Kinetics of Aldehyde Hydrogenation: Vapor-phase Flow System and Supported Nickel Catalyst

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A kinetic study of the catalytic vapor-phase hydrogenation of three aldehydes (acetaldehyde, propionaldehyde, and *n*-butyraldehyde) was made at low conversions with a commercial supported nickel catalyst. A simple initial rate equation was determined and found to agree with a mechanism suggested by the ideal kinetics of Hougen and known experimental evidence. By means of this equation the relative reactivities of the aldehydes were compared and found to agree with the predictions of organic theory. An improved reactor designed to ensure isothermal operation is described.

It would seem that experimentation in applied kinetics should have objectives in addition to the determination of a rate equation or apparent mechanism for a particular reaction. It is well known that an experimentally determined rate equation for a reaction over a given catalyst often has limited usefulness. The kinetic constants are applicable with certainty only for the one catalyst and the range of experimental conditions. It is possible, however, to develop data and concepts of general usefulness from a study of any specific reaction, particularly if certain general objectives are selected during the early stages of a project.

The objectives of the work described in this paper are listed below. The criterion for selection was the extent of their contribution to improved methods for the application of kinetics to process design and development.

OBJECTIVES

1. To determine a rate equation and rate constants for the catalytic vapor-phase hydrogenation of aldehydes to the corresponding alcohols by use of a supported nickel catalyst.
2. To determine the relative reactivities of the three aldehydes and the feasibility of correlating kinetic data for members of a family of compounds for engineering purposes.
3. To demonstrate an improved experimental reactor, designed to ensure nearly isothermal operation.
4. To reemphasize the value of theoretical organic chemistry in establishing rate equations useful for design and in comparing reaction rates of members of a family of compounds.

PREVIOUS WORK WITH ALDEHYDES

Although many aldehydes are catalytically hydrogenated to corresponding alcohols on an industrial scale, the kinetics of the reaction has received little attention. The fundamental work done thus far, however, has established that the hydrogenation of aldehydes over nickel at temperatures near 150°C. involves addition across the olefinic bond of the enol form (*2, 3, 7, 10*). Palmer (*7a*), studying the reverse reaction on copper (dehydrogenation of ethyl, *n*-propyl, and *n*-butyl alcohols), found the rates and temperature coefficients to be equal.

EXPERIMENTAL REACTOR—DESIGNED FOR ISOTHERMAL OPERATION

The usual fixed-bed experimental reactor does not have sufficient heat transfer surface for removing the heat of reaction fast enough to prevent a sizable temperature change. This is true in most cases even when the catalyst is mixed at random with inert material. An example is a reactor ½ in. in diameter by 3 in. long in which it is desired to

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hydrogenate 0.1 g.-mole of propionaldehyde/hr. If the catalyst bed temperature is 5°F. above the jacket temperature and the over-all heat transfer coefficient is 10 B.t.u./(hr.)(sq. ft./°F.), the heat transfer out of the reactor would be about 1.6 B.t.u./hr., but the heat released by the reaction is about 6 B.t.u./hr., therefore, the heat of reaction could not be removed under these conditions and the bed temperature would probably rise excessively.

A solution to this design problem is to make the catalyst section smaller in diameter but greater in length. This was accomplished by use of a $\frac{1}{4}$-in., 20 B.W.G. tube, the catalyst pellets being spaced at sufficient distances to permit removal of the heat of reaction.

The jacketed reactor used in this study is shown in Figure 1. It is made of a length of $\frac{1}{4}$-in. 20 B.W.G. type-304 stainless steel tubing. Heating, vaporizing, and mixing of the reactants takes place in the upper section. Twelve catalyst pellets ($\frac{1}{8}$- by $\frac{1}{8}$-in. cylinders) are spaced by $\frac{7}{8}$-in. spacers made from a $\frac{1}{8}$-in. rod of type-304 stainless steel. Two thermowells provide catalyst-bed inlet and outlet temperature-measurement points. A temperature-controlled "Ucon" heat transfer fluid was circulated through the jacket at about 3.5 gal./min. The jacket inlet and outlet temperatures were held to within 1°C. Arranging and spacing the catalyst pellets as indicated in Figure 1 results in high linear velocities and good transfer of the exothermic heat of reaction to the jacket thus providing a substantially isothermal reactor if conversions are held to a reasonably low value, i.e., less than 6%. A typical set of temperatures data is as follows:

Location	Temperature, °C.
Reactor inlet (top)	150.2
Reactor outlet (bottom)	150.4
Jacket inlet (bottom)	150.2
Jacket outlet (top)	150.0

Such a small temperature rise, 0.2°C., indicates a substantially isothermal catalyst bed.

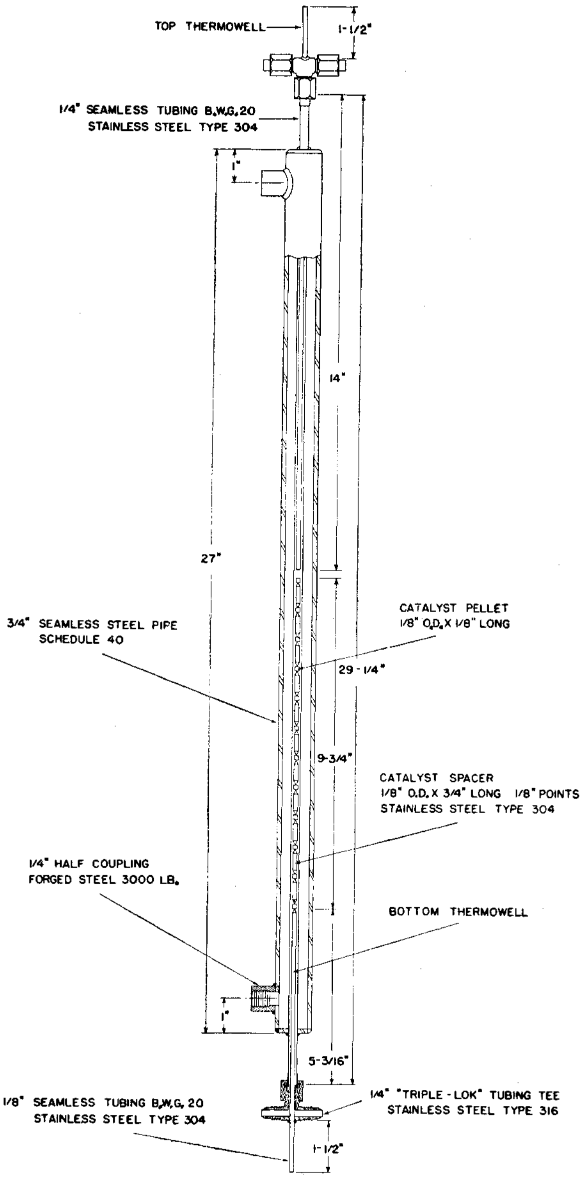

Fig. 1. Reactor drawing.

EXPERIMENTAL DETAILS

Reactants

Aldehydes manufactured by Carbide and Carbon Chemicals Company were employed. Purity limits established by infrared and chemicals methods are listed below together with methods of purification. Acetaldehyde as received was subjected to several types of analysis for purity. Comparison of its infrared spectrum with literature data indicated high purity. Peaks characteristic of water, acid, alcohol, and aldol were not found. The other aldehydes were not of equivalent purity and were distilled as indicated.

Purified propionaldehyde and *n*-butyraldehyde were redistilled 3 hr. prior to a series of runs and stored under nitrogen. Such redistillation was not found necessary for acetaldehyde.

	Maximum purity, %	Maximum water, %	Maximum acid, %	Purification method
Acetaldehyde	98	0.1	0.01	No purification required
Propionaldehyde	99	0.1	0.01	Several distillations followed by treatment with type 4A (Linde Air Products) molecular sieves
n-Butyraldehyde	99	0.1	0.01	Distillation

Analysis

A Beckman IR-2 infrared spectrophotometer was used to measure the alcohol concentration in the condensed reactor effluent. Wave lengths used were for ethanol, 2.88; *n*-propanol, 2.83; and *n*-butanol, 2.91 μ.

Catalyst

A commercial hydrogenation catalyst Ni-0101 T-$\frac{1}{8}$ in. manufactured by Harshaw Chemical Company was used. It or a similar catalyst has been used by a number of workers for hydrogenation studies (*1, 4, 6, 8, 12, 14*). The catalyst was reduced *in situ* at 250° to 350°C. and 50 lb./sq. in. abs. Hydrogen flow rate was 25 liters/(hr.) (g. of catalyst) for 16 hr. In the reduced state the catalyst is 80% nickel and 20% kieselguhr.

Experimental Procedure

A schematic flow diagram of the system is given in Figure 2. The reactor temperature was maintained by circulating Ucon fluid. Data were taken when the optical density of the reactor effluent became constant after introduction of feed or change in conditions (5 to 30 min.). At regular intervals during a series of runs feed aldehyde was introduced to the infrared cell to establish the blank optical-density reading.

Homogeneous Reaction and Catalytic Effects of Equipment

Runs made in the absence of catalyst showed no conversion of aldehyde. It can thus be concluded that the homogeneous reaction was negligible and that the metal walls of the system had no catalytic effect.

Side Reactions

At high temperatures and low space velocities, conditions would seem to be better for side reactions than under less drastic conditions. Infrared analysis of the hydrogen off gas from such runs however indicated no evidence of expected hydrogenolysis products such as hydrocarbons, carbon monoxide, and carbon dioxide. Infrared analysis of the liquid indicated the presence of only alcohol and aldehyde. Therefore, no side reactions were observed.

Mass Transfer Effects

Mass transfer was indicated to be non rate controlling by the observation that the rate of reaction was definitely dependent on total pressure. A more rigorous method of establishing mass transfer effects is to measure conversion at different combinations of flow and catalyst weight such that the time factor is maintained constant. This method was used and results showed that mass transfer effects were negligible.

TABLE 1
RUN DATA
HYDROGENATION OF PROPIONALDEHYDE

Run	Temp., °C.	Partial Pressures, lb./sq. in. abs. Aldehyde P_u	Partial Pressures, lb./sq. in. abs. Hydrogen P_H	Space velocity g. moles/(hr.)(g.) (F_u/W)	Conversion, % x	Initial rate of reaction, g. moles/(hr.)(g.) Measured	Initial rate of reaction, g. moles/(hr.)(g.) Corrected r_0
Unreduced Catalyst Weight = 0.7961 g.							
6B	150.5	10.0	10.0	2.51	2.00	0.0502	0.0502
6C	149.2	15.0	15.0	2.51	2.63	0.0660	0.0660
6D	150.6	20.0	20.0	2.51	3.04	0.0763	0.0763
6E	150.0	22.5	22.5	2.51	3.20	0.0803	0.0803
6F	149.9	25.0	25.0	2.51	3.37	0.0846	0.0846
6G	150.3	27.5	27.5	2.51	3.48	0.0874	0.0874
6H	149.8	30.0	30.0	2.51	3.60	0.0904	0.0904
7A	174.7	14.3	15.7	4.13	2.56	0.106	0.108
7B	174.9	20.0	20.0	3.79	3.05	0.116	0.118
7C	175.0	25.1	24.9	3.79	3.25	0.123	0.125
7D	174.9	30.1	29.9	3.79	3.55	0.135	0.137
7E	175.4	27.6	27.4	3.79	3.43	0.130	0.132
7F	173.8	22.6	22.4	3.79	3.12	0.118	0.120
7G	174.5	17.5	17.5	3.79	2.90	0.110	0.112
7H	175.4	10.0	10.0	3.79	2.28	0.0864	0.0880
7I	174.4	15.0	15.0	3.73	2.80	0.104	0.106
7J	173.8	12.5	12.5	3.73	2.46	0.0932	0.0949
8A	149.4	16.3	13.7	2.95	2.47	0.0729	0.0755
8B	150.4	14.4	15.6	2.95	2.23	0.0657	0.0680
8C	150.1	12.9	17.1	2.95	1.85	0.0545	0.0564
8D	150.4	11.1	18.9	2.95	1.57	0.0463	0.0479
8E	150.1	9.8	20.2	2.95	1.33	0.0392	0.0406
8F	149.2	16.3	13.7	2.95	2.47	0.0729	0.0755
8H	150.7	15.2	14.8	1.29	5.45	0.0703	0.0728
8I	148.5	15.4	14.6	3.98	1.77	0.0703	0.0728
8J	149.1	15.9	14.1	7.05	0.92	0.0648	0.0671
9A	165.5	20.2	19.8	3.83	2.48	0.0950	0.100
9B	164.8	25.2	24.8	3.83	2.79	0.1070	0.113
9C	164.1	27.2	27.5	3.83	2.87	0.1100	0.116
9D	164.2	30.3	29.7	3.83	2.96	0.1130	0.119
9E	163.6	17.7	17.3	3.83	2.34	0.0895	0.0944
9F	164.0	15.0	15.0	3.83	2.13	0.0815	0.0860
9G	164.8	10.1	9.88	3.83	1.70	0.0650	0.0686
9H	164.1	20.2	19.8	3.83	2.49	0.0953	0.1005
16A	149.9	20.4	19.6	2.61	2.64	0.0689	0.0769
16B	150.0	25.5	24.5	2.61	2.90	0.0757	0.0845
16C	150.0	30.6	29.4	2.61	3.12	0.0815	0.0910
16D	149.9	28.0	27.0	2.61	2.98	0.0778	0.0868
16E	149.4	22.9	22.1	2.61	2.78	0.0726	0.0810
16F	150.4	17.8	17.2	2.61	2.45	0.0639	0.0713
16G	149.9	12.2	12.3	2.61	2.04	0.0532	0.0594
16I	150.5	15.3	14.7	2.61	2.38	0.0621	0.0643
16J	151.1	20.4	19.6	2.61	2.65	0.0691	0.0771

Catalyst Activity

Data for the three aldehydes are summarized in Tables 1, 2, and 3*. The range of variables is as follows:

Temperature, °C.	120–180
Pressure, lb./sq. in. abs.	20–60
Mole fraction hydrogen	0.4–0.7
Space velocity, g. moles/(hr.)(g.)	1.5–7
Conversion, %	0.5–3.5

The catalyst activity was checked at regular intervals by use of propionaldehyde hydrogenation as the base reaction. All data are therefore reported as corrected to a single base activity by use of the activity factor described by Hougen and Watson. The decline in activity for propionaldehyde after 64 runs was 10.4%, for *n*-butyraldehyde after 39 runs it was 5%, and for acetaldehyde after 26 runs it was 58%. The high decline in activity for acetaldehyde was probably due to some undetected impurity.

CALCULATION OF INITIAL RATES

The usual method of determining the initial rate of reaction is to measure conversion at various time factors (W/F) and to extrapolate the data to $x = 0$ and $(W/F) = 0$. The slope of the curve at $x = 0$ is the initial rate.

$$r_0 = \left[\frac{dx_u}{d\left(\frac{W}{F_u}\right)}\right]_{x_u=0} \qquad (1)$$

In this work it was found that at conversions up to 5% a plot of x vs. (W/F) was a straight line. Since the maximum conversion encountered was 3.5%, except for the runs that established the linear relationship, initial rates were calculated as follows:

$$r_0 = \frac{x_u}{\left(\frac{W}{F_u}\right)} = (x_u)\left(\frac{F_u}{W}\right) \qquad (2)$$

DETERMINATION OF RATE EQUATION

Because of the complexities associated with catalytic reactions it is imperative that a study of relative rates be approached in the simplest manner possible. Accordingly, only initial rates were considered in this work and a simple kinetic equation was selected to represent the data.

An equation of the form $r_0 = k\,(P_u)^m(P_H)^n$ was used to correlate the data. The exponents were restricted to integral and half-integral values in order further to simplify the study and subsequent use of the rate equations. By logarithmic correlation of the data the exponents were found to be $m = 1.0$ and $n = -0.5$ for the three aldehydes. Values of k were

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*Complete tabular material has been deposited as document 5440 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

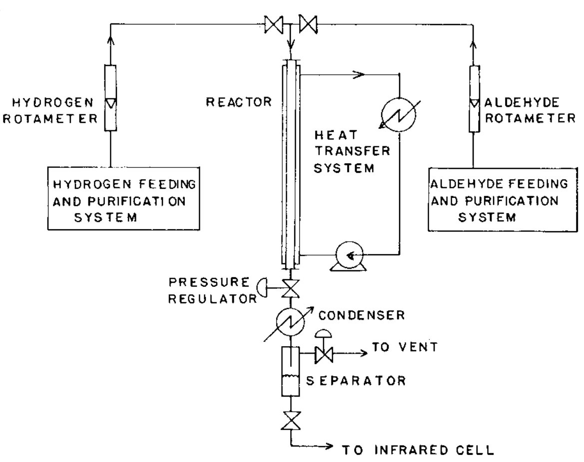


Fig. 2. Flow diagram of experimental unit.

computed by the method of least squares and fitted similarly to the Arrhenius equation. Results are summarized in Table 4.

These values show definite trends. The value of E is substantially constant for all the aldehydes and the value of A increases as the size of the aldehyde increases. This treatment, therefore, gives a quantitative measure of the reactivity of the three aldehydes. Values of k are highest for *n*-butyraldehydes and lowest for acetaldehyde.

POSSIBLE MECHANISM

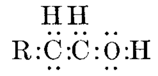
Boudart (*5*) has emphasized the value of finding a mechanism based on classical kinetics which after the necessary simplification will give the rate equation selected by the method just described. The mechanism thus selected provides a theoretical framework for subsequent reasoning and speculation.

From plots of initial rate vs. total pressure, as described by Hougen (*15*), it was concluded that the controlling step is the adsorption of the aldehyde. It is further reasonable to assume that hydrogen is atomically adsorbed on the nickel surface. The initial rate equation for expressing these conditions is, according to Hougen and his associates: $r_0 = (k_A P_u)/(1 + K_H P_H)^{1/2}$. This equation may be simplified as suggested by Boudart (*5*) to $r_0 \cong k[P_u/(P_H)]^{1/2}$, which is the equation already shown to fit the data.

COMPARISON OF RELATIVE RATES FOR THE ALDEHYDES

In a comparison of, and an attempt to correlate, applied kinetic data on members of a family of compounds, it is valuable to employ knowledge of the chemistry of the reaction. The results have indicated that the higher the molecular weight of the aldehyde, the greater the initial rate of hydrogenation, in contrast to the behavior observed for the olefins. Ethylene hydrogenates faster than propylene and propylene faster than 1-butene (*6*). The controlling step in the hydrogenation of these two homologous series, however, is different. In olefin hydrogenation the surface reaction is rate controlling (*6, 11*); whereas with aldehydes the adsorption of aldehyde controls. Thus, when a methyl group is substituted for a hydrogen atom on the ethylene molecule, the rate of surface reaction is decreased. But when a methyl group is substituted for an α-hydrogen atom on the acetaldehyde molecule, the rate of adsorption of the aldehyde is increased. There is no contradiction since different types of reactions are taking place.

Anderson and MacNaughton (*2*) and Badin and Pacsu (*3*) have found that the hydrogenation of an aldehyde involves enolization and addition on the olefinic double bond. On the basis of these findings it might be assumed that the following structure represents the carbonyl compound in a state ready for adsorption:



$$\mathrm{R{:}\overset{H}{\underset{\cdot\cdot}{C}}{:}\overset{H}{\underset{}{C}}{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{:}H}$$

The α-carbon atom is a nucleophilic center. Any structural factor which tends to increase the electron density at a nucleophilic center will enhance its reactivity (*9*). When R is a methyl group the inductive effect is one of electron release, and the electron density at the α carbon of propionaldehyde would be expected to be higher than that of acetaldehyde. Similarly, an ethyl group results in a slightly larger electron release and *n*-butyraldehyde should have

TABLE 2

RUN DATA

HYDROGENATION OF *n*-BUTYRALDEHYDE

Run	Temp., °C.	Partial pressures, lb./sq. in. abs. Aldehyde P_u	Partial pressures, lb./sq. in. abs. Hydrogen P_H	Space velocity, g.-moles/(hr.)(g.) (F_u/W)	Conversion, % x	Initial rate of reaction, g.-moles/(hr.)(g.) Measured	Initial rate of reaction, g.-moles/(hr.)(g.) Corrected r_0
		Unreduced Catalyst Weight = 0.7961 g.					
19A	160.4	20.4	19.6	1.61	2.63	0.0425	0.106
19B	160.3	25.5	24.5	1.61	2.94	0.0474	0.119
19C	160.1	30.6	29.4	1.61	3.06	0.0494	0.124
19D	159.6	28.1	26.9	1.61	3.14	0.0507	0.127
19E	159.5	23.0	22.0	1.61	2.90	0.0468	0.117
19F	159.5	17.9	17.1	1.61	2.76	0.0446	0.112
19G	159.6	12.7	12.3	1.61	2.37	0.0382	0.0955
24A	179.8	20.1	19.9	3.10	2.26	0.0702	0.181
24B	180.4	25.2	24.8	3.10	2.34	0.0726	0.187
24C	179.0	30.2	29.8	3.10	2.38	0.0740	0.191
24D	178.5	17.6	17.4	3.10	2.05	0.0636	0.164
24E	179.2	12.6	12.4	3.10	1.84	0.0572	0.147
24F	180.0	10.1	9.9	3.10	1.60	0.0497	0.128
24G	181.3	15.1	14.9	3.10	1.90	0.0590	0.152
24H	180.8	20.1	19.9	3.10	2.10	0.0652	0.168
26A	170.5	13.0	27.0	1.64	2.73	0.0450	0.117
26B	169.8	10.4	29.6	1.64	2.63	0.0433	0.113
26C	169.6	8.6	31.4	1.64	2.50	0.0412	0.107
26D	170.0	16.9	23.1	1.64	3.01	0.0496	0.129
26E	170.8	24.0	16.0	1.64	3.01	0.0496	0.129
26F	171.7	13.0	27.0	1.64	2.73	0.0450	0.117
28A	169.1	20.4	19.6	2.39	2.17	0.0517	0.136
28B	171.0	25.5	24.5	2.39	2.30	0.0548	0.145
28C	170.9	30.6	29.4	2.39	2.45	0.0584	0.154
28D	170.7	17.8	17.2	2.39	2.13	0.0507	0.134
28E	170.5	12.7	12.3	2.39	1.90	0.0452	0.119
28F	169.7	10.2	9.8	2.39	1.75	0.0417	0.110

an α-carbon atom of higher electron density than propionaldehyde. The higher the electron density of the α-carbon atom, the greater would be its affinity for centers on the catalyst of opposite charge. (In the presence of the aldehyde such sites as NiH^+ may be postulated as existing.) Therefore, on the basis of the inductive effect the rates of adsorption should increase as the size of R is increased. This prediction was substantiated experimentally.

The effect dies out rapidly as it is transmitted down a saturated chain (*9*); therefore, it would be expected that a bigger difference in rates should occur between acetaldehyde and propionaldehyde than between the latter and *n*-butyraldehyde. Initial rates calculated from the equations of Table 4 for the reaction of equimolar mixtures of hydrogen and aldehyde at 180°C. and 20 lb./sq. in. abs. indicate that relative reactivities are acetaldehyde 1.00, propionaldehyde 1.54, *n*-butyraldehyde 1.91.

Palmer (*7a*) observed constancy of rates and temperature coefficients within his experimental error for the reverse reactions on copper. In the present investigation of the forward reactions on nickel only the temperature coefficients remained constant. Because of the different catalyst and the difficulties experienced by Palmer in regulating flow rates, it is difficult to compare his findings with the initial rate data on the forward reaction of the present investigation.

Extrapolation of the observed trend in reactivity would seem dangerous since the inductive effect may become negligible in relation to steric effects, and it is certainly conceivable that the controlling step could be different in the hydrogenation of another aldehyde. It should be further emphasized that these data were taken at low conversions and that the effect of product composition has not been studied.

TABLE 3

RUN DATA

HYDROGENATION OF ACETALDEHYDE

Run	Temp., °C.	Partial pressures, lb./sq. in. abs. Aldehyde P_u	Hydrogen P_H	Space velocity, g.-moles/(hr.)(g.) (F_u/W)	Conversion, % x	Initial rate of reaction, g.-moles/(hr.)(g.) Measured	Corrected r_0
		Unreduced Catalyst Weight = 0.7784					
31A	129.5	13.8	27.3	3.12	3.04	0.0948	0.0224
31B	130.4	17.1	33.9	3.12	3.19	0.0995	0.0235
31F	130.6	8.86	17.5	3.12	2.77	0.0865	0.0204
31G	130.8	10.4	20.5	3.12	2.83	0.0884	0.0209
31H	131.6	12.1	23.8	3.12	2.98	0.0930	0.0220
31I	130.9	13.7	27.2	3.12	3.04	0.0948	0.0224
33D	121.1	17.0	33.7	3.12	1.72	0.0536	0.0154
33E	121.3	13.7	27.1	3.12	1.65	0.0514	0.0147
33F	119.2	10.5	20.6	3.12	1.54	0.0480	0.0138
33G	119.8	8.56	17.2	3.12	1.52	0.0473	0.0136
33H	120.9	12.0	23.8	3.12	1.56	0.0486	0.0139
33I	119.9	17.2	23.8	3.92	1.42	0.0556	0.0168
33J	118.9	13.2	27.8	3.92	0.99	0.0388	0.0118
33K	119.5	23.6	17.4	3.92	2.05	0.0803	0.0243
33L	121.5	20.0	21.0	3.92	1.46	0.0572	0.0173
33M	121.3	14.9	26.1	3.92	1.24	0.0486	0.0147
35D	139.9	17.4	17.7	5.90	1.35	0.0796	0.0316
35E	140.1	12.8	13.0	5.90	1.26	0.0743	0.0295
35F	139.7	11.0	11.2	5.90	1.22	0.0719	0.0285
35G	140.3	15.6	15.9	5.90	1.36	0.0802	0.0318

TABLE 4

INITIAL RATE EQUATION FOR THE HYDROGENATION OF ALDEHYDES

$$r_0 = k\frac{P_u}{(P_H)^{1/2}}$$

$$\ln k = -\frac{E}{RT} + \ln A$$

	Acetaldehyde	Propionaldehyde	*n*-Butyraldehyde
E*	$+7.8 \pm 0.1 \times 10^3$	$+7.8 \pm 0.1 \times 10^3$	$+7.8 \pm 0.1 \times 10^3$
ln A	+4.94	+5.17	+5.31
Average deviation, %	±13.6	±5.1	±6.9

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*Actual values obtained are 7,890, 7,810, and 7,730, respectively.

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NOTATION

A = constant of the Arrhenius equation
E = constant of the Arrhenius equation
F = feed rate, g.-moles/hr.
K = adsorption-equilibrium constant
k = reaction-velocity constant
L = total number of molal-adsorption sites per mass of unreduced catalyst
P = partial pressure, lb./sq. in. abs.
r = reaction rate, g.-moles/(hr.)(g. unreduced catalyst)
R = gas constant
T = temperature, °K.
W = unreduced catalyst weight, g.
x = conversion of aldehyde, moles per mole fed
π = total pressure, lb./sq. in. abs.

Subscripts

H = hydrogen
u = aldehyde
o = initial

LITERATURE CITED

1. Akers, W. W., and R. R. White, *Chem. Eng. Progr.*, **44**, 553 (1948).
2. Anderson, L. C., and N. W. MacNaughton, *J. Am. Chem. Soc.*, **64**, 1456 (1942).
3. Badin, E. J., and E. Pacsu, *ibid.*, **66**, 1953 (1944).
4. Binder, G. G., and R. R. White, *Chem. Eng. Progr.*, **46**, 563 (1950).
5. Boudart, Michel, *A.I.Ch.E. Journal*, **2**, 62 (1956).
6. Fair, J. R., Jr., Ph.D. dissertation, Univ. of Texas, Houston (1955).
7. Friedman, Lewis, and J. Turkevich, *J. Am. Chem. Soc.*, **74**, 1669 (1952).

7a. Palmer, W. G., *Proc. Roy. Soc.* (*London*), **107A**, 255 (1925).

8. Pursley, J. A., R. R. White, and C. M. Sliepcevich, *Chem. Engr. Prog. Symposium Series* No. 4, **48**, 51 (1952).
9. Royals, E. E., "Advanced Organic Chemistry," Prentice-Hall, New York (1954).
10. Sabatier, Paul, *Compt. rend.*, **136**, 738, 921, 983 (1903).
11. Sussman, M. N., and Charles Potter, *Ind. Eng. Chem.*, **46**, 457 (1954).
12. Tschernitz, J. L., S. Borstein, R. B. Beckmann, and O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*, **42**, 883 (1946).
13. Weller, Sol, *A.I.Ch.E. Journal*, **2**, 59 (1956).
14. Wilson, J. M., J. W. Otves, D. P. Stevenson, and C. O. Wagner, *Ind. Eng. Chem.*, **45**, 1480 (1953).
15. Yang, K. H., and O. A. Hougen, *Chem. Eng. Progr.*, **46**, 146 (1950).