

important in governing the rate, since the hydrogen must pass through the layer of residues extending away from the catalytic surface in order to be adsorbed and subsequently react. The rate at which hydrogen is adsorbed on the catalyst may be rate-determining for the hydrogenation process. This is in line with the first-order dependence on hydrogen pressure, and would explain the fact that substituents near the phenyl groups slow down the hydrogenation process. If one assumes that, in molecules such as diphenylacetic acid or triphenylacetic acid, only one phenyl group may be adsorbed at any given instant, the slow rates observed for these compounds, and also the equality of the rates for diphenylacetic and phenylcyclohexylacetic acids are understandable.

Linstead¹⁰ noted that the "open chain" derivatives of diphenic acid all hydrogenate in the coiled or pseudo-tricyclic phase, but was unable to explain this fact. The conception of edgewise adsorption with the carboxyl groups oriented away from the catalyst might explain this result.

The picture of hydrogenation advanced in the foregoing discussion should be regarded only as a tentative hypothesis. It is advanced since it does explain the rates of hydrogenation reported in this and in the two following articles.

Summary

A study has been made of the kinetics of the catalytic hydrogenation of phenyl-substituted aliphatic acids. The reactions were carried out in acetic acid solution using Adams platinum catalyst.

It was shown that the reaction rate is first order with respect to hydrogen pressure, zero order with respect to the concentration of phenyl-substituted acid, and directly proportional to the amount of catalyst. First-order reaction rate constants, all referred to one gram of platinum oxide, are given for eleven acids.

The factors influencing the relative rates of catalytic hydrogenation are discussed.

KNOXVILLE, TENN.

RECEIVED JUNE 17, 1944

[CONTRIBUTION NO. 42 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Catalytic Hydrogenation of the Benzene Nucleus. II. The Hydrogenation of Benzene and Mono-alkylbenzenes

BY HILTON A. SMITH AND E. F. H. PENNEKAMP

In the first paper of this series,¹ a study of the hydrogenation of a number of phenyl-substituted aliphatic acids was described. The purpose of the present paper is to report further kinetic studies involving the catalytic hydrogenation on platinum of a series of mono-alkylbenzenes. Since these latter compounds are liquids, their purity cannot be established readily by melting points, and, of course, neutral equivalents cannot be used. Instead, one must rely on distillation ranges and refractive indices.

Experimental

Benzene was purified by fractionation of thiophene-free Merck reagent benzene in a five-foot spiral column.

Toluene was prepared from Eastman Kodak Co. practical grade material by the method described by Fieser.² The hydrocarbon from this treatment was fractionated in the five-foot spiral column.

Ethylbenzene, isopropylbenzene and *n*-butylbenzene were purified by fractionation of the best grade of Eastman chemicals in the five-foot spiral column.

n-Propylbenzene, *s*-butylbenzene, and *t*-butylbenzene were obtained from the best grade of Eastman chemicals by fractional distillation in a 25-cm. Vigreux column.

n-Amylbenzene, isoamylbenzene, *n*-hexylbenzene, *n*-heptylbenzene, and *n*-nonylbenzene were prepared by a Fittig synthesis following the method outlined by Gattermann and Wieland.³ These preparations were fractionated in the 25-cm. column.

Several methods were tried in the preparation of *iso*-butylbenzene, none of which was satisfactory. The material used for hydrogenation purposes was prepared by the method outlined by Wreden,⁴ but the compound certainly cannot be regarded as pure.

Table I gives the distillation range and refractive index of the compounds used for hydrogenation runs. The distillation temperatures represent the temperature readings in the still-heads, all of which were of a total reflux, variable take-off construction. These readings were corrected to 760 mm. pressure by means of Trouton's rule and the Clausius-Clapeyron equation.

After each hydrogenation was complete, the acetic acid solution was separated from most of the catalyst by decantation. Water was added to the solution, and the hydrocarbon layer (with the exception of *n*-nonylcyclohexane) was steam-distilled. The hydrocarbon layer in the distillate was washed with sodium bicarbonate solution, and then fractionated in the 25-cm. Vigreux column.

Steam distillation was found to be impractical for the *n*-nonylcyclohexane. This compound was separated from the acetic acid solution by dilution with water, and subsequently distilled.

Refractive indices for the products, together with their corrected distillation ranges, are also given in Table I.

As in earlier work, the acetic acid solvent for the hydrogenation runs was prepared by fractionation, and the platinum catalyst was prepared by standard methods.⁵ The hydrogenations were carried out in a low-pressure Parr catalytic reduction apparatus in the manner already described.¹

Experimental Calculations and Results

It was established, as in previous work, that the hydrogenation reaction was first order with respect to hydrogen pressure, zero order with

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

(2) Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., 1941, p. 364.

(3) Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Company, New York, N. Y., 1932, p. 107.

(4) Wreden and Znatovics, *Ber.*, **9**, 1606 (1876).

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

TABLE I
 PHYSICAL CONSTANTS OF REACTANTS AND PRODUCTS

Compound	n_{20}^D	Distillation head temperature (corrected to 760 mm.)	References to previously reported compounds
Reactants			
1 Benzene	1.5002	79.9	
2 Toluene	1.4947	110.8	
3 Ethylbenzene	1.4955	136.5	
4 <i>n</i> -Propylbenzene	1.4899	158.9-159.1	<i>a</i>
5 <i>n</i> -Butylbenzene	1.4891	183.7	<i>a</i>
6 <i>n</i> -Amylbenzene	1.4874	205.3-205.5	<i>a</i>
7 <i>n</i> -Hexylbenzene	1.4855	225.6-225.9	<i>a</i>
8 <i>n</i> -Nonylbenzene	1.4838	281.7-282.2	<i>b</i>
9 <i>i</i> -Propylbenzene	1.4907	154.7	<i>c</i>
10 <i>i</i> -Butylbenzene	1.4852	172.8-173.1	<i>d</i>
11 <i>s</i> -Butylbenzene	1.4890	174.5-175.2	<i>c</i>
12 <i>t</i> -Butylbenzene	1.4922	169.3-169.4	<i>c</i>
13 <i>i</i> -Amylbenzene	1.4899	198.9-199.0	<i>c</i>
Products			
1 Cyclohexane	1.4256	80.9	<i>e</i>
2 Methylcyclohexane	1.4225	101.4-101.6	<i>e</i>
3 Ethylcyclohexane	1.4324	131.8-132.0	<i>e</i>
4 <i>n</i> -Propylcyclohexane	1.4363	156.7	<i>e</i>
5 <i>n</i> -Butylcyclohexane	1.4403	181.3-181.4	<i>e</i>
6 <i>n</i> -Amylcyclohexane	1.4430	203.7-203.9	<i>e</i>
7 <i>n</i> -Hexylcyclohexane	1.4454	224.6-224.7	<i>f</i>
8 <i>n</i> -Nonylcyclohexane	1.4520	281.4-281.6	<i>g</i>
9 <i>i</i> -Propylcyclohexane	1.4403	154.3-154.9	<i>e</i>
10 <i>i</i> -Butylcyclohexane	1.4380	171.5-171.6	<i>e</i>
11 <i>s</i> -Butylcyclohexane	1.4454	179.6-179.8	<i>e</i>
12 <i>t</i> -Butylcyclohexane	1.4463	171.7-171.8	<i>e</i>
13 <i>i</i> -Amylcyclohexane	1.4418	196.5-196.6	<i>e</i>

^a Schmidt, Hopp and Schoeller, *Ber.*, **72**, II, 1895 (1939). ^b Shen, Ju and Wood, *J. Inst. Petroleum*, **26**, 475-487 (1940). ^c McKenna and Sowa, *THIS JOURNAL*, **59**, 471 (1937). ^d Schramm, *Monatsh.*, **9**, 616 (1888). ^e Signaigo and Cramer, *THIS JOURNAL*, **55**, 3331 (1933). ^f Bourguet, *Bull. soc. chim.*, [4] **41**, 1475 (1927). ^g Not previously reported.

respect to the concentration of hydrocarbon, and directly proportional to the amount of catalyst

 TABLE II
 EFFECT OF VARIABLES ON RATE OF HYDROGENATION OF BENZENE HYDROCARBONS

For all runs, 50 ml. of acetic acid was used as solvent.

Compound	Moles	Grams of catalyst	Initial pressure	$k_{20} \times 10^3$ (reciprocal minutes)	$k_{20}^\circ \times 10^{3a}$
Benzene	0.05	0.2000	64.4	13.01	65.05
Benzene	.10	.2000	64.4	12.84	64.2
Benzene	.05	.1000	64.4	6.35	63.5
Benzene	.05	.2000	39.3	11.96	59.8
Toluene	.05	.2000	64.4	8.03	40.15
Toluene	.05	.1000	64.4	3.76	37.6
<i>t</i> -Butylbenzene	.05	.2000	64.4	3.11	15.55
<i>s</i> -Butylbenzene	.025	.2000	64.3	2.99	14.95
<i>i</i> -Butylbenzene	.022	.2000	32.4	2.96	14.80

^a k_{20}° represents rate constant referred to one gram of standard platinum oxide as catalyst.

used. This is demonstrated for several different compounds in Table II.

Since benzene hydrogenates faster than any compound previously studied, a check was made on the effect of the rate of shaking on its rate of hydrogenation. It was found that a change from 180 to 250 cycles per minute in the shaking had no effect on the rate of hydrogenation. A few runs were also made at 20 and 50°. These indicated an activation energy for the hydrogenation of benzene of around 8000 calories per mole, which is the same as that found for phenyl-substituted aliphatic acids.

The values of the reaction rate constants listed in Table II and also those listed in Table III were calculated by plotting $\log p_0/p$ against time, and multiplying the slope of the line by 2.303. Figure 1 shows typical plots for hydrogenation of the mono-alkylbenzenes, and Table III gives the standard hydrogenation rate constants for the compounds included in this research.

 TABLE III
 STANDARD HYDROGENATION RATE CONSTANTS FOR MONO-ALKYLBENZENES

Compound	$k_{20}^\circ \times 10^4$ (reciprocal minutes)
Benzene	650
Toluene	402
Ethylbenzene	294
<i>n</i> -Propylbenzene	265
<i>n</i> -Butylbenzene	244
<i>n</i> -Amylbenzene	263
<i>n</i> -Hexylbenzene	250
<i>n</i> -Nonylbenzene	252
<i>i</i> -Propylbenzene	216
<i>i</i> -Butylbenzene	150
<i>s</i> -Butylbenzene	189
<i>t</i> -Butylbenzene	166
<i>i</i> -Amylbenzene	274

Discussion

Table III is particularly instructive when compared with the rate of hydrogenation of phenyl-substituted aliphatic acids.¹ In that series, all acids which were terminal-substituted normal aliphatic acids had the same rate constants. For the benzene series, the rate of hydrogenation of the parent member is much the fastest, with toluene considerably slower. Higher normal-alkylbenzenes all have much the same rate. Furthermore, this latter rate is about the same as for the series of phenyl-substituted normal-aliphatic acids.

This is readily explained on the basis of steric hindrance to the approach of hydrogen to the catalyst surface. When the adsorbed hydrocarbon is pictured with the benzene nucleus adsorbed on the platinum surface, and the saturated residue extended outward, it is easy to see that there will be none of this type of hindrance for the molecules of benzene itself. For toluene, the methyl groups will hinder the hydrogen, while for

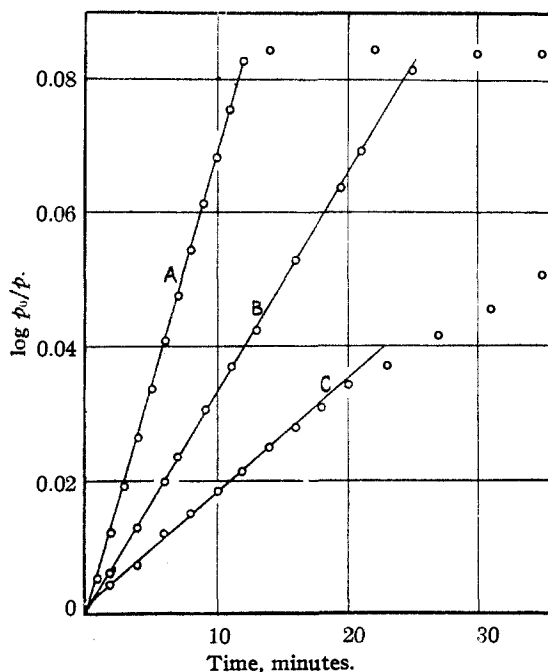


Fig. 1.—Hydrogenation plots for benzene series. For each run, 0.05 mole of hydrocarbon, 0.2 g. of PtO_2 , 50 ml. of acetic acid, and 64.3 lb. initial hydrogen pressure were used: A, benzene; B, toluene; C, *s*-butylbenzene.

ethylbenzene, still greater hindrance will be found. However, beyond that point, little change will be expected. Furthermore, the hindrance offered by the carboxyl group will be much the same as that for ethylbenzene and higher members of the benzene series. It is rather hard to understand how these results can be explained as caused by inductive influences, since the effect of carboxyl and alkyl groups would be quite different.

It may also be noted that substitution in the position alpha to the benzene ring cuts down the rate of hydrogenation, although the effect does not seem to be as marked for the benzene series as for the phenyl-substituted aliphatic acids.

A comparison of these results with those previously obtained by Lozovoy and Diakova⁶ reveals much similarity. These workers hydrogenated a series of benzene hydrocarbons on a nickel-alumina (Zelynsky) catalyst, at a pressure of 35 atmospheres, and a temperature of 150°. The reaction was followed by withdrawing samples

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

of the reaction mixture at definite time intervals, and analyzing by means of refractive index readings. Under these conditions, the catalytic reduction is in a transition period from a zero to first order dependence on hydrogen pressure (zero order below 110°, first order above 200°).⁷

Table IV gives a comparison of the relative rates of hydrogenation of several benzene hydrocarbons as found by Lozovoy and Diakova, and as found in this research.

TABLE IV

Hydrocarbon	Relative rate of hydrogenation	
	This research	Lozovoy and Diakova ⁶
Benzene	100	100
Toluene	62	50
Ethylbenzene	45	43
<i>n</i> -Propylbenzene	41	45
<i>n</i> -Butylbenzene	38	44
<i>n</i> -Amylbenzene	40	41
<i>n</i> -Hexylbenzene	38	
<i>n</i> -Octylbenzene		40
<i>n</i> -Nonylbenzene	39	

The agreement between these results is rather noteworthy considering the great difference in experimental conditions and in method. It not only serves to confirm the method here used, which is much simpler and more generally applicable than that used by Lozovoy and Diakova, but also indicates that the results may be extrapolated over a wide range of catalytic conditions.

More work along these lines is now in progress.

Summary

A study has been made of the kinetics of the catalytic hydrogenation of a series of mono-alkylbenzenes. 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 for 13 compounds.

The relative rates of hydrogenation were compared with those previously obtained for a series of phenyl-substituted aliphatic acids, and also with a series of benzene hydrocarbons studied by Lozovoy and Diakova⁶ under considerably different experimental conditions.

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

KNOXVILLE, TENN.

RECEIVED JUNE 17, 1944

(7) Lozovoy and Diakova, *ibid.*, **7**, 2977 (1938).