

vapor pressure measurements. At higher concentrations, the progressive divergence between the two sets of data may be attributed to the increased solubility of the lead phosphate in the more concentrated acid.

The standard potentials of the lead amalgam-

lead phosphate and lead-lead phosphate electrodes are as follows:

Pb(2-phase amalgam),  $\text{PbHPO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ;  $E_{25}^0 = 0.2448$  volt

Pb,  $\text{PbHPO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ;  $E_{25}^0 = 0.2507$  volt.

WILSON DAM, ALABAMA RECEIVED NOVEMBER 4, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## High Pressure Hydrogenations with Adams Catalyst

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Extensive application of Adams platinum oxide has proved its value as a catalyst for low pressure hydrogenation,<sup>2</sup> but little is known of its utility at high hydrogen pressure. Some indication that it may be useful at high pressure is found in the reduction of L-mannonic lactone to L-mannitol,<sup>3</sup> and in the reduction in this laboratory of phenacylpyridinium bromide to the alcohol.<sup>4</sup> This paper reports an extension of the high pressure method to some simple aromatic compounds.

It was found that the simple benzenoid hydrocarbons may be reduced at room temperature on a preparative scale in a practical period of time. As a specific example 21 g. of toluene dissolved in 25 ml. of glacial acetic acid was completely hydrogenated at 2000 lb. over 0.67 g. of platinum oxide within twenty minutes at 25°. Benzene and *m*-xylene were hydrogenated even more rapidly, and phenol, *o*-cresol and 2-naphthol were only slightly slower. Thus the method was more rapid than the low pressure method of Adams and Marshall<sup>5</sup> in which hours were required for many aromatic nuclei. In addition it should be useful in the reduction of acids and other compounds which poison nickel but not platinum or of other compounds in acid medium.

It was hoped that the great increase in rate occasioned by high pressure would allow a practical rate of hydrogenation of the aromatic nucleus even in the absence of the acidic solvent. Experience has shown, however, that benzene was not reduced over platinum in the absence of solvent or when dissolved in ethanol or dioxane and heated to 180° at 2000 lb. This was in sharp contrast to the rapidity of reduction in glacial acetic acid solution at 25° and clearly demonstrated that the well-known promoting effect of acids on Adams catalyst applies at high as well as at low pressure.

Recent investigations of Smith and co-workers<sup>6,7</sup> with this catalyst at low pressure re-

vealed the facts that the rate was first order with respect to hydrogen pressure, zero order with respect to acceptor and directly proportional to the amount of catalyst. They found that the phenyl-substituted aliphatic acids and the alkylated benzenes followed the rate equation

$$\log p_0/p = kt/2.303$$

When the constant,  $k$ , was referred to a constant quantity of catalyst, one gram, its magnitude was dependent only upon temperature and the nature of the compound under investigation and it was designated as  $k_t^0$ .

Although the evaluation of  $k_t^0$  at high pressure was more difficult than at low pressure the data presented in Table I indicated that for benzene it was independent of pressure in the range of 1000-2980 lb. of hydrogen.

TABLE I  
HYDROGENATION OF BENZENE, 0.0226 MOLE, IN GLACIAL ACETIC ACID, 4 ML., OVER PLATINUM OXIDE IN THE 43-ML. BOMB

Initial pressure, lb./sq. in.	Catalyst, mg.	$t$ , °C.	Time, min.	$k_t^0 \times 10^3$
1000	64	27	41	66
1050	127	26	18	67
1380	63	25	35	47
1470	67	28	21	64 <sup>a</sup>
1670	62	30	21	73 <sup>a</sup>
1990	66	27	15	57
2480	64	26	15	51
2980	63	26	12	51

Average 60

<sup>a</sup> These reactions were run at a shaking rate of 24 cycles per minute in order to show that the usual 40 cycles was sufficient to make the hydrogenation rate independent of rate of shaking.

Although the  $k_t^0$  values were not comparable unless the experiments were made with a constant hydrogen void, they had more significance than such measurements as total time of hydrogenation, time required for the reduction of the middle third, etc. With the  $k_t^0$  values it was possible to study either the activity of the catalyst or the reactivity of the hydrogen acceptor. Thus in the preparative scale in reductions of the compounds

(1) Abstracted from the Ph.D. Thesis of Robert D. Schuetz.

(2) For a general review of this and other catalysts see Adkins and Shriner in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 779.

(3) Baer and Fischer, *THIS JOURNAL*, **61**, 761 (1939).

(4) Riegel and Witteoff, *ibid.*, **68**, 1805, 1913 (1946).

(5) Adams and Marshall, *ibid.*, **50**, 1970 (1928).

(6) Smith, Alderman and Nadig, *ibid.*, **67**, 272 (1945).

(7) Smith and Pennekamp, *ibid.*, **67**, 276, 279 (1945).

TABLE II  
HYDROGENATIONS AT 25° WITH ADAMS CATALYST IN 25 ML. OF ACETIC ACID IN THE 300 ML. BOMB

Compound	Moles	Cat., g.	Initial pressure, lb./sq. in.	Time, min.	$k_t^0 \times 10^3$	% Products
Benzene	0.28	0.83	1960	15	180	95 Cyclohexane
Toluene	.23	.97	2000	12	100 <sup>a</sup>	92 Methylcyclohexane
<i>m</i> -Xylene	.20	.58	1620	18	136 <sup>b</sup>	87 (23% <i>cis</i> -, 77% <i>trans</i> -1,3-dimethylcyclohexane) <sup>12</sup>
Naphthalene <sup>c</sup>	.12	.35	1850	95	27 <sup>d</sup>	92 (23% <i>trans</i> -, 77% <i>cis</i> -Decalin)
Tetralin	.18	.52	1700	90	12 <sup>d</sup>	91 <i>cis</i> -Decalin
Phenol	.21	.58	1720	30	62	47 Cyclohexanol
<i>o</i> -Cresol	.24	.69	1700	45	51	66 <i>cis</i> -2-Methylcyclohexanol
2-Naphthol <sup>c</sup>	.14	.66	1580	63	46 <sup>d</sup>	89 <i>trans</i> -Decahydro-2-naphthol
Aniline	.27	.90	1750	1245	8	17 Cyclohexylamine, 23 dicyclohexylamine

<sup>a</sup> Average of two runs. <sup>b</sup> Average of four runs at 1350, 1550, 1620 and 1700 lb. The largest value was 139 and the smallest 134. <sup>c</sup> It was necessary to add 20 ml. of ether to these to complete solution. <sup>d</sup> These are pseudo values determined at the beginning of the reaction, cf. Fig. 1.

shown in Table II the  $k_t^0$  values reflected comparative ease of hydrogenation.

At low pressure Smith and Pennekamp found that the relative rates of benzene, toluene and *m*-xylene were 100/62/49,<sup>7</sup> whereas our results were 100/55/75. The benzene-toluene ratio was about as close as could be expected but *m*-xylene appeared definitely out of line. This may be due to the greater ease of desorption of the product when in competition with hydrogen at high pressure. The predominant product, *trans*-dimethylcyclohexane, would be expected to be little absorbed to the catalyst surface or less so than methylcyclohexane. Adams and Marshall<sup>8</sup> thought the product of the low pressure reduction was predominantly the *trans* isomer, but they were unable to separate the isomeric mixture. Our separation and reference to the accepted physical properties of the *cis-trans* isomers confirms their view.<sup>12</sup> Since the rate of reduction follows strictly the first order law there is little reason to believe that any intermediate stable enough to leave the catalyst surface is formed, and so our results are in contradiction to the generally accepted view that compounds which hydrogenate completely at one sitting on the catalyst lead predominantly to the *cis* isomers.<sup>8</sup>

Figure 1 shows graphically the rate of change of hydrogen pressure. Although the phenols were hydrogenated more slowly than the simple hydrocarbons, the rate governing factor seems to be the hydroxyl group, for all three studied had about the same rate. This was further borne out by a comparison of naphthalene and 2-naphthol. Whereas the former hydrogenated much more slowly than benzene the latter was reduced much more rapidly than naphthalene and just slightly less readily than phenol. The 2-naphthol curve is seen to be a composite of two straight lines with slightly different slopes which obviously was due to the formation of an intermediate of fair stability, probably the *ac*-tetrahydro compound.

(8) For a recent summary of the stereochemistry of hydrogenation compare Linstead and co-workers, THIS JOURNAL, 64, 1985ff (1942).

Naphthalene presented an even stranger case in that it did not begin to obey the first order requirement until about 40% of the hydrogen had been added. Shortly after the beginning of the reaction there was a deceleration of the rate which may be due to a poisoning of the catalyst by the intermediate, tetralin. Tetralin itself confirmed this interpretation, the curve taking the same general form and slope as the last 60% of the naphthalene curve. Quantities of materials and pressures were selected so as to require approximately the same time for hydrogenation of these two substances to decalin, yet the proportion of stereoisomers was different. The production of approximately 30% of *trans*-decalin from naphthalene may be due to a different mechanism of reduction.<sup>8</sup>

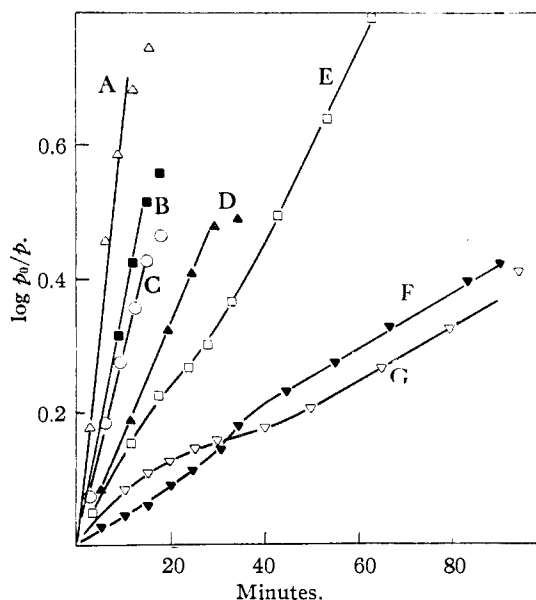


Fig. 1.—Rates of hydrogenation, cf. experiments in Table II: A, benzene; B, *m*-xylene; C, toluene; D, phenol; E, 2-naphthol; F, tetralin; G, naphthalene. The line for *o*-cresol was almost coincident with D.

The reduction of aniline, and presumably other aromatic amines, by this procedure was entirely unsatisfactory. The reaction was too slow to be practical and the yields were poor.

### Experimental

**Purification of Compounds.**—Benzene and toluene were prepared free from sulfur compounds by extraction with sulfuric acid, three times, followed by refluxing first with sodium and then with Raney nickel. They were then fractionated at reflux ratios of 10/1 in ten-plate columns. The source of the *m*-xylene is unknown; its melting point (bulk) was  $-47$  to  $-45^\circ$ , reported<sup>9</sup>  $-47.4^\circ$ . Naphthalene was purified by the method of Willstätter and Hatt.<sup>10</sup> An amount of 250 g. was crystallized from acetic acid, then acetone, and then from ethanol; the series of crystallizations was repeated four times to yield 50 g. of the sulfur-free compound. Tetralin of commercial grade was fractionated from Raney nickel in a ten-plate column. Phenol and *o*-cresol were distilled from Raney nickel. Sublimed 2-naphthol was crystallized three times from an equal weight of hot ethanol by adding water until crystallization began. Aniline was twice distilled from Raney nickel.

**Hydrogenations.**—The apparatus and methods were essentially those described by Adkins.<sup>11</sup> Glass liners invariably were used, and the usual procedure was to place the catalyst and solution of the hydrogen acceptor in the liner, then seal the bomb and admit hydrogen, taking care to avoid shaking until the normal shaking could be started. The pressure drop during the first five to ten seconds of shaking was considered to be due to solution of hydrogen and reduction of catalyst and was discounted. The catalyst was taken from a single lot obtained from American Platinum Works, Newark, N. J.

A comparison of the activity of our catalyst with that of Smith and Pennekamp<sup>7</sup> was made by hydrogenating benzene under their conditions in the Parr low-pressure apparatus. In three successive runs at 60, 60 and 30 lb. initial pressure our catalyst (calculated to one g.) gave  $k_{25}^0$  values of 21.8, 22.2 and  $25.5 \times 10^{-3}$ , which by comparison with their value at  $30^\circ$ ,  $65 \times 10^{-3}$ , shows our catalyst to be less than one-half as active as theirs.

**Recovery of Products.**—The hydrocarbons and amines were recovered by filtering off the catalyst, pouring the filtrate into aqueous sodium hydroxide solution, and extracting with ether. The alcohols were boiled for a time with excess alkali before extraction in order to hydrolyze the possible acetate esters.

*cis*- and *trans*-1,3-dimethylcyclohexanes were separated by fractionation of the mixture in a Podbielniak Hyper-Cal column having a Heli-Grid-packed section, 22 mm. by 91 cm., with a rating in excess of 100 plates.

(9) Timmermans and Hennaut-Roland, *J. chim. phys.*, **27**, 401 (1930).

(10) Willstätter and Hatt, *Ber.*, **45**, 1471 (1912).

(11) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937.

A reflux ratio of 150/1 and a distillation rate of approximately 3 g. per hour was used to produce 34 g. of the *trans* isomer in ten fractions with  $d^{20}_4$  0.765–0.766 and an eleventh intermediate fraction of 3 g. with  $d^{20}_4$  0.770. The residue from this still was subjected to 20-plate distillation to yield 17 g. of the *cis* isomer in two fractions,  $d^{20}_4$  0.783–0.785. The densities reported for the *trans* and *cis* isomers are 0.76628 and 0.78348, respectively.<sup>12</sup>

*cis*- and *trans*-decalins resulting from the hydrogenation of naphthalene were separated by fractionation at 2 mm. in a Podbielniak 8 mm. by 46 cm. Heli-Grid column rated at 50 plates. Two fractions,  $n^{20}_D$  1.4687 and 1.4700 weighing 5 g., of pure *trans*, two intermediate fractions 13 g., and then eight fractions of *trans*,  $n^{20}_D$  1.4808–1.4810 weighing 51 g., were collected. The reported constants are  $n^{20}_D$  1.46968 and 1.48113, respectively.<sup>13</sup>

The decalin obtained from tetralin was distilled and determined to be wholly *cis* by its physical properties,  $n^{20}_D$  1.4810 and  $d^{20}_4$  0.8951; Skita<sup>14</sup> reported 0.8963 for this compound.

*trans*-Decahydro-2-naphthol was not purified since the material obtained by evaporation of the ether extract had m. p.  $72$ – $74^\circ$ . The reported values is  $75^\circ$ .<sup>15</sup>

### Summary

1. Adams and Marshall's method for the reduction of aromatic compounds has been extended to hydrogen pressures as high as 3000 p.s.i. The reductions in acetic acid solution go rapidly at room temperature and it is possible to prepare the perhydro compounds on a preparative scale within a few minutes.

2. The kinetics of the reductions of the monocyclic compounds are consistent with a first order dependence on hydrogen pressure and a zero order dependence on the hydrogen acceptor.

3. The stereochemistry of the reaction has been investigated for *m*-xylene, *o*-cresol, naphthalene and tetralin. The first of these produces a mixture of 77% *trans*- and 23% *cis*-1,3-dimethylcyclohexane. *o*-Cresol and tetralin produce *cis* derivatives, but naphthalene produces a mixture of 23% *trans*- and 77% *cis*-decalin.

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RECEIVED DECEMBER 23, 1946

(12) Miller, *Bull. soc. chim. Belg.*, **44**, 513 (1935); *C. A.*, **30**, 2180 (1936). Note added in proof; Pitzer and Beckett, *THIS JOURNAL*, **69**, 977 (1947), have suggested that this assignment of structures may be incorrect.

(13) Seyer and Walker, *THIS JOURNAL*, **60**, 2125 (1938).

(14) Skita, *Ann.*, **431**, 1 (1923).

(15) Leroux, *Compt. rend.*, **140**, 590 (1905); Hüchel, *Ann.*, **441**, 1 (1925).