TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-METHYL-1-BUTENE[a]

T, °K.	$(F°_0 - H°_0)/T$, cal. deg.$^{-1}$	$(H° - H°_0)/T$, cal. deg.$^{-1}$	$H° - H°_0$, kcal.	$S°$, cal. deg.$^{-1}$	$C_p°$, cal. deg.$^{-1}$	$\Delta Hf°$,[b] kcal.	$\Delta Ff°$,[b] kcal.	log Kf[b]
0	0	0	0	0	0	− 2.29	− 2.29	Infinite
273.16	−63.00	15.92	4.349	78.92	24.61	− 8.22	+13.66	−10.93
298.16	−64.43	16.72	4.985	81.15	26.28	− 8.68	15.68	−11.49
300.00	−64.53	16.78	5.034	81.31	26.41	− 8.71	15.84	−11.54
400	−69.80	20.04	8.016	89.84	33.20	−10.44	24.29	−13.27
500	−74.63	23.30	11.65	97.93	39.40	−11.89	33.14	−14.49
600	−79.16	26.44	15.86	105.60	44.72	−13.07	42.25	−15.39
700	−83.45	29.39	20.57	112.84	49.26	−13.99	51.55	−16.09
800	−87.56	32.12	25.70	119.68	53.15	−14.69	60.96	−16.65
900	−91.50	34.64	31.18	126.14	56.52	−15.20	70.44	−17.11
1000	−95.27	36.97	36.97	132.24	59.43	−15.52	79.99	−17.48
1100	−98.89	39.14	43.05	138.03	61.96	−15.68	89.54	−17.79
1200	−102.38	41.14	49.37	143.52	64.15	−15.71	99.11	−18.05
1300	−105.75	42.98	55.87	148.73	66.05	−15.69	108.66	−18.27
1400	−109.00	44.69	62.57	153.69	67.71	−15.57	118.23	−18.46
1500	−112.14	46.27	69.40	158.41	69.15	−15.43	127.78	−18.62

[a] To retain internal consistency, some values are given to one more decimal place than is justified by the absolute accuracy. [b] For the reaction $5C(c, graphite) + 5H_2(g) = C_5H_{10}(g)$.

3450 cal. mole^{-1}, also is reasonable, but not much significance can be attached to the actual numerical value. From the value obtained for the energy difference, the concentration of molecules in the high-energy conformation was calculated to be 0.15 mole % at 300°K. This result is consistent with the earlier conclusion that only one or two of the most intense vibrations of the high-energy conformation can be detected spectroscopically.

BARTLESVILLE, OKLAHOMA

[CONTRIBUTION FROM THE GULF RESEARCH & DEVELOPMENT COMPANY]

The Evaluation of Activation Energies Using a Rising Temperature Flow Reactor. The Dehydrogenation of Cyclohexane over WS_2, Pt/Al_2O_3, Cr_2O_3/Al_2O_3, $NiWO_4/Al_2O_3$ and Cr_2O_3

BY JOANNE M. BRIDGES AND G. HOUGHTON

RECEIVED DECEMBER 11, 1957

A rising temperature flow reactor has been used to evaluate the apparent activation energies and kinetics for the dehydrogenation of cyclohexane over WS_2, Pt/Al_2O_3, Cr_2O_3/Al_2O_3, $NiWO_4/Al_2O_3$ and Cr_2O_3. The method has also been used to compare rapidly the activities of the various catalysts. On the basis of equal volumes of catalyst, the order of the activities is approximately Pt/Al_2O_3 > water washed Cr_2O_3/Al_2O_3 > Cr_2O_3/Al_2O_3 > $NiWO_4/Al_2O_3$ > Cr_2O_3 > WS_2. However, on the basis of equal surface areas, the order of the activities is Pt/Al_2O_3 > water washed Cr_2O_3/Al_2O_3 > Cr_2O_3 > $NiWO_4/Al_2O_3$ > WS_2 > Cr_2O_3/Al_2O_3. Electron irradiation from a Van de Graaff accelerator has been found to have no permanent effect on the activity of Pt/Al_2O_3. The thermal cracking of cyclohexane over Vycor wool has been found to proceed in the temperature range 566–700° with an activation energy of 49 ± 5 kcal./g. mole.

Introduction

The literature in the field of catalysis indicates that one of the major obstacles to the investigation and comparison of solid catalysts is the time required to obtain the data. This difficulty has been overcome by the development of what the authors term a rising temperature flow reactor. If the reactor temperature is continuously increased with time at a steady rate of 1–10° per minute in the range 25–700°, the reactor will automatically locate the narrow band of temperature in which catalytic activity measurements can be made. Hauffe, Glang and Engell[1] have used a similar method to compare the activities of various oxides for the decomposition of nitrous oxide. Recently P. Kofstad[2] has used a rising temperature technique to investigate the kinetics of oxidation of various metals. In the present investigation the dehydrogenation of cyclohexane has been chosen for study, since the work of Kasansky and Plate,[3] Herington and Rideal[4] and Balandin and Rubinstein[5] indicates that this reaction is relatively free from complicating side reactions and the production of large quantities of intermediates.

Experimental

Equipment.—A flow diagram for the rising temperature reactor is shown in Fig. 1.

Nitrogen was used as the carrier gas and was purified by passing it over 100 mesh copper gauze at 300° to remove oxygen and then through a drying tube containing magnesium perchlorate. The nitrogen was metered by a cali-

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[1] K. Hauffe, R. Glang and H. J. Engell, *Z. physik. Chem.*, **201**, 221 (1952).

[2] P. Kofstad, *Nature*, **179**, 1362 (1957).

[3] B. A. Kasansky and A. F. Plate, *Ber.*, **67**, 1023 (1934).

[4] E. F. G. Herington and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **190**, 289 (1947).

[5] A. A. Balandin and A. M. Rubinstein, *Z. physik. Chem.*, **A167**, 431 (1933).

brated rotameter at a pressure of 4 lb./sq. in. gauge which was more than sufficient to maintain the desired flow rate. All the flow rates reported in the text are reduced to S.T.P.

The purified nitrogen was bubbled through cyclohexane (99.94 mole %, Phillips Research Grade) held at 15 ± 0.02° in a constant temperature bath. Mass spectrometric analyses of the gas leaving both the saturator and the reactor showed that the stream entering the reactor contained 7.62 ± 0.07 mole % cyclohexane at a total pressure of 750 mm. The feed composition was independent of nitrogen flow rate in the range 30–330 cc./min.

The reactor was constructed of Vycor and could hold 20 cc. of catalyst. The catalyst temperature was measured by an iron–constantan thermocouple inside a thin-walled thermowell and recorded on a Leeds and Northrup Speedomax recorder with a precision of ±1°. It was found that the temperature drop across the catalyst bed was usually less than 3°.

The catalyst temperature could be increased or decreased linearly with time by a temperature programing circuit. In this circuit the thermoelectric e.m.f. of a sensing couple was continuously compared with a steadily changing reference e.m.f. The unbalance was amplified and used to drive the Variac which supplied current to the furnace windings. The catalyst temperature could be increased continuously at a rate of 1–10° per minute over the temperature interval 25–700° and decreased at the same rate in the interval 200–700° in both cases with a deviation from linearity of less than 5%. Below 200°, linear changes in temperature occurred only at the slowest cooling rates.

On leaving the reactor the product gas was passed through a Gow-Mac thermal conductivity gauge which provided one arm of a Wheatstone bridge. In the opposite arm of the bridge was a reference cell through which purified nitrogen was passed. A system of bubble-type pressure regulators containing 85% phosphoric acid maintained a constant flow through the cells independent of the flow from the reactor. The two thermal conductivity cells were maintained at constant temperature in an air-bath. Differences in thermal conductivity between the product stream and pure nitrogen were detected by the Wheatstone bridge which was operated from a stabilized voltage supply. The signals were continuously recorded on a Leeds and Northrup Azar recorder. All connecting lines from the reactor to the thermal conductivity cell were constructed from 1 mm. bore capillary to reduce the time lag for flow from the reactor to the detector. Experiments have shown that this time lag becomes significant only at rates of temperature rise greater than 5° per minute.

The pressure drop across the catalyst bed was measured by a differential manometer containing 85% phosphoric acid.

Calibration.—The conversion recorder was calibrated by first bypassing the reactors and setting the zero per cent. conversion point on the Azar recorder by balancing the Wheatstone bridge. The reactant stream was then passed through a calibrating reactor containing Pt/Al$_2$O$_3$ at such a temperature (340°) that virtually 100% conversion to benzene and hydrogen would occur, as determined by mass spectrometric analyses of product gases. The current through the Gow-Mac cell was then adjusted until 100 divisions on the recorder chart corresponded to 100% conversion. The conversion scale was calibrated by passing the feed stream through Pt/Al$_2$O$_3$, Cr$_2$O$_3$/Al$_2$O$_3$ and WS$_2$ catalysts and taking samples for analysis by a mass spectrometer at various conversion intervals. Apart from nitrogen, cyclohexane, benzene and hydrogen, no other materials were detected in the products except in the case of thermal cracking over Vycor wool. A calibration curve was drawn by plotting per cent. conversion *versus* recorder scale reading. All points fit the curve which was approximately exponential in shape—a fact which would indicate that the greatest sensitivity in determining per cent. conversion was obtained in the low conversion region.

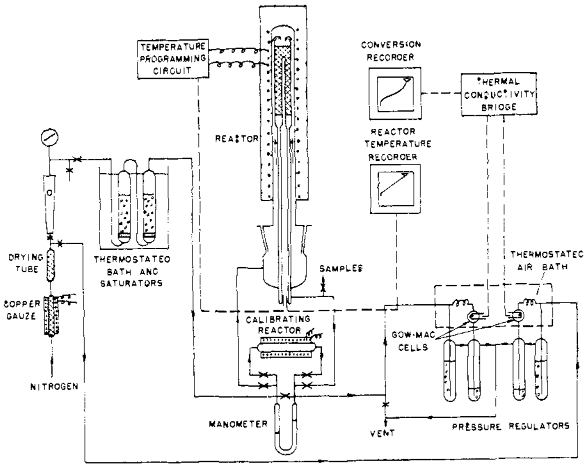

Fig. 1.—Rising temperature reactor.

Procedure.—In making a determination the feed rate was set at a standard value of 110 cc./min. of nitrogen, and, while the catalyst was stabilized in the presence of the reactant stream, the temperature of the catalyst was continuously increased until 100% conversion was obtained. The temperature of the catalyst was then cycled between 0 and 100% conversion until the conversion–temperature curves gave reproducible results thus indicating that the catalyst had been stabilized. During this pretreatment the rate of temperature change ranged from about 7 to 10° per min. At such a rate a time lag existed between reaction and analysis except at the fastest feed rates. This lag was evident when heating and cooling runs gave slightly different conversion–temperature curves. Such a lag was unimportant during stabilization runs. However, when it became apparent that the catalyst had reached constant activity, the rate of temperature change was decreased to about 2° per min. The data then obtained were used for actual comparison of catalytic activities and evaluation of activation energies. Using this slower rate of temperature change eliminated the time lag. Since the heating curves agreed with the cooling curves obtained at a low rate of temperature change, and since data obtained at the low rate of temperature change agreed with those taken at the more rapid ones (corrected for time lag), it was assured that the rates of temperature change were sufficiently low that a steady state was actually being secured at each temperature.

In investigating the stabilized catalyst the rising temperature runs were made at a feed rate of 110 c./min. of nitrogen. The falling temperature runs were made at varying feed rates.

Since the rising temperature runs were reproducible, it was assured that the data obtained were for a catalyst of constant activity.

Catalysts. A. **Pt/Al$_2$O$_3$.**—The catalyst was in the form of $^1/_{16}$ in. beads and contained 0.3% Pt, 0.25% Cl, 0.35% F, 0.12% S and less than 0.01 wt. % SiO$_2$.

B. **Cr$_2$O$_3$.**—Baker C.P.

C. **Cr$_2$O$_3$/Al$_2$O$_3$.**—This catalyst was prepared by vacuum impregnating Alcoa (H-42) activated alumina with chromium nitrate solution, drying at 120° and heating in air at 535° for 10 hr. The charge to the reactor was a 12–80 mesh powder containing 14.7% Cr$_2$O$_3$ and 4.8 wt. % SiO$_2$, the rest being alumina.

D. **Water-washed Cr$_2$O$_3$/Al$_2$O$_3$.**—Catalyst C above was washed continuously with water for 150 hr. to remove hexavalent chromium. The water-washed catalyst contained 11.0 wt. % Cr$_2$O$_3$.

E. **NiWO$_4$/Al$_2$O$_3$.**—Alcoa (H-42) activated alumina was vacuum impregnated with a sodium tungstate solution, the product dried at 150° and further impregnated with a nickel nitrate solution. After washing with water and drying at 150°, the catalyst was heated in air at 650° for 16 hr. The catalyst contained 2.98% Ni, 8.9% W and less than 1.0 wt. % Na. The Ni/W ratio was 0.332 as compared with the theoretical value of 0.319 for nickel tungstate. The charge to the reactor was a fine powder.

F. **WS$_2$.**—The catalyst was a German 5058 tungsten disulfide containing 88.4% WS$_2$, 7.8% S, 1.98% H, 0.16% C, 0.07% N, 0.034% Fe$_2$O$_3$ and 0.014 wt. % SiO$_2$. The charge to the reactor was 8–16 mesh powder.

Theory

Considering the case of a flow reactor (*cf.* Hougen and Watson[6]) and assuming that the rates

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[6] O. A. Hougen and K. M. Watson, "Chemical Process Principles," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1943.

of longitudinal and radial diffusion in the gas phase are negligible compared with the rate of reaction, a differential material balance can be made across an incremental area of catalyst surface at any cross-section

$$r\,dA = F d\chi_\alpha \qquad (1)$$

where

r = reaction rate, moles per unit area per unit time
A = surface area of catalyst
F = feed rate, mass per unit time
χ_α = moles of reactant α converted per unit mass of feed

It is common practice to consider that the kinetics of many catalytic reactions are such that they can be represented by a rate equation of the form

$$r = k_n p^n \qquad (2)$$

where

p = partial pressure of gaseous reactant α
n = order of the reaction
k_n = velocity constant

For the decomposition of nitrous oxide over various oxide catalysts, Hauffe, Glang and Engell[1] have found that n can have values of 3/4, 1, 3/2 and 2.

The temperature coefficient of the velocity constant, k_n, may be given by the Arrhenius equation

$$k_n = Be^{-E/RT} \qquad (3)$$

where E is the apparent energy of activation and B is a frequency factor.

The partial pressure p of cyclohexane is related to χ_α by the equation

$$p = \frac{P(n_{\alpha 0} - \chi_\alpha)}{(n_0 + \delta\chi_\alpha)} \qquad (4)$$

where

P = total pressure
n_0 = moles of feed per unit mass of feed
$n_{\alpha 0}$ = moles of reactant α per unit mass of feed
δ = increase in no. of moles of the reacting system per mole of reactant α converted. For cyclohexane dehydrogenation, $\delta = 3$.

Combining equations 1, 2, 3 and 4, we obtain

$$\ln F + \ln \psi_n = -E/RT + \ln(AB) \qquad (5)$$

$$\ln (F/A) + \ln \psi_n = -E/RT + \ln B \qquad (5a)$$

where

$$\psi_n = \int_0^{\chi_\alpha}\left[\frac{(n_0 + \delta\chi_\alpha)}{P(n_{\alpha 0} - \chi_\alpha)}\right]^n d\chi_\alpha \qquad (6)$$

According to equation 6 ψ_n is solely a function of total pressure, feed composition and conversion. Therefore, if these three variables are held constant, equations 5 and 5a show that a plot of ln F or ln (F/A) *versus* $1/T$ should be a straight line of slope, $-E/R$. The apparent activation energies can be computed from the slopes of these plots without a knowledge of the order of the reaction. If the reaction kinetics cannot be represented by a simple order over the whole temperature range or if the reverse reaction is of appreciable rate, then ψ_n will become a function of temperature, and the plot of ln F or ln (F/A) *versus* $1/T$ will not be linear. However, if the heats of reaction, adsorption and desorption are not too high, then it might be expected that ψ_n would be a slowly varying function with temperature. As a consequence, plots of ln F or ln (F/A) *versus* $1/T$ might still be linear over moderate temperature ranges even for more complex kinetics.

If the plots of ln F *versus* $1/T$ are linear, equation 5a can be used to compare catalysts on the basis of equal surface area. Figure 3 shows conversion–temperature curves replotted at the same feed rate per unit area. This procedure assumes either that the active surface area of the catalyst is independent of temperature or that the active surface is an exponential function of temperature of the form

$$A = A_0 e^{-\epsilon/RT} \qquad (7)$$

where A_0 is the BET surface area and ϵ is an activation energy that would be combined with the apparent activation energy, E.

Equations 5 and 5a show that at constant feed rate a plot of ln ψ_n *versus* $1/T$ will also be a straight line of slope, $-E/R$. However, linear plots will be obtained only if the correct rate equation has been chosen. Integration of equation 6 for various assumed orders shows that ψ_n is the product of a constant β_n and a function ϕ_n which depends upon the conversion

$$\psi_n = \beta_n \phi_n \qquad (8)$$

Zero order, $n = 0$

$$\beta_0 = y n_0 \qquad (9)$$

$$\phi_0 = \chi \qquad (10)$$

First order, $n = 1$

$$\beta_1 = n_0/P \qquad (11)$$

$$\phi_1 = -[y\delta\chi + (1 + y\delta)\ln(1 - \chi)] \qquad (12)$$

In the above equations y is the mole fraction of cyclohexane in the entering feed, and χ is the fraction of cyclohexane converted (*i.e.*, $\chi_\alpha/n_{\alpha 0}$). Since the constant β_n depends only upon the feed composition and the total pressure which are invariant, the authors have used plots of log ϕ_n *versus* $1/T$ to evaluate the order and apparent activation energy.

Results and Discussion

The data obtained for the catalysts studied are summarized in Table I. Representative plots of log F *versus* $1/T$ and log ϕ_n *versus* $1/T$ are shown in Fig. 2 for Cr_2O_3/Al_2O_3, and Table II summarizes the results of all $\log_{10}\phi_n$ *versus* $1/T$ plots for Cr_2O_3 on Al_2O_2.

Thermal Decomposition.—Kasansky and Plate[3] studied the thermal decomposition of cyclohexane in a quartz tube at temperatures from 590–800° and contact times ranging from 0.5–20 sec. They detected the presence of aliphatics, acetylene and benzene in the pyrolysate. It was found that in this investigation the thermal breakdown of cyclohexane was not appreciable below 600°. Samples of the product gas taken at 700° and at a feed rate of 112 cc./min. showed the presence of ethylene, propylene, butenes, butadiene, benzene, hydrogen and unreacted cyclohexane. An average activation energy of 49 ± 5 kcal./g. mole was calculated from the plots of log F *versus* $1/T$. In obtaining this value, it was assumed that a particular reading on conversion recorder corresponded to only one composition, irrespective of feed rate and temperature.

TABLE I

SUMMARY OF CATALYST DATA AND APPARENT ACTIVATION ENERGIES

Catalyst	Surface area, m.²/g. Fresh[a]	Surface area, m.²/g. Used	Wt. catalyst, g.	Length of catalyst bed, cm.	Order and apparent activation energy: Temp. range, °C.	Order	E, kcal./g. mole
Pt/Al_2O_3	190	188	13.0	11.5	156–280	...	21.0 ± 2[b]
						...	17.6–19.3[c]
Irradiated							
Pt/Al_2O_3	194	189	12.5	11.4	.....	...	....
Cr_2O_3	5.8	5.4	22.3	11.0	450–550	Zero	33.8 ± 2[c]
Cr_2O_3/Al_2O_3	248	132	22.6	11.1	392–632	...	27.0 ± 2[b]
					362–632	First	29.2 ± 2[c]
Water washed							
Cr_2O_3/Al_2O_3	...	108	18.4	9.5	374–535	Zero	20.0 ± 2[d]
$NiWO_4/Al_2O_3$	264	162	5.9	4.0	470–608	Zero	26.0 ± 2
WS_2	86	35	45.1	9.7	381–650	...	19.3 ± 2[b]
					345–698	Zero or first	19.5 ± 2[c]
Vycor wool	...	...	..	12.0	566–695	...	49 ± 5

[a] Heated to 200° *in vacuo* for 1 hr. [b] Calculated from plot of log F *versus* $1/T$. [c] Calculated from plot of log ϕ_n *versus* $1/T$. [d] Hysteresis was observed.

TABLE II

APPARENT ACTIVATION ENERGIES AND ORDERS FOR THE DEHYDROGENATION OF CYCLOHEXANE OVER Cr_2O_3/Al_2O_3 CALCULATED FROM PLOTS OF LOG ϕ_n *versus* $1/T$

Feed rate, cc./min.	Temp. range, °C.	Order	Activation energy, E, kcal./g. mole
41	362–543	First	27.3
82	397–563	First	29.1
155	425–596	First	30.0
219	433–609	First	29.7
330	451–632	First	30.1

Tungsten Disulfide.—Mass spectrometric analyses of the product gas indicated that only in the dehydrogenation of cyclohexane over WS_2 at 700° was there appreciable thermal cracking, and this amounted to less than 4% of the cyclohexane feed. The average activation energy from the log F *versus* $1/T$ plots for this catalyst for conversions up to 54.5% and temperatures in the range 381–650° was 19.3 ± 2 kcal./g. mole. Above 650° and at conversions greater than 54.5% there was a steep increase in activation energy up to a maximum value of 33.6 kcal./g. mole for 91.5% conversion. This may have resulted from the onset of thermal cracking.

Platinum on Alumina.—The free energy data of Rossini, *et al.*,[7] indicate that under the proposed experimental conditions 5% of the cyclohexane would be converted at 138° and 95% at 265°. All but one of the catalysts studied were active above this temperature region, and in the case of these catalysts it was not necessary to consider the reverse reaction. However, Pt/Al_2O_3 was active in the temperature region in which the reverse reaction occurred to an appreciable extent. At feed rates of less than 73 cc./min. and temperatures above 220°, it was found that the experimentally measured conversions became independent of feed rate.

Since the function ψ_n contains a term involving the temperature dependent equilibrium constant, plots of ln F *versus* $1/T$ should have given only approximations to the activation energy. These plots were linear, and it was assumed that ψ_n was a slowly varying function of temperature. The effect of temperature on ψ_n may, however, account for the variation in apparent activation energy from 17.6–22.8 kcal./g. mole as the temperature and conversion are changed. In the eval-

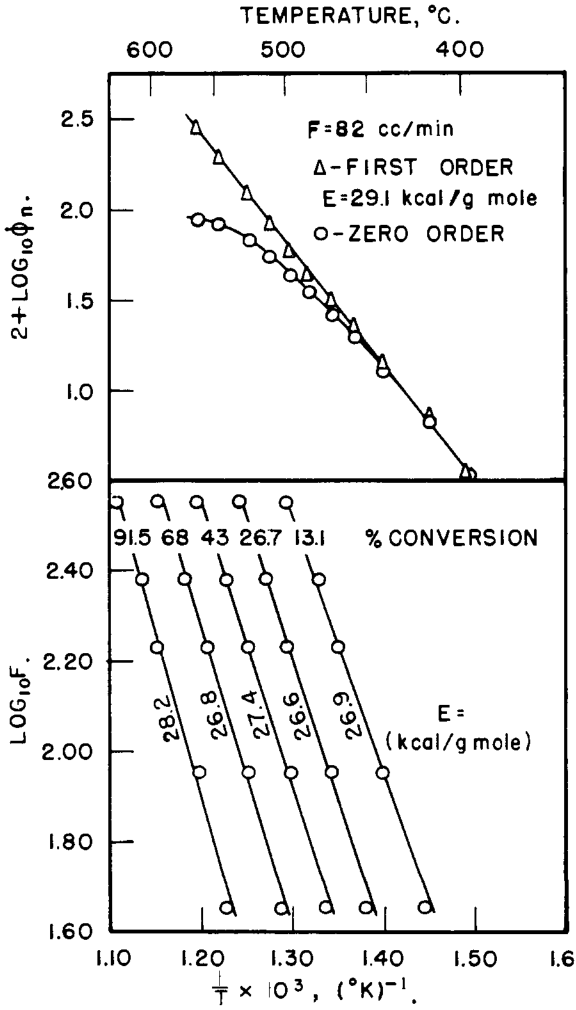

Fig. 2.—Plots of log F and log ϕ_n *versus* $1/T$ for Cr_2O_3/Al_2O_3

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(7) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbon and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

uation of the kinetics of the dehydrogenation of cyclohexane over platinum on alumina using a plot of log ϕ_n *versus* $1/T$, only the data obtained at the highest measurable feed rate of 334 cc./min. were used. Since at this feed rate the experimental conversions were somewhat smaller than the equilibrium ones, it was assumed that the reverse reaction could be neglected. It was found that the plots of log ϕ_n *versus* $1/T$ were linear for both zero- and first-order kinetics, if only conversions below 50% were considered. For conversions greater than 50% both plots were curved. The zero and first-order plots gave apparent activation energies of 17.6 and 19.3 kcal./g. mole, respectively. These values are in approximate agreement with those obtained from the plots of log F *versus* $1/T$ especially at lower conversions. It was impossible to ascertain whether the dehydrogenation reaction was zero or first order.

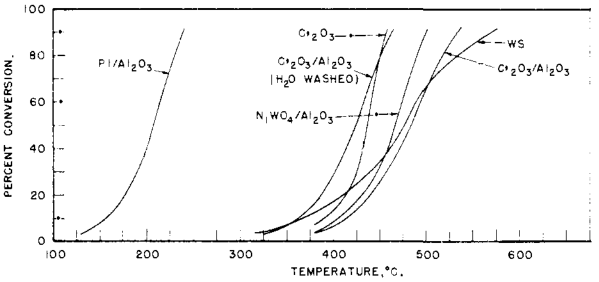

Fig. 3.—Conversion–temperature curves calculated at a feed rate per unit area of 0.0184 cc./min. m.[2].

Irradiated Platinum on Alumina.—A 25-g. sample of catalysts was divided into two equal portions, one of which was irradiated under an electron beam from a Van de Graaff accelerator to a dose of 10^{10} ergs/g. It was found that during the initial rising temperature run the irradiated catalyst was slightly more active. During the falling temperature run the two catalysts were found to have the same activity within the limits of experimental error.

Chromia on Alumina.—No complications appeared to exist in the study of unwashed Cr_2O_3/Al_2O_3. However, studies of the sample which had been water washed to remove any higher valence chromium present showed that a pronounced hysteresis existed between the rising temperature–conversion curve and the falling temperature–conversion curve. This amounted to about 20°. When order plots were made of both the rising and falling temperature–conversion curves, it was found that both gave the same activation energy (20.0 ± 2 kcal./g. mole), and the kinetics of both were best approximated by zero order. When this sample had been heated in air, the hysteresis diminished to 5°, and analysis of the data indicated that the activation energy for dehydrogenation had increased to 27.0 ± 2 kcal./g. mole and the reaction had become first order. These latter data agree with those for the unwashed sample and may indicate that the heating of the catalyst in air had oxidized some of the chromium to a higher valence state. The lower activation energy for the water washed sample which had been assumed to consist mainly of chromium in lower valence states may indicate that the lower valence states of chromium are more effective in dehydrogenation than the higher valence states.

Nickel Tungstate on Alumina and Chromium Sesquioxide.—A series of reproducible measurements were made on each of these catalysts at one feed rate only. The activation energies and reaction orders are summarized in Table I.

Comparison of Activities.—Equation 5a has been used to reduce the activities of various catalysts to an equal area basis-equal feed rate basis and the results are shown in Fig. 3. A standard value of F/A equal to 0.0184 cc./min.-m.^{2} was used; this corresponds to an actual F/A value used for Pt/Al_2O_3. The order of catalytic activity is approximately $Pt/Al_2O_3 >$ water washed $Cr_2O_3/Al_2O_3 > Cr_2O_3 > NiWO_4/Al_2O_3 > WS_2 > Cr_2O_3/Al_2O_3$. On an equal volume basis the order is approximately $Pt/Al_2O_3 >$ water washed $Cr_2O_3/Al_2O_3 > Cr_2O_3/Al_2O_3 > NiWO_4/Al_2O_3 > Cr_2O_3 > WS_2$.

With respect to the kinetics of dehydrogenation, Cr_2O_3, water washed Cr_2O_3/Al_2O_3 and $NiWO_4/Al_2O_3$ exhibited zero-order kinetics indicating that perhaps adsorption was not a rate determining step. However, in the case of unwashed Cr_2O_3/Al_2O_3 the kinetics were first-order indicating that adsorption might have been rate determining. WS_2 showed zero-order kinetics at high temperatures and approximately first-order kinetics at lower temperatures. In addition, the activation energy changed slowly with temperature. This could indicate that at low temperatures adsorption was a rate determining step and that, as the temperature was increased, the mechanism changed.

The apparent activation energies of the catalysts summarized in Table I increase in the following order: $Pt/Al_2O_3 \simeq WS_2 \simeq$ water washed $Cr_2O_3/Al_2O_3 < NiWO_4/Al_2O_3 < Cr_2O_3/Al_2O_3 < Cr_2O_3$.

Table I indicates that the most thermally stable catalyst was Pt/Al_2O_3, since its BET surface area changed only slightly with use. All other catalysts showed pronounced area changes. This was presumably due to the higher temperatures at which these catalysts operated.

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PITTSBURGH, PENNSYLVANIA