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Butene Dehydrogenation Kinetics Over Dow Type B Catalyst

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The kinetics of the dehydrogenation of butene to butadiene over a stabilized, commercial sample of Dow Type B Ca–Ni–PO_4 catalyst have been studied. The isothermal, integral reactor data were obtained over a range of space velocities from 104 to 3103 v/v/hr and a temperature range of 550–675°C. Using a 20/1 volume ratio of steam to butene, conversions ranging from 5 to 72% were obtained. Also, the effect of steam volume ratios on conversion was determined in the range of 30/1 to 7/1 at 650 and 675°C.

The results are presented in terms of space velocity and temperature. The interpretation is made in terms of the amount of the total reaction presented by various fractions of a dimensionless reactor length. An apparent activation energy of 34–43 kcal/g mole is obtained from extrapolation of the data. Finally, a thorough and comprehensive theoretical integrated rate expression is developed to evaluate the kinetic rate constants from the experimental data. Relative adsorption coefficients for butadiene plus hydrogen and steam are evaluated as 15.3 and 0.15, respectively, with the activation energy 34–36 kcal/g mole. The expression is

$$ks = 2.36 \times 10^{27} e^{-35,990/RT}$$

where k is in molecules per second and s is number of active sites per gram of catalyst.

Introduction

According to Stobaugh (*1*) annual consumption of butadiene reached 2.7 billion pounds in the United States in 1965. Recent estimates indicate the demand will reach 3.4 billion pounds per year in 1970. Production of styrene–butadiene rubber and polybutadiene rubber account for 75–80% of this consumption.

About 60% of the butadiene consumed annually is produced by catalytic dehydrogenation. The Dow process for dehydrogenating normal butenes employing Dow Type B catalyst is utilized for about 30% of the annual butadiene production.

The Dow catalyst, which is precipitated calcium–nickel phosphate promoted with chromic oxide, was described in an early paper by Britton *et al.* (*2*). A later paper by Noddings *et al.* (*3*) described the early successful commercial trials in 1951. Despite the commercial significance of the Dow process and the Dow Type B catalyst, little has been published on the kinetics of dehydrogenation utilizing this process. Firko and Alexander (*4*) have investigated the kinetics, employing a differential microreactor and a 2-g sample of Dow Type B catalyst. The results at very low conversions were compared with pilot plant data.

The purpose of the present work is to expand the fundamental knowledge concerning butene dehydrogenation kinetics and to improve the accuracy of the previous results by utilizing the newer techniques of analysis and variables control. It is also a purpose to provide numerical values of kinetic rate factors for use in a computer simulation of the process.

EXPERIMENTAL

A. Materials

Dow Type B catalyst requires a 2–3 week break-in period when first placed on stream. Thereafter, the activity declines slowly and steadily, thus requiring increasing operating temperatures to maintain a given conversion during a run. Since it was desired to characterize a well broken-in catalyst, yet with representative activity, a commercial reactor was sampled after about 100 days of use. This represents 20–30% of a normal campaign. The activity of this used catalyst was declining only slowly with time such that the effect of several days of testing was not detectable.

Phillips "Pure Grade" Butene-2 assaying 99% plus was used as the feed. The composition was approximately 66.5% *trans* and 33.5% *cis*.

The source of steam was distilled water. This was pumped to a total vaporizing chamber and heated to reaction temperature in the preheating section of the reactor described below.

B. Test Procedures

Throughout this work, the catalytic samples were tested for butene dehydrogenation activity in either of two nearly identical furnaces. Figure 1 shows a simplified sketch of the reactor furnace. The catalyst tube consisted of a one-inch i.d. Type 446 stainless steel tube 52 inches long, equipped with steam, air and butene inlets at the top and a water-cooled condenser for condensing steam in the effluent gases.

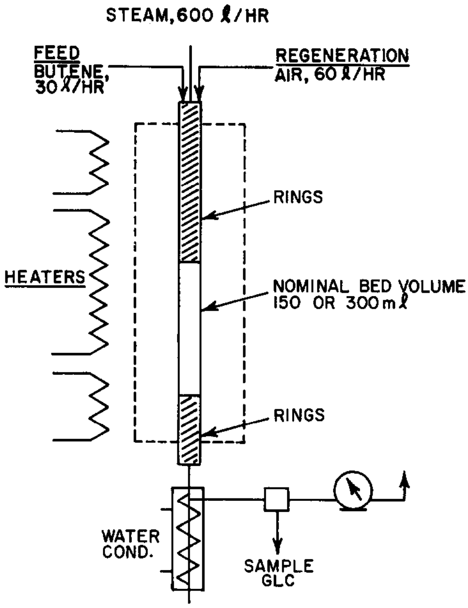

FIG. 1. Catalytic reactor.

The reactor tube was surrounded by a four-inch diameter by 42 in. long aluminum–bronze block, which in turn was surrounded by an Alundum core. Heat was supplied to the reactor and block by three electric heating elements wound on the core. The entire furnace was insulated with Johns-Manville Hi-Flo insulation.

The three furnace sections were independently controlled to the same nominal temperature with pyrometers. The temperature sensing thermocouples were inserted in holes drilled in the top, middle and bottom sections of the aluminum–bronze block.

Steam rates were controlled by the adjustable setting on the Milton Roy Minipump used for supplying distilled water to a total vaporizer. The rates were measured by collecting the water condensed from the effluent gases over a known period of time, usually thirty minutes. The flow rate of the feed was closely controlled and was measured by a wet test meter. Effluent gases, after passing through the condenser, were passed over Drierite before passing through the output wet test meter.

An automatic timer controlled the various phases of the cyclic operation which included process, fifteen minutes, steam purge, two minutes, regeneration with air and steam, eleven minutes and steam purge, two minutes. Total cycle time was thirty minutes.

The feed rate of butene during the process portion of the cycle was maintained at 30 liter/hr. During regeneration, the air rate was 60 liter/hr. Steam rates were adjusted to provide constant steam to butene ratios, according to the requirements of the various experiments. Regeneration and purge steam was maintained at the same rate as the process steam for any particular experiment.

Spot samples of the product gases for chromatographic analysis were obtained by trapping a slug of the gas in solenoid valve arrangements and sweeping the slug through the chromatographic column with hydrogen. The sampling valve arrangement was activated by a push button switch. Supplemental experiments indicated that a spot sample taken 14 min after the start of the feed portion of the cycle represented stable catalytic behavior. Thus, a 14-min spot sample was used throughout the work.

The analysis system was a conventional gas–liquid chromatograph, utilizing a thermal conductivity gauge and a fifteen-foot column of diethyl malonate on Chromosorb P at 0°C. The carrier gas was hydrogen. Areas of the various components were determined by measuring the peak width at one-half the height. Molar response factors, determined from standard known mixtures were applied to correct the areas to percent composition of the various components. The results are expressed on a H_2 free, C_4 basis. The consumption of butene, expressed as mole percent of the butene feed is the percent conversion. The production of butadiene as a mole percent of the butene consumed is the percent selectivity.

Bed sizes of 150 ml and 300 ml were used in this work. The nominal 150-ml bed was supported by inert porcelain Raschig rings ($\frac{1}{4}$ in. × $\frac{1}{4}$ in. diameter with $\frac{1}{16}$-in. wall thickness) to a height of 6 in. up from the bottom of the furnace. The space above the bed was filled with Raschig rings and served as a preheating section. For the nominal 300-ml bed, the height of the supporting rings was 9 in. up from the bottom. The beds were brought to the operating temperatures of a run in a flowing steam atmosphere.

C. Outline of Design

1. Temperature profiles for various bed sizes. The objectives of this work required the collection of integral reactor percent conversion data over a wide range of space velocities at various temperatures and steam rates. These were necessary as raw data for ultimate kinetic treatment.

The wide range of space velocities was conveniently obtained at a constant butene feed rate by varying the weight of catalyst contained in the nominal bed size. The remaining volume of the nominal bed size was made up of Raschig rings. In each case, the catalyst pellets and Raschig rings were well mixed so as to distribute the catalyst within the entire volume occupied by the nominal bed. Using a butene feed rate of 30 liter/hr (STP) and catalyst amounts ranging from 300 g to 10 g, actual space velocities from 104 to 3103 volumes of butene per volume of actalyst per hour (v/v/hr) were achieved without altering the mechanical and thermal characteristics of the reactor system.

In the first series with a nominal bed size of 150 ml, catalyst weights of 150.0, 80.0, 40.0, 20.0, and 10.0 g, mixed with Raschig rings to a volume of 150 ml, as described above, were studied. In the second series, over a nominal 300-ml bed, catalyst weights of 300.0 g and 15.0 g were added to supplement the other values listed above. The various catalyst weights in this second series were mixed with Raschig rings to provide a 300-ml volume.

Once the reactor was loaded with the desired weight of catalyst, a temperature profile was run at a steam-to-feed volume ratio of 20/1. The temperature profile was started at 675°C which was the highest test temperature. Replicate activity data from at least two cycles were obtained at 675°C and at each 25°C interval as the temperature was lowered. For each bed, the profile was stopped when the percent conversion fell in the range of 5–10%. Upon completion of the temperature profile the temperature was again raised to the initial conditions of 675°C. The catalyst activity was redetermined to assure that it had remained constant during the test. A separate sample of the catalyst stock was used for each run. This eliminated the necessity of using a single bed to the extent that its activity was altered. The longest test conducted on the same catalytic bed was approximately 180 hr, while the average test was only 40 hr.

The two samples taken at each condition served as an error check on the system. If they did not agree, more samples were taken until satisfactory replication was achieved. The average values were recorded.

The bed size–temperature combinations studied are shown in Table 1. The *x* indicates the run conditions for which data were collected. The lower temperatures were not used for the smaller beds due to the difficulties of measuring the greatly reduced activity.

2. Variation of steam to feed ratio. In addition to the above work, the effect of steam to feed ratio was studied in a separate series of experiments. Since the kinetic treatment to be invoked later utilizes an approximation which is valid only at low conversions, catalyst weights of only 10 g were used in the nominal bed sizes of 300 ml. These beds were operated at 650°C and 675°C, respectively. Replicate chromatographic data were again collected at each condition of steam to feed ratio. Nominal volume ratios of 30/1, 25/1, 20/1, 16/1, 13/1, 10/1, and 7/1 were thus studied at the two reactor temperatures. The steam ratios were determined from the quantities of condensed steam collected during the sample cycle.

TABLE 1
Run Combinations for Temperature Profile Studies

Catalyst weight, g	Bed size, ml	Temperature, °C					
		675	650	625	600	575	550
300.0	300	x	x	x	x	x	x
150.0	300	x	x	x	x	x	x
	150	x	x	x	x	x	x
80.0	300	x	x	x	x	x	
	150	x	x	x	x	x	x
40.0	300	x	x	x	x		
	150	x	x	x	x		
20.0	300	x	x	x			
	150	x	x	x			
15.0	300	x	x	x			
10.0	300	x	x				
	150	x	x				

Results and Discussion

A. Variation of Activity with Feed Space Velocity

The temperature-profile data obtained for the various catalyst weights for the 300-ml bed runs are summarized in Table 2. Similar, but less extensive data for the 150-ml bed runs are listed in Table 3. For each catalyst weight, there is a corresponding feed space velocity, F_1, and a percent conversion. The values of F_1 for the same catalyst weights vary somewhat because of the slight variation in butene feed rate between replicates.

The percent selectivity is also listed for each condition. Inspection of the values at the two highest temperatures of 650°C and 675°C shows a maximum, apparently correlated with catalyst weight or space velocity. The lower selectivities shown by the 10- and 20-g beds may be due to a small amount of decomposition over the larger quantity of Raschig rings present. The lower selectivity for the 300-g beds at 650°C and 675°C may arise from the longer contact time for butadiene with the catalyst bed. At temperatures below 650°C, the percent selectivity values are uniformly high.

Loss in selectivity can arise through a direct decomposition of the feed butene, or

TABLE 2
SUMMARY OF DATA
300-ML BED RUNS AT 20/1 STEAM RATIO

Temp., °C	$10^3/T$ °K	Catalyst weight, g	F_1 v/v/hr	Conv. %	Select. %	$\ln\left(\ln\frac{1}{1-x}\right)$	F_1x	$\log\left(\frac{1}{1-x}\right)^{F_1}$
675	1.055	300	103.8	72.44	90.29	+0.254	75.2	58.1
		150	205.2	56.81	93.49	−0.175	116.6	74.8
		80	387.9	38.77	93.08	−0.712	150.4	82.6
		40	767.1	24.01	91.89	−1.293	184.2	91.4
		20	1546.5	15.25	89.46	−1.799	235.8	111.1
		15	2048.2	12.04	89.57	−2.053	246.6	114.1
		10	3103.0	10.31	85.43	−2.218	319.9	146.6
650	1.083	300	99.1	63.38	93.50	+0.005	62.8	43.2
		150	203.6	46.01	95.57	−0.484	93.7	54.5
		80	390.4	29.86	95.86	−1.037	116.6	60.1
		40	763.8	17.98	96.34	−1.618	137.3	65.7
		20	1544.8	10.76	92.98	−2.173	166.2	76.4
		15	2042.9	8.61	94.22	−2.408	175.9	79.9
		10	3064.1	6.33	92.35	−2.727	194.0	87.4
625	1.114	300	102.7	51.44	95.25	−0.325	52.8	32.2
		150	203.3	36.83	96.66	−0.778	74.9	40.6
		80	390.1	22.63	97.36	−1.360	88.3	43.5
		40	767.2	13.26	97.26	−1.950	101.7	47.4
		20	1552.8	7.65	96.48	−2.531	118.8	53.7
		15	2041.2	5.50	98.52	−2.872	112.3	50.2
600	1.146	300	104.1	38.78	96.71	−0.712	40.4	22.2
		150	206.3	24.78	97.86	−1.256	51.1	25.5
		80	387.9	15.38	97.97	−1.790	59.7	28.1
		40	777.0	8.90	99.08	−2.373	69.2	31.5
575	1.179	300	104.5	27.04	97.49	−1.154	28.3	14.3
		150	204.3	17.51	97.90	−1.648	35.8	17.1
		80	387.0	10.12	99.38	−2.238	39.2	17.9
550	1.215	300	105.0	17.26	98.12	−1.664	18.1	8.6
		150	203.9	10.66	97.56	−2.238	21.7	10.0

by decomposition of the product butadiene, or some combination of both routes. If butene is first converted to butadiene which then decomposes, the percent conversion of butene would be appropriate to use in the kinetic expression for the reaction. However, if the decomposition is a competing reaction, then only the conversion to butadiene (percent conversion of butene times percent selectivity) should be used. Detailed investigation of the importance of these two alternates is beyond the scope of this investigation. In the absence of contrary evidence, the decomposition products were considered to arise from the butadiene and the percent conversion was used directly in the later sections when dealing with the kinetics for the reaction of butene to butadiene.

Data from Table 2 are plotted in Fig. 2 to form a family of curves, showing the percent conversion vs feed rate, F_1, at the various temperatures. Figure 3 is a similar plot of percent conversion vs feed rate, F_1, for the 150-ml bed runs (Table 3). These curves in which the results are expressed in the usual engineering units strikingly show the wide range of conversion (5–72%) and space velocities (104–3103 v/v/hr) achieved in this study.

TABLE 3
SUMMARY OF DATA
150-ML BED RUNS AT 20/1 STEAM RATIO

Temp., °C	$10^3/T$ °K	Catalyst weight, g	F_1 v/v/hr	Conv. %	Select. %	$\ln\left(\ln\frac{1}{1-x}\right)$	F_1x	$F_1 \log\left(\frac{1}{1-x}\right)$
675	1.055	150	206.7	53.35	91.71	−0.271	110.3	68.5
		80	389.5	36.85	93.85	−0.777	143.5	77.7
		40	768.7	24.11	93.19	−1.288	185.3	92.1
		20	1547.0	13.02	90.26	−1.970	201.4	93.7
		10	3094.4	9.75	85.75	−2.277	301.7	137.9
650	1.083	150	204.7	44.48	95.59	−0.530	91.1	52.3
		80	386.2	28.02	95.97	−1.112	108.2	55.1
		40	763.2	18.69	95.71	−1.576	142.6	68.6
		20	1536.6	9.50	95.03	−2.304	146.0	66.6
		10	3058.9	6.27	90.83	−2.737	191.8	86.0
625	1.114	150	206.0	32.94	96.53	−0.917	67.9	35.7
		80	384.5	22.75	97.16	−1.354	87.5	43.1
		40	770.2	14.18	97.10	−1.878	109.2	51.1
		20	1529.2	6.84	95.24	−2.647	104.6	47.1
600	1.146	150	206.0	23.35	97.32	−1.325	48.1	23.8
		80	387.1	13.98	98.10	−1.893	54.1	25.3
		40	769.4	9.21	99.07	−2.337	70.9	32.3
575	1.179	150	206.2	16.47	97.93	−1.715	34.0	16.1
		80	381.3	9.50	99.24	−2.304	36.2	16.5
550	1.215	150	205.3	10.78	96.49	−2.171	22.1	10.2
		80	385.5	6.02	99.16	−2.779	23.2	10.4

B. Utilization of the Catalyst Along the Bed Length

An alternate view of the experimental data is helpful in understanding the relative amount of the total conversion carried by the various portions of the bed.

The measurements were made using a constant 30 liter/hr feed rate of butene, varying the amount of catalyst in the bed to achieve the range of space velocities. However, the data can be applied to isothermal beds of any length by expressing these results in terms of fractional bed length. The normalizing can be accomplished in the following manner, using the 675°C conversion data for the 300-ml bed runs (Table 2) as an example. The 10 g (9.66 ml) of catalyst, expressed as a volume, is 9.66/300 of a 300-ml bed but 9.66/200 of a 200-ml bed and 9.66/100 of a 100-ml bed. The conversion obtained over the 10 g catalyst weight represents that which would have been obtained at the above fractional lengths of beds, but at space velocities corresponding to those calculated

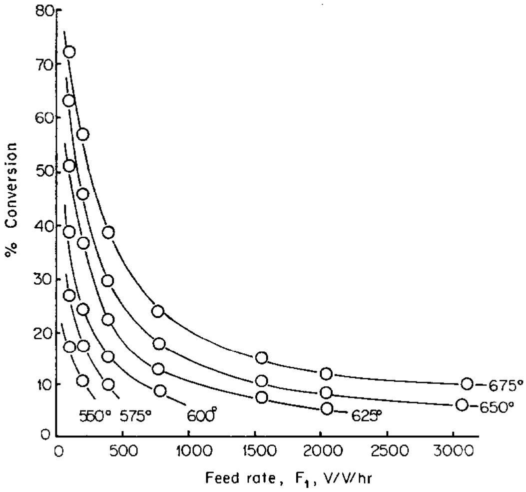

FIG. 2. % Conversion vs feed rate, 300-ml bed.

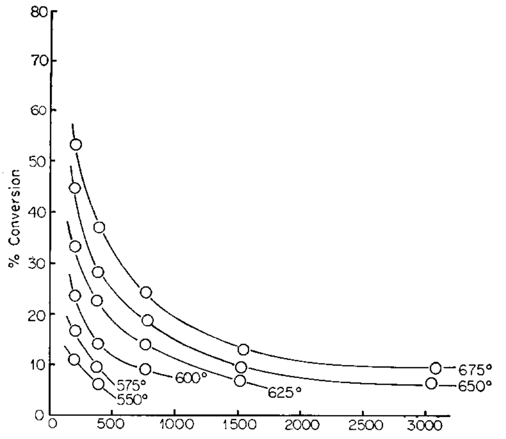

FIG. 3. % Conversion vs feed rate, 150-ml bed.

for 30 liter/hr over bed volumes of 300, 200, and 100 ml, that is, at 100, 150, and 300 v/v/hr. Proceeding in this way, Table 4 has been constructed and the corresponding calculated values of fractional or dimensionless bed length are shown in Fig. 4 with the corresponding conversions and space velocities.

As seen in Fig. 4, the slope of the conversion is steep in the first portion of the bed and tapers off as the flow proceeds along the bed length. Thus, the later sections of the catalyst bed are less effective in converting butene. This is due to the decreasing concentration of butene and to the increasing concentrations of butadiene and hydrogen which compete for the active catalyst sites.

Also, reduced space velocities result in higher conversions at all portions of the bed. Similar curves can be constructed for the other reaction temperatures listed in Table 2. In each case, a similar relationship exists, although the conversions are lower at the lower temperatures. These results can be applied to isothermal beds of any length because of the normalization to a dimensionless bed length.

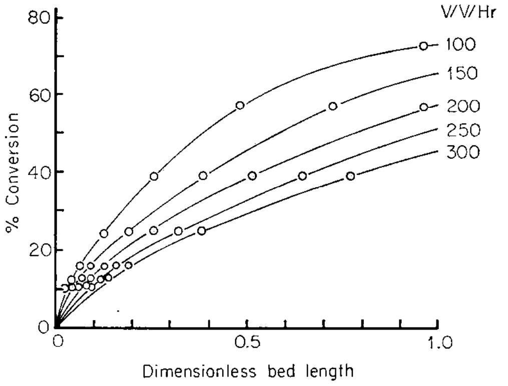

FIG. 4. Conversion throughout bed length, 675°C.

C. *Apparent Activation Energy*

According to the Arrhenius equation, the reaction rate constant, k, can be expressed as

$$k = Ae^{-E/RT} \quad (1)$$

where A is the frequency factor
E is the energy of activation
R is the gas constant and
T is the absolute temperature

or in logarithmic form,

$$\ln k = \ln A - (E/RT) \quad (2)$$

In the integrated rate expression for simple first order kinetics, the reaction rate

TABLE 4
DIMENSIONLESS BED LENGTH

Bed size, ml	Feed rate v/v/hr	Catalyst weight, g						
		10	15	20	40	80	150	300
300	100	0.032	0.048	0.064	0.128	0.257	0.483	0.966
200	150	0.048	0.072	0.097	0.193	0.386	0.725	
150	200	0.064	0.096	0.128	0.256	0.514	0.966	
120	250	0.081	0.121	0.161	0.322	0.644		
100	300	0.097	0.145	0.193	0.386	0.773		
% Conversion, 675°C		10.31	12.04	15.25	24.01	38.77	56.81	72.44

constant, k, is directly proportional to the quantity $\ln 1/(1 - x)$, where x is the fractional conversion. Then, $\ln (\ln 1/(1 - x))$ can be substituted for $\ln k$ in Eq. (2). Thus, the data from the 300-ml bed runs (Table 2) and the 150-ml bed runs (Table 3) can also be plotted as shown in Figs. 5 and 6. In these figures, $\ln (\ln 1/(1 - x))$ is plotted vs $10^3/T$°K, for each catalyst weight. Note that these integral reactor data do not form straight lines, as the Arrhenius equation would predict. Instead, the points fall along shallow curves depicted by dashes in the figures. The curvature arises as the apparent activation energy changes over a range of conversions. In each case, however, the first three points, representing the three highest temperatures, fall along straight lines. Since these temperatures are common to most catalyst weights, it was decided to obtain apparent activation energies from the slopes through these points.

The straight lines shown in Figs. 5 and 6 were derived by the least-squares method using the three data points at $10^3/T$°K equals 1.055, 1.083 and 1.114 for each catalyst weight. The apparent activation energies associated with the various catalyst weights were calculated from the slopes of these lines by multiplying by 1.986. This gives E in kcal/g mole. In the case of the 10-g beds, only the first two temperatures could be used for this calculation.

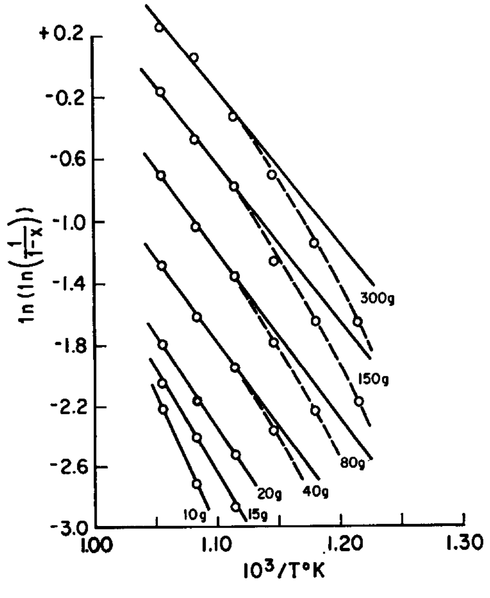

FIG. 5. Arrhenius plot, 300-ml bed.

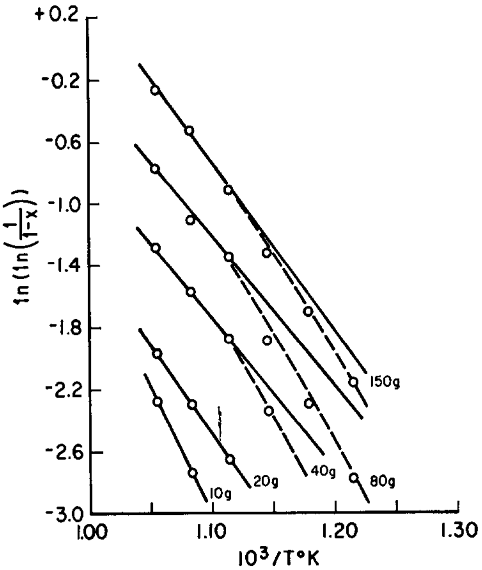

FIG. 6. Arrhenius plot, 150-ml bed.

Table 5 lists the calculated values of the apparent activation energy, E_{app}, for the various catalyst weights in the 300-ml bed runs and the 150-ml bed runs. Figure 7 shows the combined data, in which the values of E_{app} are plotted vs catalyst weight. The 300-ml bed data are shown as triangles and the 150-ml bed data are shown as circles. Extrapolation of this curve to zero catalyst weight should provide a value of E_{app} representing the activation energy for a differential reactor. The extrapolation is best accomplished by fitting the first

TABLE 5
APPARENT ACTIVATION ENERGY

Catalyst weight, g	E_{app} kcal/g mole 300-ml Bed	 150-ml Bed
300	19.52	—
150	20.29	21.81
80	21.80	19.36
40	22.12	19.85
20	24.61	22.79
15	27.60	—
10	36.12	32.63

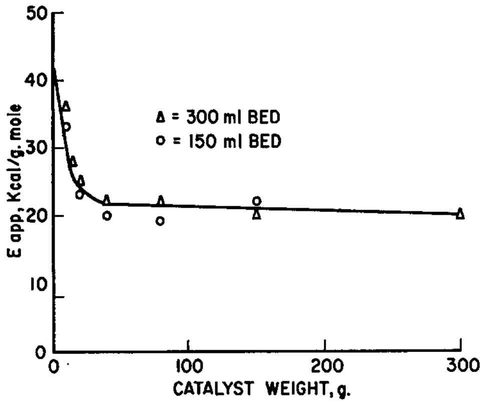

FIG. 7. Apparent activation energy.

several points to a straight line and determining the intercept. For the first 5 points, the least squares straight line has an intercept of 44.8 kcal/g mole. Using the first 7 points, the corresponding least-squares line has an intercept of 35.1 kcal/g mole. Although the extrapolation of integral reactor data to a differential bed size of zero weight is somewhat empirical, these values are later seen to be quite reasonable.

D. Kinetic Equations for Rate of Reaction

The treatment is similar to that by Balandin (*5*) and Firko and Alexander (*4*). However, here the kinetic factors are determined directly from the integrated equation. The reaction is considered to be first order in all the elements of the reactor. Thus, for any element the rate is given by

$$-\frac{dn}{dt} = kS_eS_1 \qquad (3)$$

where n = number of molecules reacted,
t = seconds,
k = $Ae^{-E/RT}$, molecules × sec^{-1},
S_e = number of catalyst active sites in the element,
S_1 = fraction of active sites covered by butene.

Alternately, the fraction of butene reacted, x, of the butene molecules, N_e, fed to the element may be used in the rate expression.

$$\frac{dx}{dt} = kS_eS_1/N_e \qquad (4)$$

Since the ratio S_e/N_e equals the total number of sites, S, over the total molecules of butene, N_1,

$$\frac{dx}{dt} = kSS_1/N_1 \qquad (5)$$

Rearrangement and integration gives

$$\int_0^x \left(\frac{1}{S_1}\right) dx = \int_0^{t_c} \left(\frac{kS}{N_1}\right) dt \qquad (6)$$

where the upper limits of the integrals are the exit conversion and contact time, respectively. The fraction of sites covered by butene in the mixture is given by Langmuir's isotherm,

$$S_1 = P_1/(P_1 + P_2Z_2 + P_3Z_3 + P_4Z_4) \qquad (7)$$

where P_1, P_2, P_3, and P_4 are partial pressures of butene, butadiene, hydrogen and steam, respectively, and Z_2, Z_3, and Z_4 are adsorption coefficients of butadiene, hydrogen, and steam, respectively, relative to butene.

This partial pressure of butene may be expressed in terms of the total number of molecules present, ΣN_r.

$$P_1 = N_1(1 - x)/\Sigma N_r \qquad (8)$$

Under conditions where no extra butadiene and hydrogen are added, and the reaction of butene produces stoichiometric quantities of these compounds,

$$P_2 = P_3 = N_1x/\Sigma N_r \qquad (9)$$

Using the mole ratio, R_4, of steam to butene in the feed,

$$P_4 = N_1R_4/\Sigma N_r \qquad (10)$$

By substitution,

$$S_1 = \frac{(1 - x)}{(1 - x) + x(Z_2 + Z_3) + R_4Z_4} \qquad (11)$$

Substitution of this expression in Eq. (6) followed by integration and combining terms gives

$$(Z_2 + Z_3 + R_4Z_4)\ln\left(\frac{1}{1 - x}\right) - (Z_2 + Z_3 - 1)x = kSt_c/N_1 \qquad (12)$$

The number of molecules of butene fed is commonly expressed in terms of a feed rate, F_1, or volumes of butene at standard conditions per bulk volume of catalyst per hour, where

$$F_1 = N_1\left(\frac{22{,}400 \text{ ml}}{6.02 \times 10^{23} \text{ molecules}}\right) \Big/ G\left(\frac{1 \text{ ml}}{1.0357 \text{ g}}\right) t_c \left(\frac{1 \text{ hr}}{3600 \text{ sec}}\right) \quad (13)$$

$$= N_1/Gt_c(7.21 \times 10^{15})$$

where G = weight of catalyst, g. Thus,

$$(Z_2 + Z_3 + R_4Z_4) \ln\left(\frac{1}{1-x}\right) - (Z_2 + Z_3 - 1)x = \frac{kS}{F_1G(7.21 \times 10^{15})} \quad (14)$$

or

$$F_1 \ln\left(\frac{1}{1-x}\right) = \frac{ks}{(7.21 \times 10^{15})(Z_2 + Z_3 + R_4Z_4)} + \frac{(Z_2 + Z_3 - 1)F_1x}{(Z_2 + Z_3 + R_4Z_4)} \quad (15)$$

where s equals number of active sites per gram of catalyst.

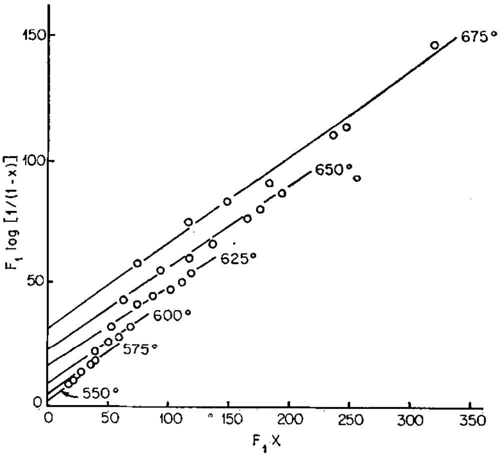

FIG. 8. Evaluation of kinetic rate factor, 300-ml bed runs.

This is the equation of a straight line with slope β and intercept, α where

$$\alpha = ks/(7.21 \times 10^{15})(Z_2 + Z_3 + R_4Z_4) \quad (16)$$

$$\beta = (Z_2 + Z_3 - 1)/(Z_2 + Z_3 + R_4Z_4) \quad (17)$$

Table 2 contains values of F_1x and F_1 log $(1/1 - x)$ for various catalyst weights at each temperature for the 300-ml bed runs. Figure 8 shows a plot of F_1 log $(1/1 - x)$ vs F_1x. The data result in a family of straight lines, one for each temperature studied. The values of α for each line

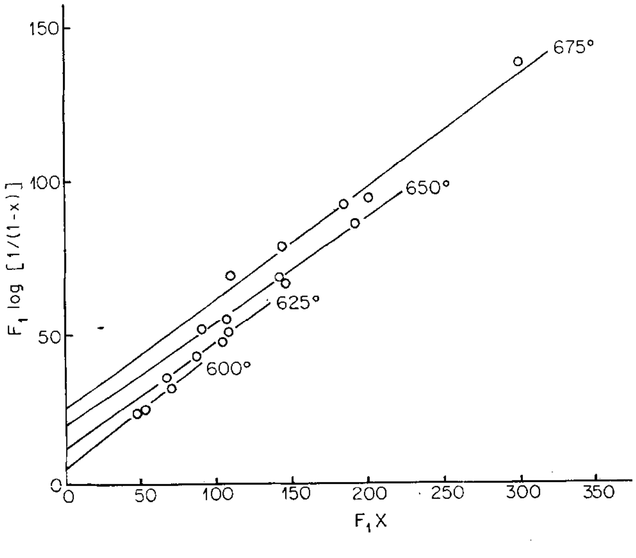

FIG. 9. Evaluation of kinetic rate factor, 150-ml bed runs.

TABLE 6
KINETIC RATE FACTOR, α

Temp., °C	$10^3/T$ °K	300-ml Bed α	300-ml Bed $\log \alpha$	150-ml Bed α	150-ml Bed $\log \alpha$
675	1.055	70.97	1.851	58.31	1.766
650	1.083	51.76	1.714	44.83	1.652
625	1.114	37.90	1.579	28.39	1.453
600	1.146	21.06	1.323	11.69	1.068
575	1.179	11.09	1.045	—	—
550	1.215	3.59	0.555	—	—

were calculated by multiplying the intercept, obtained from the least-squares straight line, by the factor 2.303 to convert back to natural logarithms. The values are listed in Table 6. Evaluation of β from 2.303 times the average slope of the six essentially parallel lines gives a value of 0.78.

Corresponding values for the 150-ml bed runs are listed in Table 3 and plotted in Fig. 9. The values at 550°C and 575°C were discarded due to poor accuracy at the lower conversions. The values of α from these data are included in Table 6 also. The corresponding value for β is 0.82.

With the relative adsorption coefficients and number of sites per gram of catalyst in Eq. (16) considered to be constant throughout the temperature range studied, it can be seen that α is directly proportional to the reaction rate constant, k. Thus, the values of α obtained at the different temperatures may be used in the Arrhenius equation to obtain a value for the activation energy, as before. Values of $\log \alpha$ are plotted vs $10^3/T$°K for each bed size in Fig. 10. The triangles represent the 300-ml bed runs and the circles represent the 150-ml bed runs. The data have been fitted by the least-squares method. The corresponding equations for the two beds are

$$\log \alpha_{300} = 10.252 - \frac{7.869 \times 10^3}{T°\mathrm{K}} \qquad (18)$$

$$\log \alpha_{150} = 9.720 - \frac{7.496 \times 10^3}{T°\mathrm{K}} \qquad (19)$$

The activation energies E_{300} and E_{150} have been calculated by multiplying the slopes by 2.303×1.986. Thus $E_{300} = 35.99$ kcal/g mole and $E_{150} = 34.28$ kcal/g mole. The range 35.1–44.8 kcal/g mole obtained by the empirical method described earlier is thus seen to be in good agreement with the values which arise from the kinetic equations derived here. Both methods of evaluating the activation energy are in good agreement with the 33.68 value given by Firko and Alexander.

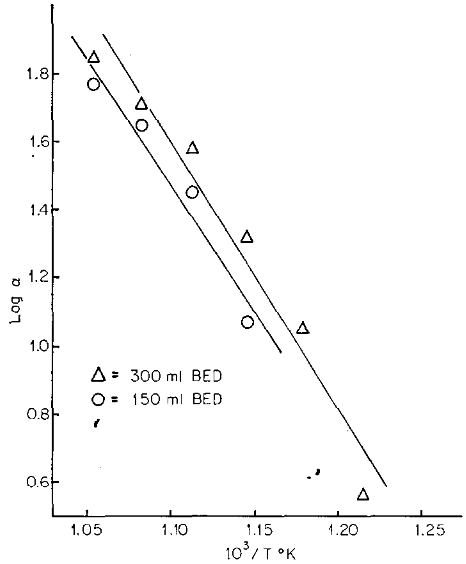

FIG. 10. Arrhenius plot using kinetic rate factor α.

In Fig. 10 the separation between the results from 300- and 150-ml bed sizes is attributed to differences in effective temperature for the two beds while operating at the same nominal temperature.

E. Steam Relative Adsorption Coefficient

The data obtained for various steam to butene mole ratios are summarized in Table 7. The conversion and selectivity are the average of at least two replicate determinations at each condition. The selectivity decreased rapidly at steam ratios below the 7/1 level reaching 54% at 4.2/1 ratio. The latter values were discarded.

The kinetic treatment is simplified at low conversions, where

$$-\ln(1 - x) \cong x. \qquad (20)$$

TABLE 7
SUMMARY OF RUNS AT VARIOUS STEAM RATIOS, 300-ML BED

Temp., °C	Catalyst weight, g	F_1 v/v/hr	Conversion %	Selectivity %	$1/x$	Steam ratio, R_4
675	10	3105	7.35	87.73	13.61	30.1
			8.74	87.32	11.44	24.8
			10.35	84.74	9.66	20.2
			12.54	83.39	7.97	15.6
			14.43	80.60	6.93	12.5
			16.86	78.31	5.93	9.6
			19.50	71.08	5.13	6.9
650	10	3105	4.74	93.52	21.10	30.38
			5.09	95.12	19.65	25.16
			6.15	92.26	16.26	20.31
			7.45	92.35	13.42	16.19
			9.08	89.95	11.01	13.38
			9.91	86.70	10.09	10.37
			11.89	83.52	8.41	6.96

Substitution of Eq. (20) in Eq. (15), with rearrangement gives the linear equation

$$R_4 = \frac{ks}{F_1(7.21 \times 10^{15})}\left(\frac{1}{Z_4}\right)\left(\frac{1}{x}\right) - \frac{1}{Z_4} \quad (21)$$

Figure 11 is a plot of R_4 vs $(1/x)$. The intercept, $(-1/Z_4)$, evaluated by a least-squares linear fit to the data, was −6.53 and −6.56 for the 675°C and 650°C data, respectively. The corresponding values for Z_4 are 0.153 and 0.152. These are considerably different from the 0.27 and 0.38 values observed at 625°C and 650°C by Firko and Alexander but correspond more closely with the 0.17 value reported at 600°C.

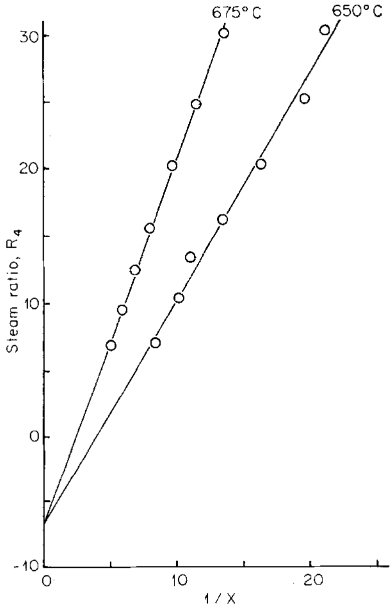

FIG. 11. Steam adsorption coefficient.

F. *Evaluation of Kinetic Rate Constant*

The values so far presented may be combined to evaluate the kinetic rate constant. Substitution of Z_4 equals 0.152, R_4 equals 20 and β equals 0.78 into Eq. (17) gives a value of 15.3 for $(Z_2 + Z_3)$. Earlier, β was shown to be constant over the temperature range of 550–675°C. Considering Z_4 constant over this same range, the sum Z_2 plus Z_3 is constant. If compensating changes in the adsorption coefficients of butadiene and hydrogen are absent, then Z_2 and Z_3 are constant also. This presents a simpler picture of the adsorption, namely that all the species maintain an unchanging adsorption coefficient relative to butene, regardless of the temperature.

The catalyst system is such that the rate constant, k, cannot be separated from the number of active sites per gram of catalyst. However, the product ks can be evaluated. The value of log α_{300} from Eq. (18) may be equated with the logarithmic equivalent of Eq. (16).

$$\log(ks/7.21 \times 10^{15}) - \log(Z_2 + Z_3 + R_4Z_4) = 10.252 - \frac{7.869 \times 10^3}{T°\text{K}} \quad (22)$$

Substitution of values gives

$$\log ks = 27.373 - (7.689 \times 10^3/T°\text{K}) \quad (23)$$

or

$$ks = 2.36 \times 10^{27} e^{-35.990/RT} \quad (24)$$

Evaluation of ks at the various temperature levels is summarized in Table 8. The values determined here have the units molecules × sites × $\sec^{-1} \times g^{-1}$. Also, the corresponding values with units moles × sites × $hr^{-1} \times g^{-1}$ are listed in the last column of Table 8. These correspond quite well with the $K_1 \times 10^3$ values of 50.5, 27.35, and 18.4 at 650, 625 and 600°C, respectively, as determined by Firko and Alexander for their catalyst.

TABLE 8
EVALUATION OF RATE CONSTANT

Temperature °C	$ks \times 10^{-13}$ molecules × sites × $\sec^{-1} \times g^{-1}$	$ks \times 10^3$ moles × sites × $hr^{-1} \times g^{-1}$
675	11.80	70.6
650	7.05	42.2
625	4.07	24.3
600	2.29	13.7
575	1.24	7.4
550	0.65	3.9

CONCLUSIONS

1. Data from conversion of butene to butadiene and hydrogen over Dow B catalyst fits the kinetic model wherein the conversion rate is proportional to the number of active sites on the catalyst and to the fraction of the active sites covered by butene.

2. The adsorption coefficients relative to butene in the competition for active sites are 0.15 for steam and 15.3 for butadiene plus hydrogen.

3. The rate of conversion along the bed length decreases as the decreased partial pressure of butene and increased concentrations of butadiene and hydrogen in the gas both lead to less butene adsorbed on the active sites.

4. Decreased flow rates of butene gives increased % conversion. However, the increase is not linear with space velocity due to the above decreased concentration of butene on the active sites as the conversion increases.

5. The activation energy is 35–45 kcal/g mole as determined by extrapolation of apparent activation energy data to zero bed weight and 34 to 36 kcal/g mole as determined from the integrated rate equation.

6. The inseparable product of the rate constant, molecules/sec, and the number of active sites per gram of catalyst, s, is

$$ks = 2.36 \times 10^{27} e^{-35,990/RT}$$

7. The above rate expressions are valid over the range tested of 104–3103 v/v/hr and 550–675°C at 20/1 volume ratio of steam to butene to give 5–72% conversion. Also, the steam relative adsorption coefficient is constant over the range tested of 30/1 to 7/1 at 650–675°C. Below 7/1 steam ratio the selectivity decreases markedly.

8. These rate expressions are in a form which can be used to simulate the operation of an adiabatic reactor. This requires a mathematical model for the heat balance along the catalyst bed as the butene reacts (endothermic) and heat transfer occurs between the gases and the catalyst, combined with evaluation of the rate of reaction at each temperature level within the bed.

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