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The Hydrogenation of Cyclopropane on Hydrogen Covered Metal Powders

I. Gas Chromatographic Study of the Hydrogenation of Cyclopropane on Rhenium

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The hydrogenation of cyclopropane on rhenium powder was investigated using the microcatalytic technique. Using hydrogen as the carrier gas the reaction was pseudo first order. In addition to propane, methane and ethane were also observed in equimolar quantities in the products. It was shown that the rate-determining step was the cleavage of the cyclopropane ring followed by rapid hydrogen addition and cracking reactions. The apparent activation energy for ring cleavage was 12.5 ± 0.5 kcal/mole.

INTRODUCTION

The observation of methane and ethane in the reaction products of the hydrogenation of cyclopropane (*1–3*), indicates that the mechanism of the reaction is more complicated than was originally supposed (*4*). Much of the work on this reaction has been carried out using catalysts deposited on supposedly inert supports such as pumice, silica, alumina, and silica–alumina. However the existence of catalyst–support interactions (*5*, *6*) indicates the desirability of examining this reaction over a wide range of high purity metal powders. To date the study of cyclopropane hydrogenation on metal powders has been limited to nickel (*1*), platinum black (*3*) and promoted iron (*7*). The present paper (Part I of this series) discusses the experimental technique and its application to rhenium.

The development of the "microcatalytic technique" (*8*, *9*) makes possible the rapid investigation of a wide range of catalysts with accurate monitoring of all reaction products. Although helium has been used as a carrier gas in the microcatalytic study of hydrogenation reactions (*8*), its use leads to serious experimental difficulties. Taylor *et al.* (*10*) have noted that hydrogen is strongly chemisorbed on noble metal surfaces, and even at higher temperatures, significant quantities of hydrogen remained on the surface after 1 hr in a helium flow system. It has been observed in this laboratory that sufficient hydrogen remains on the surface to vary the hydrogen coverage from one pulse to the next, thus causing irreproducible results. These shortcomings can be overcome by using hydrogen as the carrier gas, which also serves as one of the reactants. The reaction is thus constrained to be pseudo first order, allowing easier mathematical analysis.

THEORETICAL

The mathematics of a first order reaction in a microcatalytic reactor has been discussed by Bassett and Habgood (*9*). If the initial partial pressure of the reactant in the pulse is P^0, then the partial pressure of the reactant as the pulse emerges from the reactor will be $P^0(1 - x)$, where x is the frac-

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tional conversion of the reactant to product. At any point in the catalyst bed, the change in partial pressure of the reactant will be given by

$$\frac{-dP}{dt} = kP, \tag{1}$$

where P is the reactant partial pressure and k is the first order rate constant. Integrating throughout the length of the catalyst bed we obtain,

$$\ln\left(\frac{1}{1-x}\right) = kt, \tag{2}$$

where t is the residence time of the pulse. Catalyst residence time is difficult to measure, but it bears a relationship to the flow rate. Bassett and Habgood (*9*) have derived the relationship

$$k'K = \frac{F^0}{273RW}\ln\left(\frac{1}{1-x}\right), \tag{3}$$

where k' is the first order rate constant for the surface reaction, K is the adsorption equilibrium constant, F^0 is the carrier gas flow rate (ml at STP/sec), R is the ideal gas constant, and W is the weight of the catalyst. If a constant flow rate is maintained for all runs, Eq. (3) may more simply be expressed as

$$k'K = C\ln\left(\frac{1}{1-x}\right), \tag{4}$$

where C is a constant. A plot of $\ln[\ln(1/(1-x))]$ versus $1/T$ may be used to calculate the apparent activation energy of the reaction. More correctly, a temperature correction must also be included to allow for a change in residence time with a change in reaction temperature, under conditions of constant molar flow rate (*11*). Assuming that the carrier gas pressure is maintained constant, a more precise plot would be one of

$$\log\left[\frac{T}{273}\left(\ln\left(\frac{1}{1-x}\right)\right)\right] \text{ versus } 1/T.$$

However, when two or more reactions are proceeding simultaneously, the treatment becomes more complex. It is therefore necessary to consider two other cases: (i) the presence of two or more parallel reactions and (ii) two or more parallel reactions preceded by a common rate determining step.

Consider first two parallel first order reactions with rate constants k_1 and k_2:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B},$$

$$\mathrm{A} \xrightarrow{k_2} \mathrm{D}.$$

It follows that

$$\frac{-dP_A}{dt} = (k_1 + k_2)P_\mathrm{A}. \tag{5}$$

In this case, the partial pressure of A as the pulse leaves the reactor is $P_\mathrm{A}{}^0\,(1 - x_1 - x_2)$ where x_1 and x_2 are the fractions of A converted to B and D, respectively. Integrating throughout the length of the column,

$$\ln\left(\frac{1}{1-x_1-x_2}\right) = (k_1 + k_2)t, \tag{6}$$

$$(k_1 + k_2) = C\ln\left(\frac{1}{1-x_1-x_2}\right). \tag{7}$$

A plot of $\log\ [(T/273)\ (\ln(1/(1-x_1-x_2)))]$ versus $1/T$ will be a curve which is *concave upwards,* as in the case of Arrhenius plots for any other parallel reactions (*12*). Since

$$\frac{k_1}{k_2} = \frac{x_1}{x_2}, \tag{8}$$

it follows that the activation energies of the two reactions may be obtained by plotting

$$\log\left[\frac{T}{273}\left(\frac{x_1}{x_1+x_2}\right)\ln(1/(1-x_1-x_2))\right] \text{ vs. } 1/T,$$

and

$$\log\left[\frac{T}{237}\left(\frac{x_2}{x_1+x_2}\right)\ln(1/(1-x_1-x_2))\right] \text{ vs. } 1/T.$$

In the case of several parallel reactions preceded by a common rate determining step

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{D},$$

$$\mathrm{B} \xrightarrow{k_3} \mathrm{E},$$

$$\frac{-dP_A}{dt} = k_1 P_A, \qquad (9)$$

carrying out a similar integration as in Eq. (6),

$$\ln\left(\frac{1}{1 - x_1 - x_2}\right) = k_1 t, \qquad (10)$$

or

$$k_1 = C \ln\left(\frac{1}{1 - x_1 - x_2}\right). \qquad (11)$$

Thus a plot of log $[(T/273)\ (\ln(1/(1 - x_1 - x_2)))]$ versus $1/T$ will be a straight line, which will yield the activation energy for the rate-determining step. In this case, the plots of log $[(T/273)\ \ln(1/(1 - x_1))]$ and log $[(T/273)\ \ln(1/(1 - x_2))]$ versus $1/T$, will be curves which are *concave downwards* and will have no significance. Activation energies of the subsequent steps cannot be calculated.

EXPERIMENTAL METHODS

Materials

The carrier gas was tank electrolytic hydrogen which was further purified by passing through a Deoxo catalytic purifier, then through two drying columns containing potassium hydroxide pellets and magnesium perchlorate, respectively, and finally through a series of glass bends immersed in liquid nitrogen.

Cyclopropane was medical grade (USP), supplied by Canadian Liquid Air. Propane, ethane, and methane were C.P. grade gases supplied by Matheson of Canada Ltd. All gases were more than 99% pure, and were further purified by multiple vacuum distillation where the first and last thirds were discarded while the center third was retained. This process was repeated on the retained portion until a sample of gas showed no evidence of impurities by GC analysis.

The rhenium catalyst was Johnson-Mathey rhenium sponge certified to be more than 99.999% pure.

Apparatus and Experimental Procedure

The apparatus was constructed according to the principles established by Hall and Emmett (*8*). To prevent entry of mercury vapor into the reactor, the gases were passed through a U trap immersed in a Dry Ice–acetone bath. The partial pressure of cyclopropane used in these experiments was considerably less than its vapor pressure at this temperature [6.23 cm Hg (*13*)], so the problem of cyclopropane condensation in the trap was avoided.

The reactor was a 6-mm Pyrex glass U tube immersed in a thermostated oil bath. For catalyst reductions, the oil bath was substituted by an electric furnace. The GC column was a 2.5 ft × 6-mm Pyrex tube containing "Porapac Q" and was maintained at 50°C. The reactor could be bypassed to allow the column to be calibrated for various gases.

The catalyst (0.476 g) was held in place in the reactor by means of plugs of Pyrex glass wool. Catalyst reductions were carried out *in situ* at 500°C in a flow of hydrogen for 2 hr prior to use. Known amounts of cyclopropane were injected into the reactor and the effluent gases were analyzed by the gas chromatograph. In this manner, a series of pulses of different partial pressures was injected with the catalyst temperature being held constant. Then the temperature was altered and the process was repeated. Temperatures were chosen at random, with no pattern of rising or falling temperature sequence. The pressure of hydrogen was maintained at a constant 1250 Torr with a constant flow rate to atmosphere of 60 ml at STP/min.

RESULTS

Methane, ethane, and propane in addition to cyclopropane, were observed in the effluent gases from the reactor. The methane and ethane were detected in a 1:1 molar ratio. The propane peak heights were plotted versus the partial pressure of cyclopropane injected, as shown in Fig. 1. For any one temperature, a straight-line relationship characteristic of a first order reaction, was observed. The calibration line for propane was also included in Fig. 1. For

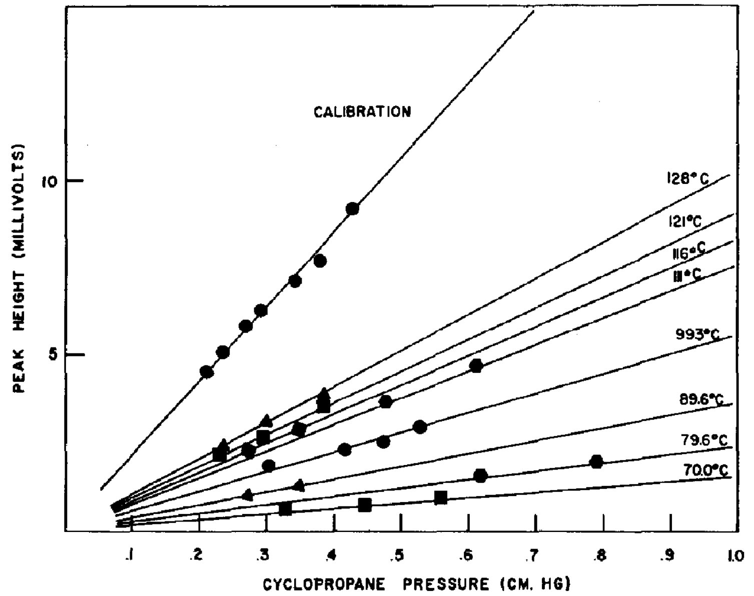

FIG. 1. Plot of propane peak height versus the partial pressure of cyclopropane injected.

any temperature the conversion of cyclopropane to propane can be calculated by dividing the slope of the line at that temperature by the slope of the propane calibration line. A similar plot for ethane is shown in Fig. 2. No propane or ethane hydrocracking was observed when these gases were used instead of cyclopropane, in the temperature range used (70–128°C).

DISCUSSION

Arrhenius plots based on the individual reactions of hydrogenation (as measured by propane formation) and cracking (as measured by ethane formation) are shown in the two lower curves of Fig. 3. A distinct curvature is apparent. The upper line represents a plot of log [(T/273) (ln(1/(1 —

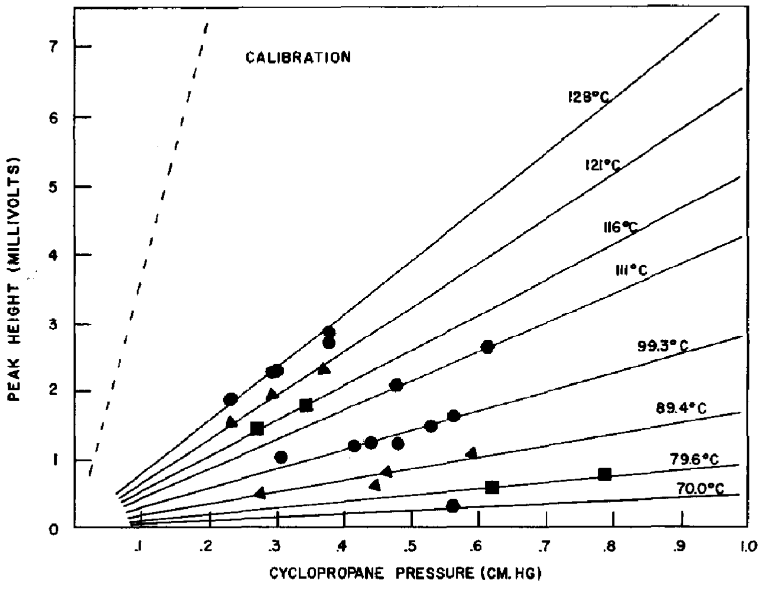

FIG. 2. Plot of ethane peak height versus the partial pressure of cyclopropane injected.

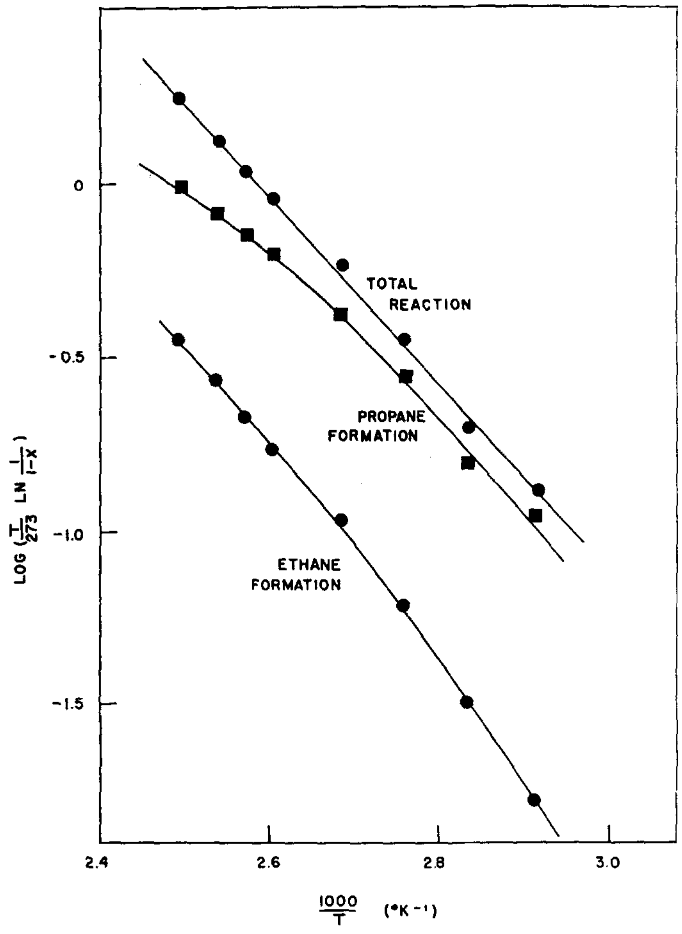

FIG. 3. Arrhenius plots for total reaction, propane formation (hydrogenation), and ethane formation (hydrocracking).

x_t)))] versus 1000/T where x_t is the total conversion of cyclopropane, which is the sum of conversions for the cracking and hydrogenation reactions. A linear relationship was observed which gave an apparent activation energy of 12.5 ± 0.5 kcal/mole. The confidence intervals were calculated using a "Students' *t*" distribution, such that there is a 95% probability that the calculated value of the activation energy falls between the two limits.

It is now generally accepted that the rate-determining step in the hydrogenation of cyclopropane is the cleavage of the cyclopropane ring (*4*, *14*), followed by more rapid addition of hydrogen to the adsorbed propyl species. McKee (*3*) and Anderson and Avery (*2*) have postulated that the ethane and methane result from hydrocracking of these adsorbed propyl species. The results of this study confirm this mechanism for rhenium. Both the hydrogenation and the cracking reactions proceed competitively at a faster rate than ring cleavage. The relative amounts of hydrogenation or cracking depend upon the relative rates of these two reactions. Mechanisms for the ring cleavage, hydrogenation and cracking reactions will be reported in subsequent parts of this series (*15*).

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REFERENCES

1. Knor, Z., Ponek, V., Herman, Z., Polejsek, Z., and Cerny, S., *J. Catal.* **2,** 299 (1963).
2. Anderson, J. R., and Avery, N. R., *J. Catal.* **8,** 48 (1967).
3. McKee, D. W., *J. Phys. Chem.* **67,** 1336 (1963).
4. Bond, G. C., and Newham, J., *Trans. Faraday Soc.* **56,** 1501 (1960).
5. Sinfelt, J. H., *J. Phys. Chem.* **68,** 344 (1964).
6. Sinfelt, J. H., *Chem. Eng. Progr. Comp. Ser.* **63,** 16 (1967).
7. Hayes, K. E., and Taylor, H. S., *Z. Phys. Chem.* (*Frankfurt am Main*) **15,** 127 (1958).
8. Hall, W. K., and Emmett, P. H., *J. Amer. Chem. Soc.* **79,** 2091 (1957).
9. Bassett, D. W., and Habgood, H. W., *J. Phys. Chem.* **64,** 769 (1960).
10. Taylor, G. F., Thomson, S. J., and Webb, G., *J. Catal.* **8,** 388 (1967).
11. Habgood, H. W., *in* "The Solid Gas Interface" (E. A. Flood, ed.), Vol. 2, p. 632. Dekker, New York, 1967.
12. Hinshelwood, C. N., "The Kinetics of Chemical Change," p. 45. Oxford Univ. Press, London/New York 1940.
13. Ruehrwein, R. A., and Powell, T. J., *J. Amer. Chem. Soc.* **68,** 1063 (1946).
14. Benson, J. E., and Kwan, T., *J. Phys. Chem.* **60,** 1601 (1956).
15. Wallace, H. F., and Hayes, K. E., to be submitted for publication.