite in partial fulfillment of the requirements for the Ph.D. degree at the University of Pittsburgh, January, 1951.

(2) This work was assisted by the Office of Naval Research and the Atomic Energy Commission.

(3) J. M. Singer and W. E. Wallace, *J. Phys. Colloid Chem.*, **52**, 999 (1948); paper I.

(4) F. A. Trumbore, W. E. Wallace and R. S. Craig, THIS JOURNAL, **74**, 132 (1952); paper II.

(5) T. M. Buck, Jr., W. E. Wallace and R. M. Rulon, *ibid.*, **74**, 136 (1952); paper III.

(6) D. A. Edwards, W. E. Wallace and R. S. Craig, *ibid.*, **74**, 5256 (1952); paper IV.

(7) J. C. Southard and F. G. Brickwedde, *ibid.*, **55**, 4378 (1933).