used for compounds III, IV and V. Method B[2] was used in the other cases. In the isolation of I, when methanol was added to the extract residue, 1.5 g. (7.1%) of yellow needles formed, identified as VII. The filtrate yielded no other crystalline product. Distillation gave fractions boiling in the ranges: 95° (35 mm.) (phenol) about 10 g.; 80–110° (1 mm.) (mostly phenyl benzoate), about 15 g.; 110–150° (1 mm.). The last fraction was redistilled to give I.

The pyrrolidine-enamine procedure of Stork[7] was employed. Cyclopentanone pyrrolidine-enamine (0.2 mole, 27.4 g.) in dioxane was treated with benzoyl chloride (0.1 mole). The mixture was stirred at room temperature and then at reflux. The product of this reaction was hydrolyzed and the organic portion distilled as above to give 10.0 g. (53%) of I. The copper chelate IX formed in 83% yield and melted at 225–228°.

The residue from the distillation on crystallization from methanol gave yellow needles, VIII, m.p. 121–122°. Analytical data are listed in Table I.

Percentage Enol Determination.—The method of Smith and Shriner[25] was used with the reported[2] modification for equilibriation in absolute methanol.

Measurement of Spectra.—The ultraviolet spectra were determined using a Cary recording spectrophotometer, model 11. Procedure used was according to the manufacturer's instructions. Matched quartz cells were used. The spectrophotometer was housed in a constant temperature room at 28°. The concentration employed was 10^{-4} molar in all cases. The solutions were freshly prepared and, for equilibrium data, were stored in the dark. Data obtained are listed in Table IV.

The infrared spectra were measured using a Perkin–Elmer model 21 double-beam recording spectrophotometer, with a sodium chloride prism. The control settings were maintained constant at: resolution, 926; response 1; gain, 5; speed, 4; suppression, 4. The concentration used was 10 mg./ml. Matched 1-mm. cells were used in standard double beam operation. Data obtained are listed in Table III.

(25) W. T. Smith, Jr., and R. L. Shriner, "The Examination of New Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 101.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE, KNOXVILLE, TENN.]

Competitive Catalytic Hydrogenation of Benzene, Toluene and the Polymethylbenzenes on Platinum

BY CHARLES P. RADER AND HILTON A. SMITH

RECEIVED SEPTEMBER 13, 1961

The competitive catalytic hydrogenation of benzene, toluene and all of the possible polymethylbenzenes has been studied on a platinum catalyst. The relative ease of adsorption of each of these hydrocarbons on the active catalyst surface has been measured by a method based on Langmuir kinetics. It has been found that the relative ease of adsorption does not necessarily parallel the relative rates of reduction of the individual hydrocarbons. The ease of adsorption decreases with increasing nuclear substitution except in the case of hexamethylbenzene which is slightly more strongly adsorbed than pentamethylbenzene. For a given isomeric set of polymethylbenzenes, the ease of adsorption always decreases with increasing symmetry of substitution. It is suggested that the relative ease of adsorption may result from the relative amount of steric strain arising from the flatwise adsorption of the nucleus on the active surface.

Introduction

The ease with which the benzene nucleus is reduced on a platinum surface is known to be a function of the amount and symmetry of nuclear substitution. On Adams platinum catalyst the rate of hydrogenation decreases with increasing nuclear substitution and increases with symmetry of substitution. Much of this work has been previously summarized.[1]

Smith and Pennekamp[2] hydrogenated benzene, toluene and all of the polymethylbenzenes over Adams platinum in glacial acetic acid at room temperature and hydrogen pressures of 1–4 atmospheres. They found that the reduction rate was zero order in the concentration of hydrogen acceptor and first order in hydrogen pressure under conditions where diffusion processes did not affect the velocity of the reaction. The rate constants for the reduction of these hydrocarbons clearly reveal a decrease in the rate of hydrogenation as nuclear substitution is increased, and within any group of isomers, an increase in rate as the symmetry of substitution increases. These effects upon the reduction rate have also been observed in the hydrogenations on platinum of the methyl

and polymethylbenzoic acids,[3] the methoxybenzenes[4] and the hydroxybenzenes.[5]

It has been suggested that the relative reduction rate depends upon the steric interference caused by the methyl substituents preventing ready attack of the hydrogen on the benzene nucleus[6] or by steric interference by the methyl groups with activated adsorption of the benzene ring on the active catalyst surface.[1] This latter type of hindrance should be reflected in the relative ease of adsorption of various methylbenzenes on the active portion of the catalyst surface. As the steric hindrance is increased the ease of adsorption should decrease. Thus, a measurement of the relative ease of adsorption of benzene and its methyl substituted derivatives should enable one to examine the relation between steric influence on adsorption and reduction rate.

The basic purpose of this research was, then, to measure the relative ease of adsorption of benzene, toluene and the polymethylbenzenes on the active platinum surface and to compare the relative ease of adsorption with the relative reduction rates

(1) H. A. Smith in P. H. Emmett, "Catalysis," Vol. V, Reinhold Publishing Corp., New York, N. Y., 1957, p. 175.

(2) H. A. Smith and E. F. H. Pennekamp, J. Am. Chem. Soc., 67, 279 (1945).

(3) H. A. Smith and J. A. Stanfield, ibid., 71, 81 (1949).

(4) H. A. Smith and R. G. Thompson, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 727.

(5) H. A. Smith and B. L. Stump, J. Am. Chem. Soc., 83, 2739 (1961).

(6) H. A. Smith, D. M. Alderman and F. W. Nadig, ibid., 67, 272 (1945).

of these hydrocarbons. This relationship should yield a more basic knowledge of the dependence of the reduction rate upon the facility with which the benzene nucleus may be chemisorbed on the active surface.

Wauquier and Jungers[7] have determined the relative ease of adsorption of benzene, toluene and the xylenes on Raney nickel at 170° by means of competitively reducing various binary mixtures of these hydrocarbons. The ease of adsorption on the active surface was found to be benzene > toluene > o-xylene > m-xylene ≅ p-xylene, whereas the relative reduction rates of the individual hydrocarbons were benzene > toluene > p-xylene > m-xylene > o-xylene. In a previous investigation in this Laboratory[8] various binary mixtures of the xylenes were reduced competitively over platinum under the same experimental conditions as had been used by Smith and Pennekamp.[2] The rate data from these reductions demonstrated that the ease of adsorption of the xylenes on the active surface was o-xylene > m-xylene > p-xylene. This is the exact reverse of the relative reduction rates of the individual xylenes. An equation was derived which predicted a theoretical increase in the slope of the log hydrogen pressure *versus* time plots for the reduction of binary mixtures of the xylenes. Such an increase was observed experimentally.

Experimental

Commercial preparations of platinum oxide were obtained from the Baker Catalyst Co. of Newark, N. J. The catalyst was sifted through a 325 mesh sieve and mechanically agitated for several days to ensure sample uniformity. Du Pont reagent grade glacial acetic acid, which was used as solvent in all hydrogenations, was fractionally distilled through an 8-ft. Vigreux column. Hydrogen was obtained from Welding Gas Products Co. of Chattanooga, Tenn. It was used directly from the cylinder since previous experiments had shown further purification to be unnecessary.

Fisher certified reagent grade benzene was fractionally distilled at a reflux ratio of 30:1 in a 12-ft. column packed with glass helices. The fraction used for hydrogenation studies distilled at a constant head temperature of 79.6° (750 mm.), n^{25}_D 1.4981. Fisher certified reagent grade toluene was distilled through the same column as was used in the distillation of benzene. A middle fraction was collected at a reflux ratio of 30:1 and a head temperature of 109.7°C (742 mm.). The sample had a refractive index, n^{25}_D, of 1.4941.

The o-xylene used in this research was the Oronite commercial grade chemical. It had previously been purified by fractional distillation, azeotropic distillation with 2-methoxyethanol,[9] and subsequent fractional distillation. A pure sample was obtained by a final fractionation at a reflux ratio of 20:1 through the column used in the purification of benzene and toluene. The boiling point of the sample was 143.6° (744 mm.), n^{25}_D 1.5029. The m-xylene sample used in hydrogenation studies was Eastman white-label grade; it was purified by the previously reported procedure of selective sulfonation.[8] After a final fractionation through a 10-ft. Vigreux column at a reflux ratio of 80:1, the sample had a boiling point of 138.4° (743 mm.), n^{25}_D 1.4946. Eastman white-label grade p-xylene had previously been distilled. A second fractionation through a 10-ft. Vigreux column at a reflux ratio of 60:1 gave a constant-boiling sample at a head temperature of 137.4° (741 mm.), n^{25}_D 1.4933.

Hemimellitene and pseudocumene were samples synthesized by Shacklett[10] and purified by conversion to the respective sulfonic acids, recrystallization, and hydrolysis to the hydrocarbons. Fractionation through a 10-ft. Vigreux column at a 75:1 reflux ratio yielded a hemimellitene sample with a boiling point of 175.1° (741 mm.), n^{25}_D 1.5115. The pseudocumene sample was fractionated through a 12-ft. glass-helix-packed column at a reflux ratio of 80:1; b.p. 168.6° (744 mm.), n^{25}_D 1.5024. The mesitylene sample used in this work had been prepared by the well-known procedure of Adams and Hufferd[11] and purified by sulfonation, recrystallization, steam distillation and fractional distillation. Distillation through a 10-ft. Vigreux column at a reflux ratio of 50:1 gave a product, b.p. 164.0° (746 mm.), n^{25}_D 1.4969.

Prehnitene, isodurene and durene were obtained from the synthetic work of Shacklett.[10] The prehnitene sample was distilled through a 10-ft. Vigreux column at a reflux ratio of 80:1 and a constant head temperature of 204.0° (743 mm.). Its refractive index, n^{25}_D, was 1.5181. The sample of isodurene was fractionated through the same column and at the same reflux ratio as those used in the purification of prehnitene. It distilled at a constant head temperature of 197.5° (750 mm.), n^{25}_D 1.5110. A pure sample of durene which melted at 79.4–79.9° was obtained by recrystallizing Shacklett's preparation[10] according to the procedure of Smith.[11a]

Eastman white-label grade pentamethylbenzene was successively recrystallized from redistilled absolute alcohol, reagent grade toluene, and redistilled reagent grade methanol. The product used in hydrogenation studies had a melting point of 53.5–55.1°. Vapor-phase chromatographic analysis showed the sample to be free from hexamethylbenzene and tetramethylbenzenes, which are the expected contaminants of the pentamethylbenzene. Hexamethylbenzene was prepared according to the procedure of Cullinane, Chard and Dawkins.[12] After two recrystallizations from an ethanol–benzene mixture and a final one from reagent grade benzene, a pure sample melting at 166.1–166.8° was obtained. Vapor-phase chromatographic analysis showed it to be free of contaminants.

A Parr low-pressure reduction apparatus modified as reported previously[8] was used in all hydrogenations. The reduction vessel was an ordinary 6 oz. Coca Cola bottle. This gave the reaction system a total volume of 0.2980 l. The general procedure for the hydrogenation reactions was the same as that reported previously.[8] The reaction temperature was 30.00 ± 0.05° for all reductions, and the hydrogen pressure range was 35–60 p.s.i. Care was taken to ensure that the reaction bottle was shaken rapidly enough for the reduction rate to be unaffected by diffusion processes.

Reductions were carried out with each of the individual hydrocarbons and various binary mixtures of them. For the reduction of the individual hydrocarbons, 10.00 ml. of glacial acetic acid and 0.500 ml. of liquid hydrocarbon were used. Approximately 0.5-g. samples of the solid hydrocarbons were used for each run. Catalyst weights were 0.03 to 0.10 g. for benzene, toluene and the xylenes; for the less reactive polymethylbenzenes, catalyst weights as large as 1.0 g. were employed.

The reductions of the binary mixtures of hydrocarbons were carried out with a glacial acetic acid solution of the two aromatic hydrocarbons concerned. The concentration of each hydrocarbon was approximately 0.2 molar. For each binary mixture a series of reductions was performed under precisely the same experimental conditions, but to different degrees of completion. The reaction mixture from each reduction was diluted with reagent grade glacial acetic acid and analyzed spectrophotometrically for the concentrations of the two hydrocarbons.

The spectrophotometric method was an adaptation of that of Tunnicliff, Brattain and Zumwalt.[13] To prevent light

(7) J. P. Wauquier and J. C. Jungers, *Bull. soc., chim. France*, 1280 (1957).

(8) H. A. Smith and C. P. Rader, "Actes der Deuxieme Congres International de Catalyse," Paris, France, 1960, p. 1213.

(9) B. J. Mair, A. R. Glasgow and F. D. Rossini, *J. Research Natl. Bur. Standards*, **27**, 39 (1941).

(10) C. D. Shacklett and H. A. Smith, *J. Am. Chem. Soc.*, **73**, 766 (1951).

(11) R. Adams and R. W. Hufferd, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 341.

(11a) L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 248.

(12) N. M. Cullinane, S. J. Chard and C. W. C. Dawkins, *Org. Syntheses*, **35**, 73 (1955).

(13) D. D. Tunnicliff, R. R. Brattain and L. R. Zumwalt, *Anal. Chem.*, **21**, 890 (1949).

absorption by the solvent, only wave lengths above 260 mμ were used in the analyses. A Beckman model DU spectrophotometer was employed in all analytical work. It was modified by placing a 10,000 megohm resistor in the grid circuit of the electrometer tube to permit the use of a narrow slit width (0.20 mm.). Thermospacers were placed on each side of the cell compartment to enable it to be kept at a constant temperature (30.0 ± 0.1°C). Their use was necessitated by the large temperature coefficients of the absorbancy indexes of the hydrocarbons being studied.[14]

The analytical method was developed according to the usual procedure. The absorption spectrum of each hydrocarbon was taken between 260 and 300 mμ. Appropriate wave lengths were chosen for the analyses of each set of binary mixtures. Table I gives the wave lengths which were used with each set of mixtures. Absorbancy indexes were determined from plots of absorbancy *versus* concentration for series of standard solutions. In all cases Beer's law was valid. Care was taken to ensure that the reaction solutions were not spectrally contaminated during the hydrogenation procedure. A correction was made for the small difference in the absorption of the quartz cuvettes containing the hydrocarbon solution and standard.

TABLE I

WAVE LENGTHS USED IN THE ANALYSES OF BINARY MIXTURES OF AROMATIC HYDROCARBONS IN GLACIAL ACETIC ACID

Hydrocarbons in mixture	Wave lengths used, mμ	
Benzene–toluene	261.0	269.0
Benzene–*p*-xylene	261.0	269.0
p-Xylene–*o*-xylene	261.0	269.0
p-Xylene–*m*-xylene	262.5	269.0
o-Xylene–*m*-xylene	269.0	271.0
p-Xylene–toluene	262.5	275.0
m-Xylene–toluene	262.5	273.0
o-Xylene–toluene	269.0	271.5
Benzene–*o*-xylene	261.0	271.0
Benzene–*m*-xylene	261.0	271.0
p-Xylene–hemimellitene	262.5	275.0
p-Xylene–mesitylene	272.0	275.0
Pseudocumene–hemimellitene	262.5	276.0
Hemimellitene–isodurene	262.0	277.5
Isodurene–durene	266.0	273.5
Prehnitene–durene	266.0	273.5
Prehnitene–pentamethylbenzene	271.0	280.0
Hexamethylbenzene–pentamethylbenzene	271.0	280.0

The analytical method was verified by the analysis of binary hydrocarbon mixtures of known concentrations. These analyses revealed that the method is capable of giving a reliable accuracy of better than ±3% with the possible exception of the pentamethylbenzene–hexamethylbenzene mixtures.

Experimental Calculations

As in the work of Smith and Pennekamp,[2] the reduction of all of the hydrocarbons studied was found to be first order in hydrogen pressure and zero order in hydrocarbon concentration. Standard first-order rate constants were evaluated by the procedure reported previously.[5] All rate constants were corrected to 1.0 g. of standard catalyst in a reaction system of 1.00-l. volume. They were reproducible within 5%.

The ease of adsorption was expressed by means of the competitive adsorption equilibrium constant (*K*) used previously by the authors.[8] The expression for this constant may be derived from Langmuir kinetics. If it is assumed that the two hydrocarbons of the binary mixture compete for the same

(14) V. A. Yarborough, J. F. Haskin and W. G. Lambdin, *Anal. Chem.*, **26**, 1576 (1954).

active surface, upon which the adsorption of hydrogen and other molecular species is negligible, the Langmuir adsorption isotherm[15] yields for the fraction of surface covered by hydrocarbon A

$$\sigma_A = \frac{b_A C_A}{1 + b_A C_A + b_B C_B} \qquad (1)$$

and for the fraction covered by hydrocarbon B

$$\sigma_B = \frac{b_B C_B}{1 + b_A C_A + b_B C_B} \qquad (2)$$

where b_A and b_B are the adsorption coefficients of A and B, respectively, and C_A and C_B are their respective concentrations. Dividing eq. 1 by eq. 2 and then rearranging gives

$$b_A/b_B = C_B \sigma_A / C_A \sigma_B = K_{AB} \qquad (3)$$

where K_{AB} is the adsorption equilibrium constant for the competitive reduction of A and B. Since b_A and b_B are themselves equilibrium constants, K_{AB} is the equilibrium constant for the reaction

A (in solution) + B (adsorbed) $\rightleftharpoons$

B (in solution) + A (adsorbed) $\qquad (4)$
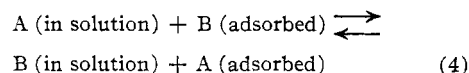
K_{AB} is a quantitative measure of the relative ease of adsorption of A and B on the active catalyst surface under conditions of equal solution concentrations.

If it is assumed that A and B are very strongly adsorbed on their portion of the active surface, eq. 1 and 2 may be added to give

$$\sigma_A + \sigma_B = 1 \qquad (5)$$

The rate expression for the competitive reduction of A and B at hydrogen pressure, *P*, and time, *t*, is

$$- \, dP/dt = \left(\frac{W_C}{V_S S}\right)(k_A \sigma_A + k_B \sigma_B)P \qquad (6)$$

where W_C, V_S and S are catalyst weight, volume of the reaction system, and catalyst standardization factor, respectively; k_A and k_B are the standard first-order rate constants for the reduction of pure A and B, respectively. The contribution to the total reduction rate by the hydrogenation of A is $k_A \sigma_A$; the contribution by the hydrogenation of B is $k_B \sigma_B$. Since A and B are reduced according to the same form of rate equation, applying the stoichiometry of the reaction and assuming hydrogen to be an ideal gas yields the expressions

$$dC_A = \frac{V_S}{3 V_l RT}\left(\frac{k_A \sigma_A}{k_A \sigma_A + k_B \sigma_B}\right) dP \qquad (7)$$

$$dC_B = \frac{V_S}{3 V_l RT}\left(\frac{k_B \sigma_B}{k_A \sigma_A + k_B \sigma_B}\right) dP \qquad (8)$$

where V_l, R and T are volume of solution of hydrocarbons in glacial acetic acid, the gas constant and absolute temperature, respectively.

K_{AB} may be quantitatively evaluated by appropriately combining eq. 3, 5, 6, 7 and 8. Dividing eq. 7 by eq. 8 and substituting eq. 3 into the resulting equation gives

$$\frac{dC_A}{dC_B} = \left(\frac{K_{AB} k_A}{k_B}\right) \frac{C_A}{C_B} \qquad (9)$$

This equation may be integrated between limits, as

(15) K. J. Laidler in P. H. Emmett, "Catalysis," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1954, p. 119.

$$\int_{C_A{}^0}^{C_A} \frac{dC_A}{C_A} = \frac{K_{AB}k_A}{k_B} \int_{C_B{}^0}^{C_B} \frac{dC_B}{C_B} \tag{10}$$

where $C_A{}^0$ and $C_B{}^0$ are the concentrations of A and B, respectively, at the beginning of the reduction. Performing the integration and rearranging yields

$$\log C_A = \frac{k_A K_{AB}}{k_B} \log C_B + \left(\log C_A{}^0 - \frac{k_A K_{AB}}{k_B} \log C_B{}^0\right) \tag{11}$$

Since the quantity within the parentheses is constant for a given competitive reduction, eq. 11 predicts a linear variation between log C_A and log C_B. From the slope of a log–log plot of hydrocarbon concentrations in a mixture during reduction, K_{AB} may be evaluated since k_A and k_B are already known.

The competitive adsorption equilibrium constant may also be determined from a knowledge of hydrogen pressure as a function of time. Substituting eq. 5 into eq. 3 and 6

$$\frac{-\left(\frac{V_s S}{W_c P}\right)\left(\frac{dP}{dt}\right) - k_A}{k_B - k_A} = \sigma_B = \frac{C_B}{K_{AB} C_A + C_B} \tag{12}$$

rearranging eq. 12

$$K_{AB} = \frac{C_B}{C_A} \frac{\left[k_B + \left(\frac{V_s S}{W_c P}\right)\frac{dP}{dt}\right]}{\left[-k_A - \left(\frac{V_s S}{W_c P}\right)\frac{dP}{dt}\right]} \tag{13}$$

Equation 13 was used to evaluate K_{AB} from hydrogen pressure–time data; dP/dt was approximated by measuring the pressure drop between reaction times 1.00 and 2.00 minutes; C_A, C_B and P were measured directly at a reaction time of 1.50 minutes. The k_A and k_B values used in eq. 13 were not obtained from the log P versus time plots for the reduction of the pure hydrocarbons. They were obtained by rearranging the rate expression into the form

$$k_A = -\left(\frac{V_s S}{W_c P}\right)\frac{dP}{dt} \tag{14}$$

As with the competitive reductions, the reaction increment between reduction times of 1.00 and 2.00 minutes was chosen for the evaluations of k_A and k_B. The use of eq. 13 for the evaluation of K_{AB} is inferior to the method embodied in eq. 11. It does, however, provide an independent check for the K_{AB} value obtained from the log–log plot of hydrocarbon concentrations.

Results

Hydrogenation of Individual Hydrocarbons.—A prerequisite to the evaluation of the competitive adsorption equilibrium constants was the determination of the standard first-order rate constant of each of the hydrocarbons to be reduced competitively. These rate constants are given in Table II. A comparison between the rate constants in Table II and those previously obtained by Smith and Pennekamp[1] reveals satisfactory agreement between them. The single exception to this agreement is the relative reduction rates of durene and isodurene. In the previous work the reduction rate of isodurene was between those of prehnitene and durene. In this investigation it was equal to that of durene within experimental error. The data of Table II show this apparent exception to

the general rule that the rate of hydrogenation increases with increasing symmetry of substitution within a given group of isomers. It should be remembered that the previous workers used laboratory preparations of Adams platinum oxide catalyst, whereas commercial platinum oxide was used in this research.

TABLE II

STANDARD RATE CONSTANTS FOR THE REDUCTION OF INDIVIDUAL HYDROCARBONS AT 30°

Compound	k, min.$^{-1}$ g.$^{-1}$ l.
Benzene	0.205
Toluene	.147
o-Xylene	.091
m-Xylene	.126
p-Xylene	.158
Hemimellitene (1,2,3-trimethylbenzene)	.0446
Pseudocumene (1,2,4-trimethylbenzene)	.089
Mesitylene (1,3,5-trimethylbenzene)	.149
Prehnitene (1,2,3,4-tetramethylbenzene)	.024
Isodurene (1,2,3,5-tetramethylbenzene)	.052
Durene (1,2,4,5-tetramethylbenzene)	.051
Pentamethylbenzene	.015
Hexamethylbenzene	.0029

Competitive Hydrogenation of Benzene, Toluene and the Xylenes.—The competitive reductions of the various binary mixtures of benzene, toluene and the xylenes were used as a critical test of the theoretical treatment of the experimental data.
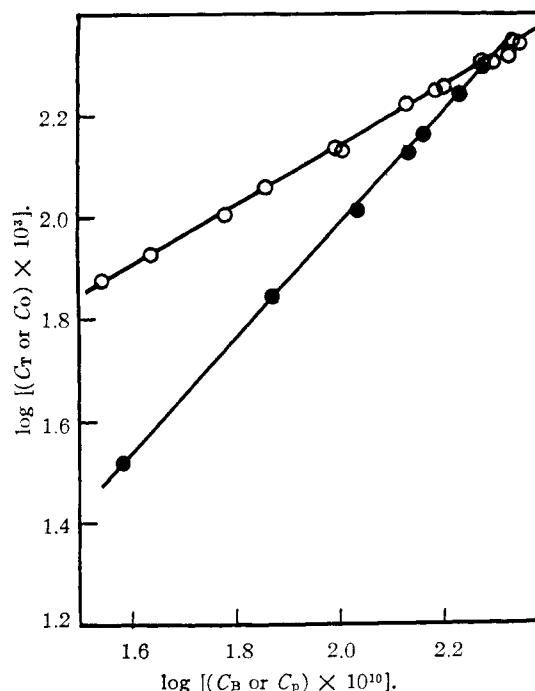

Fig. 1.—Plots of log toluene concentration (C_T) versus log benzene concentration (C_B) and log o-xylene concentration (C_O) versus log p-xylene concentration (C_P) for the competitive hydrogenation of toluene versus benzene (O) and o-xylene versus p-xylene (●), respectively.

The possible binary combinations of these compounds, ten in all, were reduced competitively. As predicted by eq. 11, all of the log–log plots

TABLE III

SUMMARY OF THE EXPERIMENTAL VALUES OF THE COMPETITIVE ADSORPTION EQUILIBRIUM CONSTANTS FOR THE COMPETITIVE HYDROGENATION OF BENZENE, TOLUENE AND THE XYLENES

K and its definition[a]	Direct exptl. value of K	Values of K as detd. from other sets of competitive hydrogenation			Values of K from hydrogen pressure–time data
$K_{BT} = C_{B\sigma T}/C_{T\sigma B}$	0.80	$K_{BO}/K_{TO} = 0.70$	$K_{BM}/K_{TM} = 0.75$	$K_{BP}/K_{TP} = 0.68$	1.19
$K_{BO} = C_{B\sigma O}/C_{O\sigma B}$	.335	$(K_{TO})(K_{BT}) = 0.382$	$(K_{BM})(K_{MO}) = 0.347$	$(K_{BP})(K_{PO}) = 0.315$	0.438
$K_{BM} = C_{B\sigma M}/C_{M\sigma B}$	.221	$K_{BO}/K_{MO} = 0.213$	$(K_{BT})(K_{TM}) = 0.235$	$(K_{BP})(K_{PM}) = 0.206$	.262
$K_{BP} = C_{B\sigma P}/C_{P\sigma B}$	.166	$(K_{BT})(K_{TP}) = 0.197$	$K_{BO}/K_{PO} = 0.176$	$K_{BM}/K_{PM} = 0.178$	.195
$K_{TO} = C_{T\sigma O}/C_{O\sigma T}$	.478	$K_{BO}/K_{BT} = 0.419$	$(K_{TM})(K_{MO}) = 0.462$	$(K_{TP})(K_{OP}) = 0.467$	.481
$K_{TM} = C_{T\sigma M}/C_{M\sigma T}$	.294	$K_{BM}/K_{BT} = 0.276$	$K_{TO}/K_{MO} = 0.304$	$(K_{TP})(K_{MP}) = 0.308$	.701
$K_{TP} = C_{T\sigma P}/C_{P\sigma T}$	.246	$K_{BP}/K_{BT} = 0.208$	$K_{TO}/K_{OP} = 0.252$	$K_{TM}/K_{MP} = 0.237$	...[b]
$K_{OP} = C_{P\sigma O}/C_{O\sigma P}$	1.90	$K_{BO}/K_{BP} = 2.02$	$K_{TO}/K_{TP} = 1.94$	$(K_{OM})(K_{MP}) = 1.95$	3.36
$K_{OM} = C_{M\sigma O}/C_{O\sigma M}$	1.57	$K_{BO}/K_{BM} = 1.52$	$K_{TO}/K_{TM} = 1.63$	$K_{OP}/K_{MP} = 1.53$	3.11
$K_{MP} = C_{P\sigma M}/C_{M\sigma P}$	1.24	$K_{BM}/K_{BP} = 1.33$	$K_{TM}/K_{TP} = 1.20$	$K_{OP}/K_{OM} = 1.21$	1.41

[a] The subscripts B, T, P, M and O are used to designate benzene, tolene, p-xylene, m-xylene and o-xylene, respectively.
[b] The pressure–time K-value for the competitive reduction of toluene and p-xylene was not evaluated because the standard first-order rate constants for these two compounds are so close to each other.

of hydrocarbon concentrations during the reduction process gave well-defined straight lines. Figure 1 gives two typical examples of these plots. The K-values were conveniently obtained from these log-log plots.

In Table III is given a summary of the competitive adsorption equilibrium constants from the competitive reduction of benzene, toluene and the xylenes. Column one identifies and defines the experimental equilibrium constant given in column two. This value was obtained from the log–log plot. The next three columns give the K-values obtained from the competitive hydrogenation of each of the two compounds concerned with a third compound. Since each of these equilibrium constants is a ratio of adsorption coefficients, the K for the competitive reduction of hydrocarbons A and B (K_{AB}) should be obtained by competitively hydrogenating A and then B with a third compound, C, to obtain K_{AC} and K_{BC}, respectively; K_{AB} should result from an appropriate multiplication or division involving K_{AC} and K_{BC}.[16] Columns three, four and five furnish three independent values of each K which may be used to check the direct experimental value in column two. These columns also give the method in which the K_{AC} and K_{BC} values are combined to obtain K_{AB}. The last column in Table III gives the K-value as obtained by the use of eq. 13.

An examination of Table III reveals that the direct experimental K-value (column two) agrees with the indirect K-values (columns two, three and four) within 10% in most cases and 20% in all cases. This agreement is within experimental error since the maximum error in a given K-value is approximately 10%. The pressure–time K-values differ with their counterparts from the log–log plots by as much as a factor of two. These differences may all be ascribed to the experimental error in the pressure–time K-values. The precision with which these values may be measured depends upon the proximity of the standard rate constants of the two compounds concerned (see eq. 13). When the standard rate constants are of comparable magnitude, errors in the dP/dt values

(16) J. P. Wauquier and J. C. Jungers, Compt. rend., 243, 1766 (1956).

may be greatly magnified in the resulting K. Thus, the experimental error in the pressure–time K may be as large as 50%. The apparent differences between the pressure–time K-values and those from the log–log plots lie within the error arising from the reading of the dP/dt values (approximately 6%). This large error in the pressure–time K-values was noted in a previous work of the authors.[8]

Table III also discloses that benzene is adsorbed slightly more strongly than toluene on the active catalyst surface and that toluene is more readily adsorbed than any of the xylenes. The ease of adsorption of toluene with respect to benzene is greater than the ease of adsorption of the xylenes with respect to toluene. The relative ease of adsorption of the xylenes is found to decrease in the order of ortho, meta, para which is the exact opposite of the relative reduction rates of the individual xylenes. This result corroborates a previous finding of the authors[8] which was based only on K-values calculated from hydrogen pressure–time data.

Competitive Hydrogenation of the Trimethylbenzenes, Tetramethylbenzenes, Pentamethylbenzene and Hexamethylbenzene.—Since the theoretical treatment of the competitive hydrogenation data had received sound experimental verification from the experiments with benzene, toluene and the xylenes, this treatment was exploited in the competitive hydrogenation of the polymethylbenzenes of higher molecular weight. All of the log–log plots of hydrocarbon concentrations were linear within experimental error. The linearity of these plots was taken as evidence that the theoretical treatment was valid. Competitive adsorption equilibrium constants were evaluated only from the log–log plots. The results of these competitive reductions are summarized in Table IV. In this table are given the adsorption equilibrium constants which were determined experimentally. The K for the competitive reduction of any desired pair of polymethylbenzenes may be obtained by appropriate multiplication and/or division involving the experimental K's.

An inspection of Table IV reveals that the trimethylbenzenes are adsorbed less readily on the

active catalyst surface than the xylenes, but more readily than the tetramethylbenzenes, which have a greater ease of adsorption than pentamethylbenzenes. Surprisingly, hexamethylbenzene is more strongly adsorbed than pentamethylbenzene. With this single exception it thus appears that the ease of adsorption will decrease as additional substituents are attached to adjacent positions in the ring.

TABLE IV

SUMMARY OF COMPETITIVE ADSORPTION EQUILIBRIUM CONSTANTS FOR THE COMPETITIVE HYDROGENATION OF VARIOUS POLYMETHYLBENZENES

Compounds competitively reduced	Definition of K^a	Exptl. value of K
p-Xylene–mesitylene	$C_{PX}\sigma_{ME}/C_{ME}\sigma_{PX}$	0.157
p-Xylene–hemimellitene	$C_{PX}\sigma_{HE}/C_{HE}\sigma_{PX}$	0.517
Hemimellitene–pseudo-cumene	$C_{PS}\sigma_{HE}/C_{HE}\sigma_{PS}$	1.29
Hemimellitene–isodurene	$C_{HE}\sigma_{IS}/C_{IS}\sigma_{HE}$	0.132
Prehnitene–durene	$C_{DU}\sigma_{PR}/C_{PR}\sigma_{DU}$	2.04
Durene–isodurene	$C_{DU}\sigma_{IS}/C_{IS}\sigma_{DU}$	1.19
Prehnitene–pentamethyl-benzene	$C_{PR}\sigma_{PM}/C_{PM}\sigma_{PR}$	0.086
Pentamethylbenzene-hexamethylbenzene	$C_{PM}\sigma_{HM}/C_{HM}\sigma_{PM}$	1.42

^{a} The various polymethylbenzenes are designated with the following subscripts: p-xylene, PX; hemimellitene, HE; pseudocumene, PS; mesitylene, ME; prehnitene, PR; isodurene, IS; durene, DU; pentamethylbenzene, PM; hexamethylbenzene, HM.

For the trimethylbenzenes it is found that hemimellitene is more strongly adsorbed than pseudocumene, which is much more strongly adsorbed than mesitylene. Thus, with increasing symmetry of nuclear substitution, the ease of adsorption of the trimethylbenzenes decreases, although the relative reduction rate increases. This parallels the results obtained from the competitive reductions of the xylenes. With the tetramethylbenzenes the ease of adsorption is also found to decrease with increasing symmetry of substitution. Thus, their relative ease of adsorption is prehnitene > isodurene > durene, whereas their relative reduction rates are durene ≅ isodurene > prehnitene. Hence, it may be concluded that the ease of adsorption decreases with increasing nuclear substitution and symmetry of substitution.

Discussion

The results obtained from the competitive reduction of benzene, toluene and the xylenes provide a sound experimental verification of the mathematical treatment of the data. This verification thus confirms the mechanistic assumptions upon which the treatment is based. The successful use of Langmuir kinetics leads to the conclusion that the same active catalyst surface must be accessible to each polymethylbenzene when it undergoes reduction; however, the possibility of a given surface area being capable of chemisorbing a larger number of molecules of one hydrocarbon than of the other is not precluded by the results of this work. The adsorption of the benzene nucleus is apparently a fast, equilibrium-type step. Further, the hydrogen acceptor is strongly adsorbed upon a portion of the catalyst surface under conditions where

neither hydrogen nor solvent molecules can effectively interfere. The reaction kinetics suggest that hydrogen may be weakly adsorbed upon a portion of the active surface which is unavailable for the chemisorption of the benzene nucleus. This picture of the benzene nucleus being strongly chemisorbed on one portion of the active platinum surface and hydrogen being weakly chemisorbed upon another portion has previously been suggested by Farkas and Farkas.[17] It is in agreement with the partial inhibition which benzene is known to have upon the hydrogen–deuterium exchange reaction on platinum.[18] The reaction mechanism appears to involve the addition of weakly chemisorbed hydrogen to the strongly chemisorbed ring. It should be remembered, however, that the results of this work do not rule out the mechanism by which hydrogen attacks the chemisorbed nucleus from the van der Waals layer (Rideal mechanism).[19]

This research has clearly shown that the ease of adsorption does not necessarily parallel the relative reduction rate. This result appears quite logical when it is realized that the adsorption of the benzene nucleus and the rate-determining step seem to be separate and distinct. The relative ease of adsorption is a thermodynamic effect which is determined by the relative stability of the chemisorbed nucleus. The relative reduction rate is a kinetic effect which is determined by the relative stability of the transition state of the rate-determining step. Changes in nuclear substitution may or may not affect the relative stability of the chemisorbed species and the transition state in the same direction. It may be concluded that the relative reduction rates of benzene and its methyl substituted derivatives are not a direct consequence of the ease with which the nucleus is chemisorbed on the active catalyst surface.

The interpretation of the relative ease of adsorption with respect to the mode of adsorption and molecular structure of the aromatic compound is somewhat difficult. The main source of this difficulty lies in the meager knowledge which presently exists concerning the exact nature of the catalyst surface. It is most logical to assume that the benzene nucleus is chemisorbed flatwise, or approximately so, on the active surface with the six π-electrons interacting with the surface atoms of the catalyst. It has been shown[20] that on a nickel-silica catalyst at room temperature benzene is adsorbed by six-point attachment. On Adams platinum the resonance of the ring appears to be disrupted by chemisorption[21] prior to undergoing reduction. These are but two of the many investigations which suggest flatwise chemisorption of the nucleus.

For such adsorption the six carbon atoms of the ring will lie in or near the same plane. The specific positions taken by the groups attached to the ring are subject to much doubt. These groups, how-

(17) A. Farkas and L. Farkas, Trans. Faraday Soc., 33, 827 (1937).

(18) H. A. Smith and E. L. McDaniel, J. Am. Chem. Soc., 77, 533 (1955).

(19) E. K. Rideal, Proc. Camb. Phil. Soc., 35, 130 (1939).

(20) P. W. Selwood, J. Am. Chem. Soc., 79, 4637 (1957).

(21) H. A. Smith, D. M. Alderman and F. W. Nadig, ibid., 67, 275 (1945); H. A. Smith and H. T. Meriwether, ibid., 71, 413 (1949).

ever, should all be pushed to the side of the ring opposite the catalyst surface. As the bulk of the groups is increased, the steric strain produced during the adsorption of the nucleus will increase, and the ease of adsorption will decrease. This is observed to be the case experimentally when a methyl group is substituted for a hydrogen atom. As the number of methyl groups attached to the ring is increased, the ease of adsorption decreases. This steric strain may be divided into two distinct categories. The first category is a frontal or F type of strain which results from the mutual repulsion between the nuclear substituents and the catalyst surface. The second category embraces a back or B type of strain which results from the closer proximity of the nuclear substituents to each other. Appreciable B strain should result for substituents which are *ortho* to each other and possibly those which are *meta*. It should not result for *para* substituents.

The concept of steric strain appears incapable of explaining the relative ease of adsorption of each of the three sets of substitutional isomers studied. The relative ease of adsorption of these sets of isomers suggests that the ring may be somewhat inclined upon chemisorption with the least substituted side being closer to the catalyst surface than the more highly substituted side. The tilting of the ring may actually be a means by which the adsorbed species minimizes F strain. The ability of the ring to be inclined upon chemisorption should decrease with increasing symmetry of substitution. Thus, as the symmetry of substitution increases, the intimacy of the approach to the active surface of the least substituted side of the ring decreases. This should result in a decreased ease of adsorption as has been observed experimentally. The concept of inclined adsorption of the nucleus may also be useful in explaining the relative ease of adsorption of such homologous series as *m*-xylene, mesitylene and isodurene. The relative ease of adsorption has been rationalized on the basis of steric rather than electronic effects. The possible effect on the ease of adsorption resulting from electron release to or withdrawal from the nucleus should be ascertained by the competitive reduction of two compounds, one of which has an electron-releasing substituent and the other an electron-withdrawing substituent (*e.g.*, toluene *versus* benzoic acid).

Steric strain and inclined adsorption may be used to explain all of the relative ease of adsorption results except that of hexamethylbenzene, which appears to be slightly more strongly adsorbed than pentamethylbenzene. The most likely explanation for this apparently anomalous result is a solvent effect. Hexamethylbenzene is so slightly soluble in glacial acetic acid that it was necessary to use it as a saturated solution in the binary reductions. The amount of pentamethylbenzene in the solution was far below the saturation point. It is thus reasonable to believe that the relative chemical potentials of the two hydrocarbons are altered by the solvent to the extent that hexamethylbenzene appears to have a greater relative ease of adsorption than it would have in the absence of the solvent. This conclusion may be tested by competitively reducing these two hydrocarbons in various other solvents. The effect of the solvent upon the other series of competitive hydrogenations should be of little consequence. Jungers and Wauquier[7] have shown the absence of solvent effects in the competitive reduction of benzene, toluene and the xylenes on Raney nickel in various organic solvents.

Stereochemistry of the 1,2,3,4-Dibenzcyclonona-1,3-diene System.[1] A Note on the Racemization Barrier in Bridged Biphenyls

BY KURT MISLOW, SEYMOUR HYDEN AND HANS SCHAEFER

A nine-membered ring bridged biphenyl (I) has been synthesized, and optically activated by second-order asymmetric transformation. The ultraviolet spectrum reflects a large angle of torsion in the ground state. The barrier to racemization (24.0 kcal./mole) reflects directed interaction between non-bonded hydrogens in the transition state. A semi-quantitative treatment of the transition state conformations in the homologous series of seven-, eight- and nine-ring bridged biphenyls (IIb–IId) is presented.

A study of the stereochemistry of 1,2,3,4-dibenzcyclonona-1,3-diene-7-carboxylic acid (I) was prompted by several considerations. Spectroscopic investigations into the relation between conjugation and conformation of 2,2'-bridged alicyclic biphenyls without substituents in the 6,6'-positions have revealed that the position of the conjugation band suffers a monotonic hypsochromic shift and decrease in intensity as the size of the bridge and the angle of torsion (θ) increase: for derivatives of IIa, IIb and IIc, the conjugation band assumes values of 264 mμ (log ϵ 4.23–4.26),[2]

(1) Preliminary communication: *Tetrahedron Letters*, No. **12**, 410 (1961). Grateful acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research, and to the Alfred P. Sloan Foundation for fellowship support (K.M.).

(2) F. A. Askew, *J. Chem. Soc.*, 512 (1935); R. N. Jones, *J. Am. Chem. Soc.*, **63**, 1658 (1941); G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 854 (1952).