yield), were obtained, m.p. 139–140°; λ_{max} 217, 228 (sho.), 270, 336, 351 mμ; ($\epsilon \times 10^{-3}$ 43.3, 36.2, 36.0, 13.6, 14.2).

Anal. Calcd. for $C_{24}H_{25}N_2Cl$: C, 76.47; H, 6.69. Found: C, 76.56; H, 6.72.

10-Chloro-5,5-dimethyl-6-N-piperidino-5,6-dihydrobenz[c]acridine (XXII). Treatment similar to that described for the 9-chloro isomer, but using an excess of piperidine, gave a 73% yield of the piperidino derivative XXII as pale yellow crystals, m.p. 148–150°; λ_{max} 217, 230 (sho.), 267, 337, 352 mμ; ($\epsilon \times 10^{-3}$ 44.0, 30.9, 37.5, 12.2, 13.0).

Anal. Calcd. for $C_{24}H_{25}N_2Cl$: C, 76.47; H, 6.69. Found: C, 76.05; H, 6.87.

11-Chloro-5,5-dimethyl-6-N-piperidino-5,6-dihydrobenz[c]acridine (XXIII). This preparation was similar to that used for the 9-chloro isomer. However, three recrystallizations from acetone, with charcoal treatment, were necessary to obtain a pure product. From 1.50 g. of the bromo compound XIV was obtained 0.70 g. (46% yield) of colorless crystals of the piperidino derivative XXIII, m.p. 121.5–123°; λ_{max} 216, 273, 322, 335, 350 mμ; ($\epsilon \times 10^{-3}$ 40.9, 41.8, 10.0, 12.3, 11.1).

Anal. Calcd. for $C_{24}H_{25}N_2Cl$: C, 76.47; H, 6.69. Found: C, 76.73; H, 6.91.

Acknowledgment. This investigation was supported by a grant from the National Cancer Institute, U. S. Public Health Service, CY 2931.

LINCOLN, NEB.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORIES, MICHIGAN STATE UNIVERSITY]

A Study of Factors Influencing Catalytic Hydrogenation Kinetics[1]

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Received January 23, 1959

The rate of disappearance of hydrogen in the catalytic hydrogenation of benzene is found to obey the pseudo-first order rate law

$$-\frac{dp}{dt} = \frac{Rkp}{V_1/T_1 + V_2/T_2}$$

in which p is hydrogen pressure, t is time, R is the gas constant, V_1 and T_1 are the volume and absolute temperature of the reaction chamber, V_2 and T_2 are the volume and absolute temperature of the remainder of the apparatus, and k is the pseudo-first order rate constant. When $T_1 = T_2$ and $V_1 + V_2 = V$ (total volume of the apparatus), the expression reduces to

$$-dp/dt = RTkp/V$$

The rate of disappearance of benzene obeys the zero-order expression

$$c_0 - c = k_0t$$

in which c_0 is the initial concentration of benzene, c is the concentration of benzene at time t, and k_0 is the zero-order rate constant. The relationship between k and k_0 is examined.

The rate of a catalytic hydrogenation is first-order with respect to hydrogen pressure, zero-order with substrate concentration, and directly proportional to the weight of the catalyst,[3] apparently conforming to the simple, pseudo-first order rate equation,

$$-dp/dt = k_{app}p \text{ or } \log p_0/p = k_{app}t/2.303 \quad (1)$$

in which p is the hydrogen pressure at time t, p_0 is the initial hydrogen pressure, and k_{app} is the apparent rate constant. In order to relate the rate constants to a unit quantity of catalyst, their experimental values are customarily divided by the weights of catalyst used.

When measured in terms of hydrogen pressure, the rate of catalytic hydrogenation also shows an apparent inverse relationship to the volume of the hydrogenation apparatus. In order to obtain rate constants which are independent of the apparatus volume, Fuzek and Smith[4] have suggested, on empirical grounds, a revised rate equation which includes this volume V:

$$-dp/dt = k'p/V \text{ or } \log p_0/p = k't/2.303V \quad (2)$$

This revised equation gives satisfactory comparisons of rate constants for low-pressure hydrogenations carried out in apparatus of different volumes but at similar pressures, and at or near room temperature. Recent investigations[5] have shown, however, that Equation 2 becomes less and less applicable as the reaction temperatures are increased; moreover, puzzling discrepancies arise when attempts are made to use Equation 2 for comparison of rates of the same hydrogenation measured in different pressure ranges under otherwise similar conditions.

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(1) Abstracted in part from the doctoral dissertation of Lyman R. Caswell, Michigan State University, 1956.

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(3) H. A. Smith, D. L. Alderman, and F. W. Nadig, *J. Am. Chem. Soc.*, **67**, 272 (1945).

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In a review of methods of expressing the rates of gas reactions, Laidler[6] has pointed out that rates are commonly expressed in any of three ways: as disappearance of moles of reactant with time, $\mathrm{d}n/\mathrm{d}t$; as change of concentration with time, $\mathrm{d}c/\mathrm{d}t$; or as change of pressure with time, $\mathrm{d}p/\mathrm{d}t$. For ideal gases these methods of expression are interrelated through the equations $pV = nRT$ and $c = n/V$; these equations lead to a constant factor $1/V$ relating $\mathrm{d}c/\mathrm{d}t$ to $\mathrm{d}n/\mathrm{d}t$ at constant volume, and to a constant factor RT relating $\mathrm{d}p/\mathrm{d}t$ to $\mathrm{d}c/\mathrm{d}t$ at constant temperature. The $1/V$ factor is responsible for the observed dependence of the rate of pressure drop upon the apparatus volume, and the RT factor explains the failure of the empirically derived equation to apply satisfactorily in the comparison of rates of reactions at different temperatures. The best form of the rate expression to be used depends upon the experimental arrangement and the nature of the comparisons to be made. A rate expression is derived for the common experimental procedure in which the pressure change is measured for hydrogen in a reservoir connected to the hydrogenation bomb, which may or may not be at the reservoir temperature; the validity of the derived relationships is tested experimentally.

If ideal-gas behavior is an adequate approximation, then the number of moles n of hydrogen in the apparatus is given by

$$n = pV/RT \qquad (3)$$

in which R is the gas constant and T is the absolute temperature. Differentiation of this expression with respect to time gives the rate of disappearance of moles of hydrogen as a function of the rate of pressure drop at constant volume and temperature:

$$-\mathrm{d}n/\mathrm{d}t = -V/RT \times \mathrm{d}p/\mathrm{d}t \qquad (4)$$

If the rate of disappearance of moles of hydrogen is proportional to the hydrogen pressure, then

$$-\mathrm{d}n/\mathrm{d}t = kp \qquad (5)$$

Combination of Equations 4 and 5 then provides the relationship between the rate of pressure drop and the pressure itself:

$$-\mathrm{d}p/\mathrm{d}t = RT/V \times k_6 p \text{ or } \log p_0/p = (RT/2.303V)k_6 t \qquad (6)$$

When carrying out hydrogenations at elevated temperature, only the reaction chamber is normally heated, while the remainder of the apparatus is at room temperature. The total number of moles of hydrogen in this case is then

$$n = V_1 p/RT_1 + V_2 p/RT_2 = (V_1 T_1 + V_2 T_2)p/R \qquad (7)$$

where V_1 and T_1 are the volume and absolute temperature of the reaction chamber and V_2 and T_2 are the volume and absolute temperature of the remainder of the apparatus. For such cases, equation 6 becomes:

$$-\mathrm{d}p/\mathrm{d}t = Rk_8 p/(V_1/T_1 + V_2/T_2) \text{ or}$$
$$\log p_0/p = Rk_8 t/2.303(V_1/T_1 + V_2/T_2) \qquad (8)$$

In order to determine the applicability of Equations 6 and 8, the hydrogenation of benzene on platinum in glacial acetic acid was studied at low pressure in three different hydrogen voids over a range of temperatures. Analogous hydrogenations to those previously described were run at high pressure[7] with one void. In order to relate the rates of disappearance of benzene and of hydrogen, the rate of disappearance of benzene was independently determined for one set of low pressure conditions.

EXPERIMENTAL

Apparatus. Low-pressure hydrogenations were carried out with a modified Parr Model 3911 low-pressure hydrogenation apparatus. The pressure gage of the apparatus was replaced by a differential manometer with a 10-ft. scale ruled at 1-mm. intervals. Two special hydrogen reservoir tanks were constructed from $4^1/_2$ in. galvanized iron pipe. The total volumes of the apparatus with each tank were determined in a manner similar to that already described.[4] These volumes were: 4.615 l. for the apparatus with the standard Parr tank (large void), 1.698 l. (medium void), and 1.176 l. (small void).

The low pressure reaction chamber was a 250-ml. wide-mouth pressure bottle specially constructed by the H. T. Martin Co. of Evanston, Ill. The bottle was heated by a coil of No. 22 Nichrome wire wound around it. Temperature measurement was made by means of a copper constantan cold-junction thermocouple inserted into a thermocouple well in the stopper of the reactor bottle. The thermocouple was connected to a Weston millivoltmeter, and the temperature was controlled by means of a Variac connected to the heating coil. The average temperature variation throughout a hydrogenation was ±0.6°.

High pressure hydrogenations were carried out in an Aminco 50-ml. high pressure bomb manufactured by the American Instrument Co. The bomb was fitted with a glass liner composed of a Pyrex tube with a 10/30 standard taper joint and fitted with a perforated glass stopper. Temperature recording and control were made with a Micromax recording potentiometer connected to an iron constantan thermocouple inserted into the base of the bomb. Average temperature variation during a run was ±1.0°.

Materials. Matheson, Coleman, and Bell "thiophene-free" benzene was refluxed 24 hr. over sodium metal and fractionally distilled using a 20-plate column. The middle third, freezing point, 5.5°, and n_{D}^{25}, 1.4971, was reserved for hydrogenation. The American Petroleum Institute[8] reports freezing point at 5.333°, n_{D}^{25} 1.49792.

Baker's "analyzed" glacial acetic acid was used without further purification. All solvent samples used in the hydrogenations were taken from the same bottle.

Matheson, Coleman, and Bell cyclohexane was twice passed through a column of activated silica gel, using freshly activated silica gel with each pass. The purified cyclohexane showed no absorption when compared with distilled water at the benzene absorption maximum of 255 mμ.

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(6) K. J. Laidler, "Kinetic Laws in Surface Catalysis," Chap. 4 in "Catalysis," Vol. I., P. H. Emmett, Ed., Reinhold Publishing Corp., New York (1954), p. 120.

(7) R. H. Baker and R. D. Schuetz, *J. Am. Chem. Soc.*, **69**, 1250 (1947).

(8) American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds," Carnegie Institute of Technology, Table 5a, October 31, 1950.

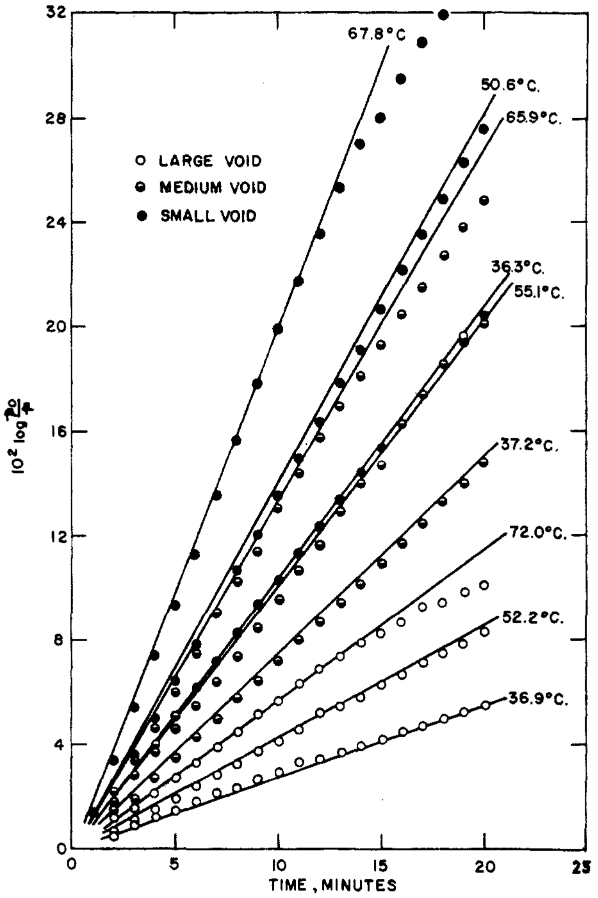

Fig. 1. Log p_0/p *vs.* time for various runs, showing effect of void on apparent rate constant at several temperatures

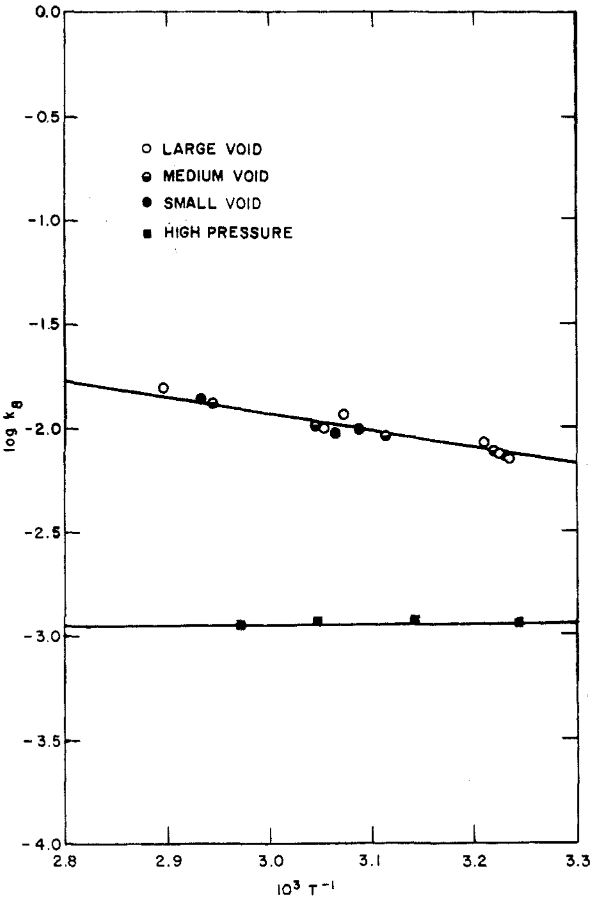

Fig. 2. Arrhenius plots of log k_8 *vs.* 1/T for low and high pressure runs

Hydrogen obtained from the Ohio Chemical and Surgical Co. was used without further purification.

Adams' platinum-oxide catalyst was obtained from the American Platinum Works. All hydrogenations were run with samples from the same batch of catalyst. Three samples of the catalyst were analyzed by reduction with hydrogen, giving an average platinum content of 79.45%. All rate constants were related to one gram of platinum by dividing them by the weight of platinum in the catalyst sample.

Hydrogenations. All low pressure hydrogenations were carried out with 4.4 g. (0.056 mole) of benzene in 10 ml. of glacial acetic acid, using 0.20 g. of platinum oxide and an average initial hydrogen pressure corresponding to a reading of 270 cm. of mercury on the differential manometer. High-pressure hydrogenations were carried out with exactly one-half these quantities of benzene, acetic acid, and catalyst, and using an initial hydrogen gage pressure of 1200 p.s.i. Pressure readings were made at 1-min. intervals during the course of each hydrogenation.

Determination of benzene. A series of low pressure hydrogenations using the largest void at 36.9° were stopped at various stages of partial hydrogenation and the reaction mixture was analyzed for residual benzene. The acetic acid was removed from the reaction mixture by two extractions of 4 ml. of the reaction mixture with 5-ml. portions of a saturated solution of sodium acetate. The hydrocarbon layer was diluted with cyclohexane and the benzene in it determined by means of the absorption at 255 mμ in a Beckman DU quartz spectrophotometer. The procedure was calibrated by use of a series of simulated hydrogenation mixtures to permit correction for the benzene lost during the extraction of the acetic acid.

DISCUSSION

Rate of disappearance of hydrogen. The values of log p_0/p were plotted against the time in minutes for all hydrogenations. The plots for nine such runs, clearly showing how void differences produce apparent differences in reaction rates, are depicted in Fig. 1. The slopes of the linear portions of these plots were determined by the method of least squares, and the values of k_{app}, k', k_6, and k_8 for Equations 1, 2, 6, and 8, respectively, were calculated from the slopes; these constants are presented in Table I. The Arrhenius plots of log k_8 *vs.* $1/T$ for the low and high pressure runs are shown in Fig. 2; the activation energy is found to be 4.3 kcal./mole at the lower pressures, and essentially zero kcal./mole in the high pressure runs.

The use of Equation 6 instead of Equation 8 leads to only a slightly higher activation energy, although the rate constants differ for the two equations. The importance of using Equation 8 becomes greater when the void and reaction chamber volumes are more nearly equal. As the reaction chamber volume becomes negligible relative to the void, Equation 8 reduces to Equation 6. In the low pressure runs reported, even the smallest void is enough larger than the reaction chamber to tend to mini-

TABLE I

RATE CONSTANTS FOR THE HYDROGENATION OF BENZENE

Temp.	Void, V, L.	10^2k_{app} Min.$^{-1}$ G.$^{-1}$	$10^2k'$ ($k' = k_{app}V$) L. Min.$^{-1}$ G.$^{-1}$	10^2k_6 ($k_6 = k_{app}V/RT$) Mole Atm.$^{-1}$ Min.$^{-1}$ G.$^{-1}$	10^2k_8 [$k_8 = k_{app}(V_1/T_1 + V_2/T_2)/R$] Mole Atm.$^{-1}$ Min.$^{-1}$ G.$^{-1}$
a. Low Pressure (Reaction Chamber Volume, 0.25 L.)					
35.8	4.60	3.78	17.4	0.709	0.746
36.3	1.16	15.2	17.6	0.716	0.868
36.9	4.60	3.99	18.4	0.749	0.788
37.2	1.68	11.0	18.5	0.752	0.860
38.4	4.60	4.50	20.7	0.843	0.887
48.1	1.68	13.4	22.5	0.909	1.04
50.6	1.16	20.7	24.0	0.966	1.16
52.2	4.60	6.23	28.7	1.16	1.22
53.1	1.16	20.1	23.3	0.937	1.13
54.1	4.60	5.24	24.1	0.981	1.03
55.1	1.68	15.0	25.2	1.02	1.16
65.9	1.68	19.6	32.9	1.32	1.49
67.8	1.16	29.3	34.0	1.35	1.61
72.0	4.60	8.37	38.5	1.56	1.63
b. High Pressure (Reactor Chamber Volume, 0.050 L.)					
35	0.04	32.6	1.30	0.0516	0.114
45	0.04	34.9	1.40	0.0534	0.116
55	0.04	36.4	1.46	0.0541	0.116
63	0.04	36.6	1.46	0.0530	0.112

mize the contribution of the correction introduced by Equation 8; even here, however, the correction does noticeably affect the magnitude reported for the rate constant, and the effect is much more pronounced at the higher pressures, where the void and reaction chamber volumes are comparable.

The striking differences in magnitude of the rate constants and the activation energies in the low and high pressure runs are not eliminated by the use of Equation 8. The lower rate constants at high pressure can most likely be attributed to the different shape of the adsorption isotherms for hydrogen on the catalyst surface in the different pressure ranges. The lower activation energy at high pressure suggests a difference in mechanism. A possible interpretation might be that the greater probability of occupancy by hydrogen of sites adjacent to benzene makes possible a lower energy activated complex. The present work does not make a definitive interpretation possible.

Rate of disappearance of benzene and its correlation with the rate of disappearance of hydrogen. The concentration of benzene, in moles per liter, remaining after time t, was found to be given by the zero-order rate equation,

$$c_0 - c = k_0t$$

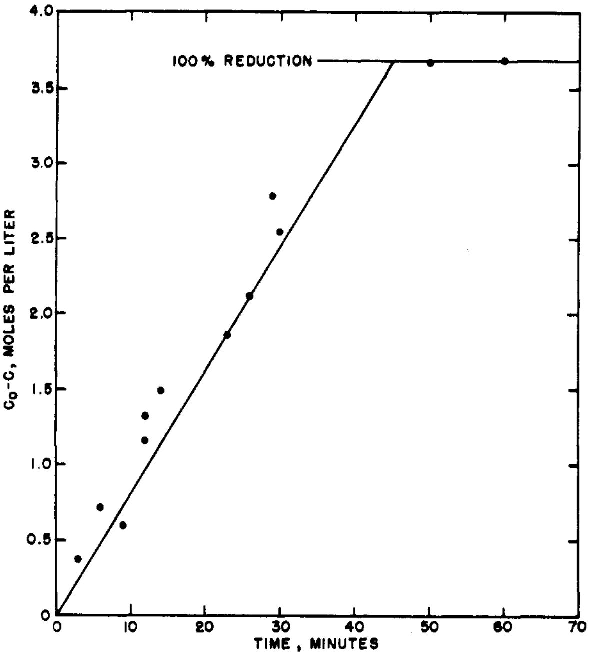

Fig. 3. Zero-order kinetics of benzene disappearance at 36.9° under hydrogen pressure of 3.31 atm.

in which c_0 is the initial concentration of benzene, c is the concentration of benzene which has reacted, and k_0 is the zero-order rate constant. The value of k_0 determined from the least-squares slope of the plot of $(c_0 - c)$ against t (Fig. 3) for 36.9° was 0.518 mole l.$^{-1}$ min.$^{-1}$ per gram of catalyst. Multiplication of this value by the volume of the reaction mixture, 0.016 l., gives 0.00828 mole min.$^{-1}$ g.$^{-1}$ According to the stoichiometry of the reaction, the average rate of disappearance of hydrogen should be three times the average rate of disappearance of benzene if the two rates are expressed in the same units. The rate constant for the hydrogenation for the same set of conditions was 0.00788 mole atm.$^{-1}$ min.$^{-1}$ g.$^{-1}$ Multiplying this constant by the average hydrogen pressure during the run, 251.3 cm., or 3.31 atm., gives the average rate of disappearance of hydrogen, 0.0261 mole min.$^{-1}$ g.$^{-1}$ Division of the average rate of disappearance of hydrogen by the average rate of disappearance of benzene gives a factor of 3.17 in good agreement with the stoichiometric expectations. This relationship cannot be obtained using the rate constant for hydrogen from either Equation 1 or Equation 2.

Acknowledgment. The authors are grateful to the Research Corp. for a Frederick Gardner Cottrell grant in support of this work.

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