styrene to the complete lack of hydrogenation of bromobenzene or naphthalene at *ca.* 350°. With the olefins the ease of hydrogenation (no. 4 > 5,7 < 6) appears to parallel the possession by the molecule in question of geometrical properties which most readily permit adsorption on the catalyst surface. The resistance of halogen substituents to hydrogenolysis by this catalyst (no. 3, 12, 23) is noteworthy. This property is shared by all rhenium catalysts we have studied. The marked effect of the solvent on the course of hydrogenation in some cases (no. 10, 11) and the absence of any significant effect in other cases (no. 15, 16) is interesting. This phenomenon has also been previously noted with other rhenium catalysts.

The carbonyl and nitro groups in separate molecules are relatively easily reduced, but the inclusion of both groups in the same molecule in the one case examined (no. 24) caused the nitro group to be resistant under conditions which would lead to easy hydrogenation otherwise.

The carboxylic acid group, which is hydrogenated with great difficulty if at all by most catalysts, is relatively easily reduced (no. 20). In this respect it is surpassed only by rhenium heptoxide reduced to the active catalyst *in situ*.[1]

Rhenium Catalysts. V. Rhenium Heptoxide–Tetrahydropyran Complex[1,2]

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Rhenium(VII) oxide reacts with boiling tetrahydropyran to form a nearly colloidal, black, voluminous, insoluble complex which has unusual activity in catalytic hydrogenations. It is relatively active in promoting saturation of aromatic hydrocarbons whereas nitro compounds are singularly inert under comparable conditions.

During an investigation of the solubility of yellow rhenium(VII) oxide in various solvents, it was observed that the oxide reacts readily with warm tetrahydropyran to form a very finely divided black, voluminous precipitate of rather indefinite composition containing 45 to 55% rhenium. The recovery of rhenium from tetrahydropyran in the form of this complex is 80–90%. This "black" is active in catalyzing the liquid phase hydrogenation of many organic compounds, particularly aromatic structures. On the other hand, nitro compounds are singularly inert to hydrogenation under these same conditions.

Nechamkin, Kurtz, and Hiskey[4] have reported that various ethers reduce rhenium(VII) oxide to rhenium(VI) oxide. In particular, dioxane forms a pearly-white crystalline complex having the composition $Re_2O_7 \cdot 3C_4H_8O_2$, which decomposes at about 145° giving a 40% yield of maroon-red rhenium(VI) oxide uncontaminated by lower or higher oxides.

The tetrahydropyran complex also decomposes on heating to form pure rhenium(VI) oxide. However, this oxide has a pattern of hydrogenation catalytic activity (to be reported in a subsequent paper of this series) entirely different from that of the black, undried, amorphous complex from which it is derived. The details of the preparation and catalytic activity of the tetrahydropyran complex are reported below.

Experimental

Rhenium(VII) oxide[5] was carefully ground to a fine powder in a mortar and pestle with strict exclusion of moisture. This substance appears to be even more hygroscopic than phosphorus(V) oxide.

Tetrahydropyran[6] was purified by extended refluxing over sodium metal ribbon followed by distillation. After a repetition of this process the distillate was stored over calcium hydride or sodium metal without discoloration occurring. It was filtered immediately prior to use.

Preparation of the Catalyst.—One and one-half grams of finely powdered rhenium(VII) oxide was added to 150 ml. of purified tetrahydropyran, and the mixture was refluxed 2 hr., cooled, and centrifuged. After decantation of the supernatant solvent, the very black, voluminous complex was washed with absolute ethanol by centrifugation and decantation and stored under absolute ethanol. The suspended complex settled very slowly. Air, water, or amines caused a change in color of the complex from black to caramel brown.

Analysis of the clear supernatant tetrahydropyran following centrifugation established that precipitation of the rhenium(VII) oxide as the tetrahydrofuran complex was 80–90% complete.

Analysis of Catalysts.—Samples were prepared for analysis in the same manner as reported in the immediately preceding paper of this series, except that it was sometimes necessary to filter off undissolved material after the initial treatment of the sample with concentrated ammonium hydroxide and 30% hydrogen peroxide and treat it again in order to dissolve it completely. The perrhenate ion was determined as its tetraphenylarsonium salt. Values for

(1) *Cf.* H. Smith Broadbent and John H. Johnson, *J. Org. Chem.*, **27**, 4400 (1962), for paper IV in this series.

(2) Support by the U. S. Air Force through their Office of Scientific Research, Contract AF 18(600)-1164 is gratefully acknowledged.

(3) This paper is based on a thesis submitted by Mr. Johnson (1956) in partial fulfillment of the requirements for the M.S. degree at Brigham Young University.

(4) H. Nechamkin, A. N. Kurtz, and C. F. Hiskey, *J. Am. Chem. Soc.*, **73**, 2828 (1951); H. Nechamkin and C. F. Hiskey, *Inorg. Syn.*, **3**, 186 (1950).

(5) Obtained as a massive yellow crystalline sublimate from Prof. A. D. Melaven, University of Tennessee, Knoxville, Tenn.

(6) Commercial material from the Electrochemicals Department, E. I. du Pont de Nemours, Inc.

TABLE I

HYDROGENATIONS CATALYZED BY RHENIUM(VII) OXIDE–TETRAHYDROPYRAN COMPLEX

No.	Substrate	Solvent	Av. temp., °C.	Av.[a] pressure, atm.	Time, hr.	Yields,[b] %	Product(s)
1	Styrene	Ethanol	107	255	2	100	Ethylbenzene
2	Styrene	Ethanol	242	308	5	24	Ethylcyclohexane
						56	Ethylbenzene
3	Styrene	None	165	245	12	51	Ethylcyclohexane
4	1-Hexene	None	135	252	1	100	Hexene
5	2-Hexene	None	122	245	3	100	Hexane
6	2,4,4-Trimethyl-1-pentene	None	91	218	3	100	2,4,4-Trimethylpentane
7	Cyclohexene	Ethanol	151	264	13	100	Cyclohexane
8	Cyclohexanone	Ethanol	113	248	5	100	Cyclohexanol
9	Acetophenone	Ethanol	162	258	3	32	Ethylbenzene
						45	Methylphenylcarbinol
10	*m*-Nitroacetophenone	Ethanol	195	302	3		No reduction
11	Capronitrile	None	240	306	7	15	Hexylamine
						16	Dihexylamine
						69	Trihexylamine
12	Acetic acid	None	195	281	4	23	Ethyl alcohol
						40	Ethyl acetate
13	Isobutyric acid	None	255	311	3	70	Isobutyl alcohol
						30	Isobutyl isobutyrate
14	Benzene	None	160	242	10	100	Cyclohexane
15	Nitrobenzene	Ethanol	250	333	4	11	Aniline
						43	Nitrobenzene
							Decomposition products
16	Nitrobenzene	None	207	278	5	33	Aniline
							Decomposition products
17	Toluene	None	174	242	15	100	Methylcyclohexane
18	Cumene	None	148	255	11	71	Isopropylcyclohexane
19	*t*-Butylbenzene	None	195	272	9	100	*t*-Butylcyclohexane
20	*p*-Xylene	None	162	240	3	89	1,4-Dimethylcyclohexane
21	*p*-Cymene	None	240	313	1	22	*p*-Menthane
						78	*p*-Cymene
22	1-Nitropropane	None	130	276	2.5		No reduction
23	Phenol	Cyclohexane	170	260	15	92	Cyclohexanol
24	Aniline	Cyclohexane	300	370	3		No reduction
25	Chlorobenzene	Cyclohexane	300	360	4		No reduction
26	Naphthalene	Cyclohexane	309	364	5		No reduction
27	Pyridine	None	228	300	4	37	Piperidine
28	Biphenyl	Cyclohexane	295	354	2		No reduction
29	4-Nitrobiphenyl	None	235	282	10	43	4-Aminobiphenyl
							Decomposition products
30	Diphenyl ether	None	160	240	19	20	Cyclohexanol
						6	Dicyclohexyl ether
						37	Cyclohexyl phenyl ether
						23	Diphenyl ether
31	4-Nitrodiphenyl ether	None	160	240	3	100	4-Aminodiphenyl ether
32	Diphenylmethane	None	208	274	9	7	Dicyclohexylmethane
						70	Cyclohexylphenylmethane
						23	Diphenylmethane

[a] Total system pressure at the average temperature in question. [b] Based on crude, recovered, reaction product.

the rhenium content ranged from 44.4 to 54.5% for various runs.

Part of the rhenium in the complex appeared to remain in a soluble form since prolonged extraction of one sample with benzene lowered its rhenium content to 37.9%.

Carbon and hydrogen as well as rhenium analyses were obtained on two samples of catalyst both before and after use in hydrogenation. The samples analyzed immediately following their preparation gave the following results[7]: (1) Re, 47.6; C, 24.1; H, 3.4; (2) Re, 44.7; C, 24.6; H, 3.5.

The same two samples analyzed after their being used to hydrogenate benzene to cyclohexane gave the following results, respectively. (1) Re, 54.7; C, 30.0; H, 3.4; (2) Re, 51.0; C, 25.9; H, 3.6.

(7) These results apply to the catalyst after vacuum drying at 100° over Molecular Sieve 4-A.

Hydrogenation Procedure.—Hydrogenations were carried out in a Parr Instrument Co., 500 ml., 36 cycle per min. rocking reactor with a glass liner using 1 g. of catalyst per mole of substrate at an initial pressure of 200 atm. of hydrogen as outlined in more detail in the previous paper. If the reaction solvent was not ethanol, the ethanol in which the catalyst was suspended for storage was removed by centrifugation and decantation and replaced by the desired solvent or by the substrate itself if no solvent was used.

The reaction product was analyzed after removal of the catalyst by fractional distillation, chemical extraction, titrimetry, and refractometry.

Discussion of Results

During hydrogenation the original rhenium(VII) oxide–tetrahydropyran complex [in which the rhen-

ium may already be wholly or partially reduced to the rhenium(VI) state] probably experiences further reduction to a lower valent state which is the active form of the catalyst, since the analyses show a 6–7% increase in rhenium content of the catalyst after hydrogenation. Variability in the composition of the complex catalyst precludes any sound conjecture about its composition at this point.

The data for a representative listing of the hydrogenations carried out with this catalyst are presented in the accompanying table.

In general, the catalytic activity of rhenium(VII) oxide–tetrahydropyran complex in liquid phase hydrogenations is lower than that for the other rhenium catalysts studied heretofore[8]; however, the *pattern* of activity toward various reducible groups is entirely different from that noted for any other catalyst.

Most surprising are the relatively mild conditions required for the hydrogenation of most aromatic rings (no. 14, 17, 18, 19, 20, 21, 30, and 32) in comparison with the relatively strenuous conditions needed to reduce the nitro group which is usually so readily reduced (no. 22). The hope that this phenomenon would permit the as yet generally unobserved selective hydrogenation of aromatic rings without concomitant reduction of nitro groups in the same molecule was not realized, however (*cf.* no. 14 and 16, 30 and 31). Apparently, the presence of a nitro group in a molecule "poisons" the catalyst toward aromatic ring hydrogenation so that the latter function is not hydrogenated at all, and a given nitroarene suffers hydrogenation of the nitro group alone and then only under conditions more drastic than would be required to hydrogenate the aromatic function in the absence of the nitro group. Moreover, the complete inertness of the aminoarenes to further hydrogenation is illustrated by aniline (no. 24). The resistance of *m*-nitroacetophenone to reduction compared with acetophenone (no. 9, 10) also illustrates the adverse effect of the nitro group.

In contrast to aniline, phenol (no. 23) was relatively easily hydrogenated. The extreme inertness of naphthalene, biphenyl, and chlorobenzene in comparison to the other aromatic compounds is noteworthy (no. 25, 26, and 28 *vs.* 14, 17, 18, 19, 20, 21, 23, 30, and 32). The chlorine atom of chlorobenzene does not undergo hydrogenolysis even at 300°.

(8) *Cf.* earlier papers in this series.

Phosphorus Compounds. III. Pyrolysis of Tertiary Phosphine Oxides[1-3]

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Pyrolytic study of a series of tertiary phosphine oxides has confirmed the high thermal stability of the carbon–phosphorus bond. Oxides containing alkyl groups with an available β-hydrogen atom apparently cleave by a cyclic mechanism to an olefin and a secondary phosphine oxide. The secondary oxides from the lower members of the series subsequently disproportionated into a secondary phosphine and a phosphinic acid. Oxides with no β-hydrogens were more stable than the preceding group at 600°, and, with the compounds examined, the phosphorus oxides all required temperatures approximately 300° above those required for similar decomposition of the corresponding amine oxides.

Since tertiary phosphine oxides appear to be one of the most stable groups of compounds in phosphorus chemistry, it was of interest to examine the thermal stability of some compounds in this class. This study was facilitated by the development in these laboratories of a general method for the preparation of a series of unsymmetrical tertiary phosphines.[1] The oxides were easily obtained by direct oxidation of the corresponding phosphines. For example, ethylmethylphenylphosphine was prepared in an over-all yield of 66% starting from phenyldichlorophosphine. Oxidation of this phosphine with hydrogen peroxide gave an 86% yield of the corresponding white crystalline phosphine oxide. The symmetrical phosphine oxides were prepared by the reactions of Grignards of alkyl halides with commercially available monosubstituted dichlorophosphines[5] or phosphorus trichloride,[6] or directly with phosphorus oxychloride.[7] It has been recorded[8] that the carbon–phosphorus bond in unsubstituted aromatic and aliphatic phosphonic acids [$RPO(OH)_2$] is both thermally and chemically stable, as might also be predicted for tertiary phosphine oxides. The carbon–phosphorus bond energy is 62 kcal.,[9] compared with 68 kcal. for carbon–silicon, 64 kcal. for carbon–carbon, and 57 kcal. for carbon–arsenic bonds.

(1) Previous paper in this series, *J. Org. Chem.*, **25**, 1996 (1960).

(2) This work was done in fulfillment of a contract with the Army Chemical Corps.

(3) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September 1961.

(4) (a) Chemical Corps Postdoctoral Fellow, 1960–1961; (b) Chemical Corps Postdoctoral Fellow, 1958–1959.

(5) G. M. Kosolapoff and R. F. Struck, *Proc. Chem. Soc.*, 351 (1960).

(6) W. C. Davies, P. L. Pearse, and W. J. Jones, *J. Chem. Soc.*, **135**, 1262 (1929).

(7) R. H. Pickard and J. Kenyon, *ibid.*, **89**, 262 (1906).

(8) L. D. Freedman and G. O. Doak, *Chem. Rev.*, **57**, 479 (1957).

(9) M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).