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The Catalytic Hydrogenation of the Benzene Nucleus. III. The Hydrogenation of Polymethylbenzenes

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In earlier papers in this series,[1,2] studies of the hydrogenation on platinum of phenyl-substituted aliphatic acids and of monoalkylbenzenes have been described. The purpose of the present paper is to report further kinetic studies involving the catalytic hydrogenation on Adams catalyst of the polymethylbenzenes.

Adams and Marshall[3] found that the hydrogenation of mesitylene on platinum in acetic acid solution proceeded somewhat faster than that of either *m*-xylene or mixed xylenes. Since in these experiments only the over-all reaction time was measured, the results may be in considerable error due to catalyst poisoning. Lozovoy and Diakova[4] included the xylenes, mesitylene, durene, and penta- and hexamethylbenzene in their study of the rate of hydrogenation of benzene hydrocarbons on a nickel–alumina (Zelynsky) catalyst. These latter authors suggested that the rate of hydrogenation of substituted benzenes could be roughly expressed by the formula $v_n = 2^{-n}v$, where v_n represents the velocity of hydrogenation of a benzene nucleus containing n substituents, and v is the velocity of hydrogenation of benzene. The results of Adams and Marshall are not in accord with this formula.

Since all of the polymethylbenzenes have been prepared, the study of the rate of hydrogenation on platinum of this complete series was undertaken.

Experimental

***o*-Xylene, *m*-xylene, *p*-xylene, mesitylene, durene, isodurene, hexamethylbenzene and *p*-methylisopropylbenzene** were all obtained from the Eastman Kodak Company, and were Eastman best grade materials. **Pentamethylbenzene** was obtained from Eastman in a practical grade. **Pseudocumene** was prepared from 4-amino-1,3-dimethylbenzene according to the method described by Smith and Lund.[5] **Hemimellitene** was prepared by the method of Smith and Spillane.[6] **Prehnitene** was prepared by a Jacobsen synthesis from pentamethylbenzene.[7]

The *o*-xylene, *m*-xylene and *p*-methylisopropylbenzene were purified by fractionation in a five-foot spiral column. *p*-Xylene, mesitylene, pseudocumene, hemimellitene, isodurene and prehnitene were purified by fractionation in a 25-cm. Vigreux column. Durene was purified by two recrystallizations from methanol, and hexamethylbenzene by two recrystallizations from a methanol–benzene solvent. Pentamethylbenzene was purified by fractional crystallization from methanol. Table I gives the appropriate physical constants of the samples used for hydrogenation purposes. The distillation temperatures in this table represent the temperature readings in the still-heads corrected to 760 mm. pressure by means of Trouton's rule and the Clausius–Clapeyron equation.

After each hydrogenation was complete, the platinum catalyst was removed from the acetic acid solution by filtration. Water was added to the solution, and the hydrocarbon layer (with the exception of durene where the layer was simply separated) was steam-distilled. The hydrocarbon layer was washed with sodium bicarbonate solution and then fractionated in the 25-cm. Vigreux column. Physical constants for the products are also given in Table I.

As in earlier work, the acetic acid solvent was prepared by fractionation in a five-foot, helix-packed still, and the platinum catalyst was prepared by standard methods.[8] The hydrogenations were carried out in a low-pressure Parr catalytic reduction apparatus in the manner already described.[1] For most runs, 0.05 mole of hydrocarbon, 0.2 g. of platinic oxide and 50 ml. of acetic acid were used. However, for isodurene, prehnitene, pentamethylbenzene and hexamethylbenzene, only 0.025 mole of hydrocarbon was hydrogenated. For hexamethylbenzene, 0.4 g. of catalyst was employed.

Experimental Calculations and Results

It has already been established[1,2] that such hydrogenations are first order with respect to

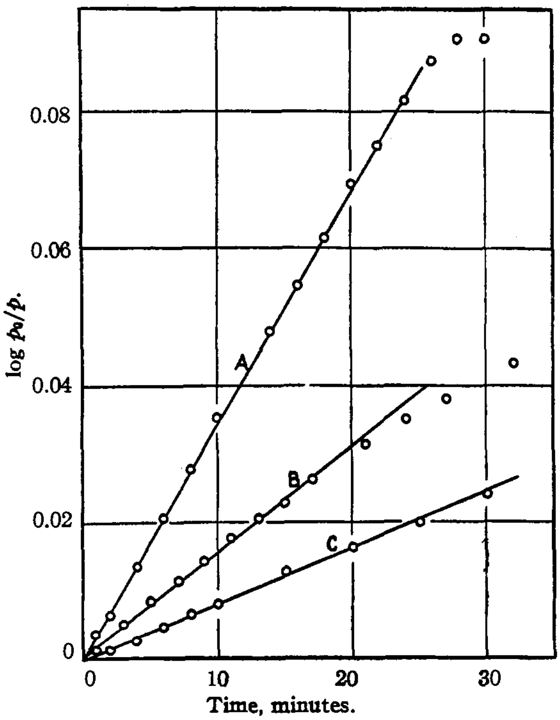

Fig. 1.—Hydrogenation plots for polymethylbenzenes. For each run, 0.2 g. of PtO_2, 50 ml. of acetic acid, and 64.3 lb. H_2 pressure were used; for A and B, 0.05 mole and for C, 0.025 mole of hydrocarbon hydrogenated: A, *p*-xylene; B, pseudocumene; C, isodurene.

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(1) Smith, Alderman and Nadig, THIS JOURNAL, 67, 272 (1945).

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

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

(4) Lozovoy and Diakova, *J. Gen. Chem.* (U. S. S. R.), 9, 895 (1939).

(5) Smith and Lund, THIS JOURNAL, 52, 4144 (1930).

(6) Smith and Spillane, *ibid.*, 62, 2639 (1940).

(7) Smith and Lux, *ibid.*, 51, 2994 (1929).

(8) Adams, Voorhees and Shriner, "Org. Syntheses," 8, 92 (1928).

TABLE I

	Compound	n^{20}_D	Distn. head temp., °C. (760 mm.)	M. p. (cor.), °C.	Refs.
		Reactants			
1	*o*-Xylene	1.5047	144.2–144.3		*a*
2	*m*-Xylene	1.4964	139.0		*a*
3	*p*-Xylene	1.4950	138.4		*a*
4	Hemimellitene	1.5130	176.4		*b*
5	Pseudocumene	1.5036	169.5–169.6		*c*
6	Mesitylene	1.4974	164.9–165.0		*a, d*
7	Prehnitene	1.5197	93.6 (25 mm.)		*e*
8	Isodurene	1.5123	110.6–110.7 (50 mm.)		*f*
9	Durene			79.8	*a, g*
10	Pentamethylbenzene			53.5–54	*a, g*
11	Hexamethylbenzene			166.6	*a, g*
12	*p*-Cymene	1.4881	180.4		*a, h*
		Products			
1	1,2-Dimethylcyclohexane	1.4334–1.4345	128.7–129.5		*a, i, j*
2	1,3-Dimethylcyclohexane	1.4239–1.4252	121.0–122.0		*a, i, j*
3	1,4-Dimethylcyclohexane	1.4260–1.4282	122.6–123.7		*a, i, j*
4	1,2,3-Trimethylcyclohexane	1.4392–1.4396	151.0–151.2		*i*
5	1,2,4-Trimethylcyclohexane	1.4329–1.4336	145.7–146.3		*i, j*
6	1,3,5-Trimethylcyclohexane	1.4263–1.4268	138.7–139.1		*a, i*
7	1,2,3,4-Tetramethylcyclohexane	1.4487–1.4500	175.7–176.4		*e*
8	1,2,3,5-Tetramethylcyclohexane	1.4401–1.4413	168.0–168.6		*i*
9	1,2,4,5-Tetramethylcyclohexane	1.4450–1.4466	172.6–174.5		*a, i*
10	Pentamethylcyclohexane	1.4538–1.4554	194.1–195.7		*a*
11	Hexamethylcyclohexane	*k*	221.6–222.0	*k*	*a*
12	*p*-Menthane	1.4404–1.4406	172.2–172.6		*a, j*

[a] Lozovoy, Diakova and Stepantseva, *J. Gen. Chem.* (U. S. S. R.) **7**, 1119 (1937). [b] Smith and Spillane, ref. 6. [c] Smith and Lund, ref. 5. [d] Smith and Cass, THIS JOURNAL, **54**, 1606 (1932). [e] Mitchell, *ibid.*, **55**, 4276 (1933). [f] Smith and Cass, *ibid.*, **54**, 1609 (1932). [g] Smith and Macdougall, *ibid.*, 51, 3001 (1929). [h] Welsh and Hennion, *ibid.*, **63**, 2604 (1941). [i] Eisenlohr, *Fortschr. Chem.*, **18**, 521 (1925). [j] Skita and Shenk, *Ber.*, **55**, 144 (1922). [k] The first 25% of distillate gave n^{20}_D 1.4660–1.4673. The remaining material crystallized on the refractometer. The whole distillate melted around 24°.

hydrogen pressure, zero order with respect to the concentration of hydrocarbon, and directly proportional to the amount of platinum catalyst present. These facts were checked for several of the polymethylbenzenes.

Rate constants were calculated by plotting log p_0/p against time, and multiplying the slope of the line thus obtained by 2.303. Figure 1 shows typical plots for hydrogenation of the polymethylbenzenes. Table II gives standard hydrogenation constants (referred to 1 g. of standard platinic oxide) for the compounds included in this research. Constants for benzene, toluene, and isopropylbenzene are included for comparison purposes.

TABLE II

STANDARD HYDROGENATION RATE CONSTANTS FOR POLYMETHYLBENZENES AND RELATED COMPOUNDS

Compound	$k^{\circ}_{W} \times 10^4$
Benzene	650[a]
Toluene	402[a]
o-Xylene	208
m-Xylene	320
p-Xylene	420
Hemimellitene (1,2,3-trimethylbenzene)	93
Pseudocumene (1,2,4-trimethylbenzene)	189
Mesitylene (1,3,5-trimethylbenzene)	375
Prehnitene (1,2,3,4-tetramethylbenzene)	63
Isodurene (1,2,3,5-tetramethylbenzene)	74
Durene (1,2,4,5-tetramethylbenzene)	118
Pentamethylbenzene	23
Hexamethylbenzene	1.3
Isopropylbenzene	216[a]
p-Cymene (*p*-methylisopropylbenzene)	279

[a] Data from Smith and Pennekamp, ref. 2.

Discussion

An inspection of Table II immediately reveals the fact that the number of methyl substituents is not the only rate-controlling factor. In fact, *p*-xylene with two substituents hydrogenates faster than toluene which has only one. Similarly, mesitylene hydrogenates more rapidly than either *o*-xylene or *m*-xylene, and durene faster than hemimellitene. The results with mesitylene and the xylenes are in line with those of Adams and Marshall[3] on these compounds.

Table III gives a comparison of the relative rates of hydrogenation of members of this series as found by Lozovoy and Diakova,[4] and as found in this research.

The formula of Lozovoy and Diakova holds as well for this research as it does for their results if only those compounds which have all methyl sub-

TABLE III

Hydrocarbon	Relative rate of hydrogenation This research	Relative rate of hydrogenation Lozovoy and Diakova[4]	From the formula $v_n = 2^{-n}v$
Benzene	100	100	100
Toluene	62	50	50
o-Xylene	32	24	25
m-Xylene	49	23	25
p-Xylene	65	31	25
Hemimellitene	14		12.5
Pseudocumene	29		12.5
Mesitylene	58	10	12.5
Prehnitene	10		6.3
Isodurene	11		6.3
Durene	18	3.8	6.3
Pentamethylbenzene	3.5	0.5	3.2
Hexamethylbenzene	0.2	Too small to record	1.6
Isopropylbenzene	33		50
p-Cymene	43	33	25

stituents adjacent to each other are considered. However, when all of the polymethylbenzenes are included, no such agreement is found.

Perhaps the most striking fact which is apparent in Table II is the role of symmetrical substitution in governing the rate of hydrogenation. Such an effect cannot be attributed to the influence of ortho, meta and para substitution since for the dimethylbenzenes *p*-xylene is much the fastest, while for the trimethylbenzenes the meta-substituted compound, mesitylene, is the fastest. One might tend to explain this symmetry effect on the basis of the Eyring theory of reaction rates. According to this theory, the reaction rate is directly proportional to the symmetry numbers of the reactants, and inversely proportional to the symmetry number of the activated complex. If one assumes that symmetry is lacking in the activated complex, a reasonable explanation of some of the results with the polymethylbenzenes might be obtained.

However, there is no assurance that symmetry is destroyed in the activated complex. Furthermore, *p*-cymene hydrogenates more readily than isopropylbenzene, and yet the symmetry of the two is the same. Also the faster hydrogenation of *m*-xylene than *o*-xylene, and of pseudocumene than hemimellitene cannot be explained in this manner.

The variation in rate of hydrogenation of this series might be caused by better fit to the catalytic surface of those compounds which have fewer methyl substituents. It is, however, rather difficult to see why on this basis mesitylene should hydrogenate faster than *m*-xylene, or *p*-cymene faster than isopropylbenzene. While such an explanation cannot be excluded, it does not appear very probable.

In earlier papers it was suggested that steric hindrance by the saturated groups on the benzene ring to the approach of hydrogen might explain certain results. This same explanation is also in general agreement with the data of Table II. Thus, when a polymethylbenzene has all of its substituent groups in adjacent positions, the benzene nucleus will be adsorbed with the methyl groups away from the metal surface, and these will form a layer through which the hydrogen must pass. However, when the groups are more symmetrically placed, the layer of saturated groups would necessarily be less continuous, and this would facilitate the approach of the hydrogen. This explanation accounts for the generally decreased rate of hydrogenation with increased number of substituents. It also accounts for the faster rate of hydrogenation of *p*-cymene when compared with isopropylbenzene. The isopropylbenzene would be adsorbed with its isopropyl group away from the active catalytic surface. However, with *p*-cymene, the para methyl group prevents such adsorption; instead, the saturated groups would tend to orient themselves away from the catalyst, the adsorption being similar to that of *p*-xylene.

Configuration of the Products.—An inspection of the latter half of Table II shows a considerable range in both the refractive index and the distillation temperature of most of these products. Since various *cis–trans* isomers are possible for the polymethylcyclohexanes and related compounds, it is believed that these variations are due to the presence of isomers rather than to other causes. The values given for the physical constants of these products represent readings taken over the middle 80% of the hydrogenated hydrocarbon.

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Summary

A study has been made of the kinetics of the catalytic hydrogenation of the polymethylbenzenes and of *p*-cymene. The reactions were carried out at low pressures, in acetic acid solution, using Adams platinum catalyst. First-order reaction rate constants, all referred to one gram of standard platinum oxide, are given.

It has been demonstrated that, while increased methyl substitution does generally decrease the rate of hydrogenation of the benzene nucleus, the position of substitution is also important. For compounds having the same number of methyl substituents, symmetrically substituted ones react the fastest.

The results have been compared with those of Lozovoy and Diakova,[4] and it has been demonstrated that their formula is not generally applicable.

The factors influencing the relative rates of hydrogenation of this group of compounds were discussed.

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