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Selectivity of Gold for Hydrogenation and Dehydrogenation of Cyclohexene*

ROBERT P. CHAMBERS† AND MICHEL BOUDART‡

From the Department of Chemical Engineering, University of California, Berkeley

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Rates of reaction of cyclohexene over a gold powder catalyst, in the presence or absence of hydrogen, were measured in a batch recirculation system between 203° and 285°C. After activation of the powder, consisting of a treatment with hydrogen first and then with oxygen, the measured rates are in excellent agreement with those previously reported on gold evaporated films. It has now been shown that, on gold, cyclohexene reacts irreversibly to form either cyclohexane or benzene. The selective production of benzene can be controlled within wide limits at a fixed temperature. It is depressed by high partial pressures of hydrogen, enhanced in the absence of hydrogen, while benzene becomes practically the sole product in the presence of small quantities of oxygen. Thus, at 203°C, the selectivity as measured by the ratio of benzene to cyclohexane is increased by a factor of 3000 when a partial pressure of hydrogen equal to 0.74 atm is replaced by a partial pressure of oxygen equal to 0.041 atm.

INTRODUCTION

A number of investigations of the catalytic behavior and properties of gold have been made.

Chemisorption studies at 10^{-3} torr by Trapnell (*1*) showed that while gold weakly chemisorbed ethylene and acetylene at room temperature, the chemisorption of molecular hydrogen at temperatures from −183°C to room temperature was not detectable. The author stated a lower detection limit of 2% coverage. Culver, Pritchard, and Tompkins (*2*) reaffirmed that gold was not capable of chemisorbing detectable quantities of molecular hydrogen, but hydrogen atoms were chemisorbed with an appreciable coverage at −183°C and 10^{-5} torr. However, upon heating to −78°C the hydrogen was completely desorbed as molecules.

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† Present address: Department of Chemical Engineering, Tulane University, New Orleans, Louisiana.

‡ To whom queries concerning this paper should be sent: Department of Chemical Engineering, Stanford University, Stanford, California.

Hydrogen–deuterium exchange rates on gold have been measured by a number of workers (*3, 4, 5*) and found to be intermediate in magnitude between rates on the transition metals and on surfaces such as germanium and glass. Ortho–para hydrogen conversion has also been studied on gold (*6–9*).

Gold catalysts exhibit activity for the dehydrogenation of formic acid (*10 11*). Sachtler and deBoer (*12*) showed that hydrogen atoms produced from formic acid decomposition underwent rapid hydrogen–deuterium exchange or could rapidly react with oxygen. In either case these induced reactions proceeded far faster than if the hydrogen had to be chemisorbed from the gas phase.

The catalytic activity of gold-evaporated films has been studied by the school of Kemball. Thus, Stoddart and Kemball have reported the hydrogenation of acetone (*13*) and the exchange of $(CH_3)_2CO$ with deuterium (*14*). More recently, Erkelens, Kemball and Galwey (*15*) studied the reactions of hydrogen and deuterium with cyclohexene on gold evaporated films. They found

fairly rapid dehydrogenation of cyclohexene to benzene accompanied by a simultaneous hydrogenation yielding cyclohexane. The selectivity of producing benzene varied markedly with temperature and hydrogen partial pressure. However, even at constant temperature and hydrogen partial pressure, the ratio of benzene to cyclohexane was found to change rapidly with time at the start of the run, asymptotically approaching a constant value after about 40% of the cyclohexene was converted. These investigators, who were primarily interested in the exchange of deuterium with cyclohexene, found that exchange proceeded more rapidly than either hydrogenation or dehydrogenation.

In view of the relative inertness of gold surfaces in chemisorption and catalysis, these findings of Kemball *et al.* appeared to us to be of much more than routine interest.

The current study was made to understand the selectivity of gold for benzene production from cyclohexene, unravel the reasons behind the change of selectivity with conversion, and increase our knowledge of the role of hydrogen in catalytic reactions on gold.

Notation

A	Total catalyst surface area (cm^2)
c	Concentration (g mole/cm^3)
k	First order surface rate constant (cm/sec)
k_A	Hydrogenation surface rate constant (cm^4/g mole sec)
k_B	Dehydrogenation surface rate constant (cm/sec)
P	Partial pressure (atm)
q	Volumetric flow rate (cm^3/sec)
r	Surface reaction rate (g mole/sec cm^2)
R	Gas constant (atm cm^3/g mole °K)
S	Selectivity, $\Delta x_B/\Delta x_A$ (dimensionless)
t	Time (sec)
T	Temperature (°K)
V	Volume (cm^3)
V_{eff}	Recirculation system volume corrected to reactor temperature, equal to $V_s(T_s/T_o) - V_r\left(\frac{T_r - T_o}{T_o}\right)$ (cm^3)
x	Mole fraction in hydrocarbon (dimensionless)

Subscripts

A	Cyclohexane
B	Benzene
E	Cyclohexene
H_2	Hydrogen
o	Portion of recirculation system outside of reactor
r	Reactor
s	Entire recirculation system, r + o

Superscripts

0	Initially
′	Hydrogenation zero order in hydrogen
″	Hydrogenation half order in hydrogen

Experimental

Kinetic data were obtained in a batch recirculation system which permitted a high space velocity with low conversion per pass, about 0.2% initially, declining with consumption of the reactants. In all cases, as could be ascertained by special calculations, isothermal operation was assured without any appreciable gradients of concentration.

The recirculation system schematically shown in Fig. 1 was constructed of Pyrex glass. Gas recirculation was achieved by means of an inert, noncontaminating magnetic pump. Recirculation rates normally provided four volume changes per minute in the 1.1-liter system.

The glass reactor contained a thermocouple well and a shallow (about 2 g) catalyst bed, supported by a fritted glass disc. The reactor was surrounded by a large aluminum block and together with the preheater was placed in a furnace.

Samples were withdrawn from the system periodically by means of a modified Wilkens Instrument and Research gas sample valve and were analyzed by a Wilkens Model 1520 gas chromatograph. The components were separated on two columns; light gases, cyclohexane, cyclohexene, cyclohexadiene, and benzene by β,β'-oxydipropionitrile; hydrogen, oxygen, and nitrogen by Type 13 X molecular sieve. Thermal conductivity detectors were used on the gross peaks while a

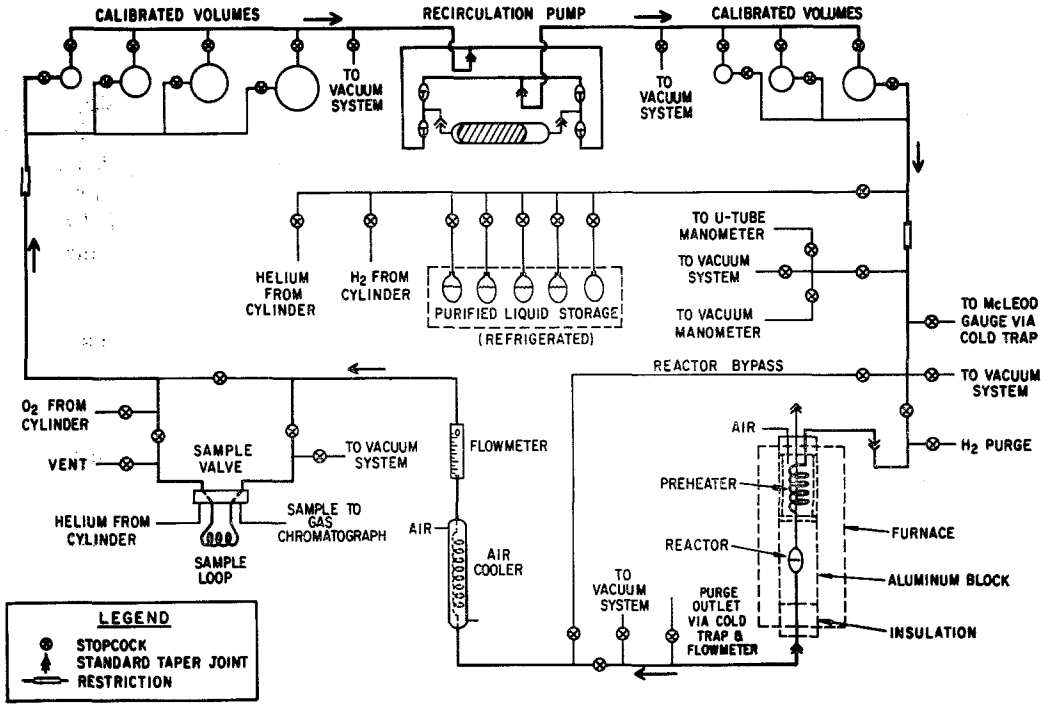


FIG. 1. Schematic diagram of recirculation system.

flame ionization detector was used for the trace components.

The catalyst employed for this study was 50–70 mesh porous gold powder obtained from Engelhard Industries, with total impurities less than 100 ppm. The specific surface area, measured by the continuous flow method (*16*) using a Perkin-Elmer Sorptometer, was 0.07 m^2/g. A detailed analysis and other properties are shown in Table 1.

Research grade cyclohexene, cyclohexane, and benzene from Philips Petroleum were purified by distillation to remove atmospheric contaminants, and stored as liquids in a refrigerated bath. Technical grade 1,3-cyclohexadiene was purified in the same manner. Analyses of each hydrocarbon are tabulated in Table 2.

Hydrogen, purified by low-temperature liquefaction, was obtained from the University of California Low Temperature Laboratory. Total impurities are believed to be less than 10 ppm. Helium, from U.S. Navy supplies, had a nominal impurity level of 100 ppm. Gas chromatographic analysis indicated less than 30 ppm air. Oxygen, research grade from The Matheson Company, contained 100 ppm argon, 20 ppm nitrogen, 7 ppm krypton, and 0.6 ppm carbon dioxide.

The catalyst activation procedure is shown on Table 3. It consisted of evacuation to 10^{-6} torr, followed by treatments in flowing hydrogen at 325°C and static oxygen at 250°C. The procedure was arrived at during the course of this work by evolutionary operation and undoubtedly contains some redundant steps. But, as described, it proved satisfactory for reproducible operation.

Before each run the separate parts of the recirculation system, excluding the reactor, were filled with known amounts of reactants. The usual pressure of hydrocarbon added to the 1.1-liter system was 4 torr. Sufficient hydrogen and/or helium was used to bring the total pressure above atmospheric. The reactants were then mixed with the recirculation pump, bypassing the reactor. The run was started by opening the evacuated

TABLE 1
GOLD CATALYST
TYPICAL ANALYSIS

Component	ppm
Au	99.99(%)
Ag	10
Fe	10
Si	10
Mg	5
Al	5
Pd	4
Ca	3
Pt	1
Re	1
Ni	1
Cr	1
Mn	1
Pb	1
Ru	n.d.
Sn	n.d.
Zn	n.d.
Sb	n.d.
	53
Powder size	50–70 mesh
Surface area	0.072 m^2/g
Bulk density	3.3 g/cm^3

reactor, containing the activated gold powder, to the recirculation system.

In the case of a first order reaction, the kinetic data can be analyzed in the following way: For the change ΔP_r in reactant partial pressure P_r due to passage of the gas through the differential reactor in the batch recirculation system, we have

$$q_r\left(\frac{\Delta P_r}{RT_r}\right) = -kA\left(\frac{P_r}{RT_r}\right) \qquad (1)$$

where q is the volumetric flow rate, k the surface rate constant with dimensions of length/time, A the total catalyst surface area, and the subscript r refers to a property in the reactor. The simplicity of Eq. (1) arises from the small changes in concentration, temperature, density, and other properties across the differential reactor which are negligible in comparison with their entrance values and are therefore eliminated.

TABLE 3
CATALYST ACTIVATION PROCEDURE

Step	Hours
Evacuation *in situ*, heat to 175°C	1
Flowing hydrogen—250 STP cm^3/min, 1000 torr Heat to 325°C	2
Flowing hydrogen—250 STP cm^3/min, 1000 torr Maintain at 325°C	6–10
Cool *in vacuo* to 250°C	1
Static oxygen—600 torr Maintain at 250°C	4–6
Heat/cool *in vacuo* to run temperature	1

Now, as a result of consumption of reactant in the reactor, a negative accumulation (loss) in the recirculation loop of constant volume can be described by

$$\frac{V_s}{RT_s}\left(\frac{dP_s}{dt}\right) = q_r\left(\frac{\Delta P_r}{RT_r}\right) \qquad (2)$$

TABLE 2
HYDROCARBONS

Compound	Freezing point (mole %)	Thiophene test	Probable impurities	Grade
Cyclohexene	99.94	—	Cyclohexane	Phillips Petroleum Research Grade
Cyclohexane	99.99	None	C_7 Hydrocarbons	Phillips Petroleum Research Grade
Benzene	99.89	None	Toluene	Phillips Petroleum Research Grade
1,3-Cyclohexadiene	90.[a]	—	9% Benzene[a] 1% Cyclohexene	Matheson, Coleman, and Bell—Technical

[a] Determined by gas chromatograph.

where V_s is the system volume and T_s and P_s are, respectively, the effective temperature and partial pressure for the entire system. For an initially well-mixed system, P_s will be essentially identical with P_r. Combining (1) and (2), we get

$$k = \frac{-V_s(T_r/T_s)}{A}\frac{d \ln P_s}{dt} \qquad (3)$$

Integrating with the initial condition, $P_s = P_s^0$ at $t = 0$, and introducing observables, we get

$$k = (-V_{eff}/At) \ln x \qquad (4)$$

where V_{eff}, the system volume corrected to reactor temperature, is equal to $V_s(T_r/T_s)$ which in turn equals

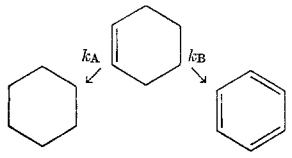
$$V_s\left(\frac{T_r}{T_o}\right) - V_r\left(\frac{T_r - T_o}{T_o}\right)$$

The subscript o refers to the portion of the recirculation system outside the reactor which in this study was maintained at room temperature, and x refers to the mole fraction of the reactant present in the hydrocarbon. For example, with $V_s = 1104$ cm^3, $V_r = 71$ cm^3, $T_r = 254$°C, then we calculate that $V_{eff} = 1900$ cm^3.

Chromatographic analysis requires the periodic removal of small samples from the system. Correction for the amount removed is not required for first order kinetics, as removal does not affect the reactant mole fraction.

Results

Determination of the network of component reactions was the first step in the experimental program. Data indicated that the selectivity S, which is the ratio of benzene to cyclohexane produced, $\Delta x_B/\Delta x_A$, in a given time interval, was constant during the first order reaction of cyclohexene in excess hydrogen, Fig. 2. Apparently the transient selectivity observed by Kemball *et al.* (*15*) arose from a small amount of cyclohexane produced at the beginning of the run before a steady state run temperature had been achieved. When benzene was substituted for cyclohexane a very slow hydrogenation apparently occurred, very much slower than with cyclohexene. Furthermore, a mixture of cyclohexene and benzene gave about the same selectivity as pure cyclohexene. The corresponding reaction paths are parallel straight solid lines in a triangular diagram as seen on Fig. 3. The correction of these lines to the same hydrogen partial pressure, 0.23 atm, is so small that the lines remain unaltered. As will be discussed later, the only network whose characteristic pattern in a triangular diagram is composed of parallel, straight line reaction paths is



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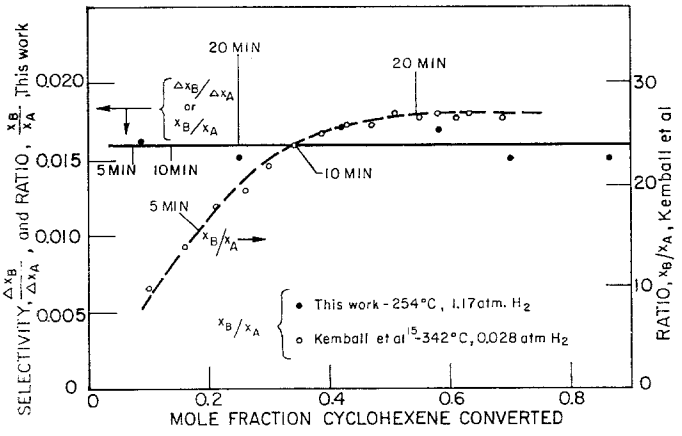


FIG. 2. Selectivity vs. conversion.

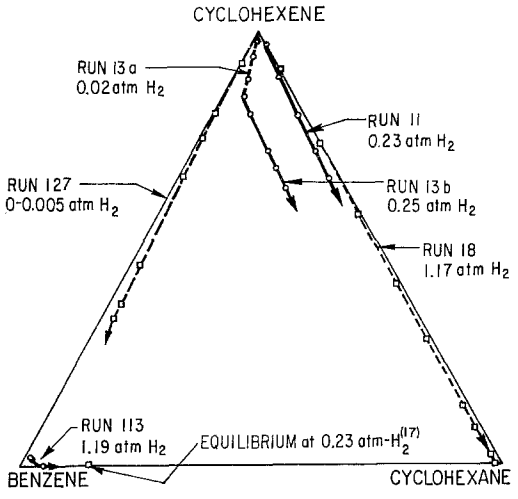


FIG. 3. Reaction paths on gold at 254°C.

Therefore, the form of the network has been established.

The orders of the two irreversible reactions were then determined. At hydrogen partial pressures of 0.3 to 1.2 atm, considerably in excess of that of the hydrocarbon, the primary reaction was hydrogenation which showed first order behavior in cyclohexene (see Fig. 4, Run 135). When cyclohexene reacted in the initial absence of hydrogen, primarily dehydrogenation took place. Dehydrogenation was also first order in cyclohexene and unaffected by the changing hydrogen partial pressure (Fig. 4, Run 127).

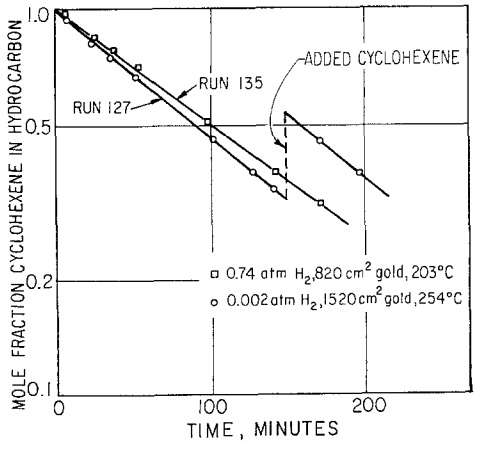


FIG. 4. First order reaction of cyclohexene on gold.

Since selectivity varied quite markedly with hydrogen partial pressure, evidently the hydrogenation reaction had to be a function of hydrogen.

The order with respect to hydrogen was determined from experimental runs, where cyclohexene was reacted in the initial absence of hydrogen, by postulating several reaction orders, integrating the rate equations, and comparing the resultant expressions with the experimental data. For example, postulating first order in hydrogen, we get

$$-\frac{V_{\text{eff}}}{RT_r}\left(\frac{dP_A}{dt}\right) = k_A A\left(\frac{P_E}{RT_r}\right)\left(\frac{P_{H_2}}{RT_r}\right) \quad (6)$$

where E refers to cyclohexene, A to cyclohexane, B to benzene, and H_2 to hydrogen. Since very little hydrogenation takes place in the initial absence of hydrogen

$$P_{H_2} \approx 2P_B \quad (7)$$

Inserting this into Eq. (6), we obtain

$$-V_{\text{eff}}\left(\frac{dP_A}{dt}\right) = 2k_A A P_E\left(\frac{P_B}{RT_r}\right) \quad (8)$$

Now, the dehydrogenation reaction yields

$$-V_{\text{eff}}(dp_B/dt) = k_B A P_E \quad (9)$$

If we multiply both sides of Eq. (9) by $2(P_B/RT_r)(k_A/k_B)$, the right-hand sides of Eqs. (8) and (9) will be identical. Equating the left-hand sides,

$$\frac{dP_A}{dt} = \frac{k_A}{k_B}\left(\frac{2}{RT_r}\right)P_B\frac{dP_B}{dt} \quad (10)$$

Integrating with respect to time,

$$P_A = \frac{k_A}{k_B}\left(\frac{1}{RT_r}\right)P_B^2 \quad (11)$$

Converting to mole fraction of total hydrocarbon yields

$$x_A = \frac{k_A}{k_B}\left(\frac{P_E^0}{RT_r}\right)x_B^2 \quad (12)$$

where P_E^0 is the initial partial pressure of cyclohexene. Therefore, if hydrogenation is first order in hydrogen, a plot of x_A versus $(P_E^0/RT_r)x_B^2$ should be linear with a slope

of k_A/k_B. But, of course, Eq. (7) is only approximate and $P_{H_2} = 2P_B - P_A$. Correcting for this effect, Eq. (12) becomes

$$x_A = \frac{k_A}{k_B}\left(\frac{P_E^0}{RT_r}\right)\left(1 - \left[\frac{x_A}{2x_B}\right]_{av}\right)x_B^2 \quad (13)$$

and x_A is now plotted versus

$$\left(1 - \left[\frac{x_A}{2x_B}\right]_{av}\right)\left(\frac{P_E^0}{RT_r}\right)x_B^2$$

A similar development leads to the following relations which would be expected if hydrogenation were zero or half order in hydrogen, respectively:

$$x_A = \frac{k_A'}{k_B}x_B \quad \text{if} \quad r_A = k_A'\left(\frac{P_E}{RT_r}\right) \quad (14)$$

$$x_A = \frac{k_A''}{k_B}\left(\frac{2\sqrt{2}}{3}\right)\left(\frac{P_E^0}{RT_r}\right)^{1/2} \times \left(1 - \left[\frac{x_A}{2x_B}\right]_{av}\right)^{1/2} x_B^{3/2} \quad (15)$$

if

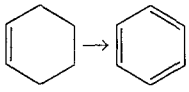
$$r_A = k_A''\left(\frac{P_E}{RT_r}\right)\left(\frac{P_{H_2}}{RT_r}\right)^{1/2}$$

Comparing how well Eqs. (13) to (15) describe the experimental data (Fig. 5), we find that Eq. (13) fits the data very well. The other equations do not. Hydrogenation is then first order in hydrogen as well as first order in cyclohexene.

Rate constants for the faster of the two reactions at the experimental conditions were calculated by Eq. (4) from first order plots like Fig. 4, and corrected for the presence of the slower reaction. Rate constants for the slower hydrogenation at low hydrogen partial pressures were obtained from selectivity data by means of Eq. (13). At higher hydrogen partial pressures, where dehydrogenation was the slower reaction, the dehydrogenation rate constant was simply determined from

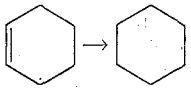
$$k_B = k_A\left(\frac{P_{H_2}}{RT_r}\right)\left(\frac{\Delta x_B}{\Delta x_A}\right) \quad (16)$$

Rate constants for each run are listed in ref. 25. Arrhenius plots, Fig. 6, yielded an activation energy of 22 kcal/g mole for dehydrogenation and 14.5 kcal/g mole for hydrogenation. The reaction orders and rate constants are summarized below, rates r being expressed in g moles/cm² sec



$$r = k_B c_E$$

$$k_B = 2 \times 10^5 \exp(22\,000/RT_r) \text{ cm/sec}$$



$$r = k_A c_E c_{H_2}$$

$$k_A = 1.5 = 10^8 \exp(-14\,500/RT_r) \text{ cm}^4/\text{g mole sec}$$

Preexponential factors refer to rate constants determined in the initial absence of hydrogen. When the hydrogen partial pres-

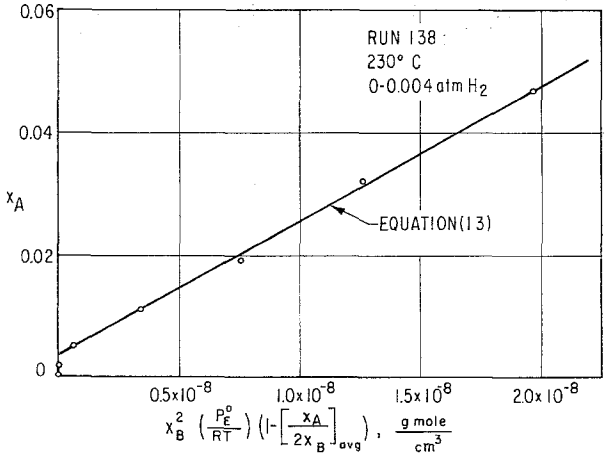


FIG. 5. Hydrogenation first order in hydrogen.

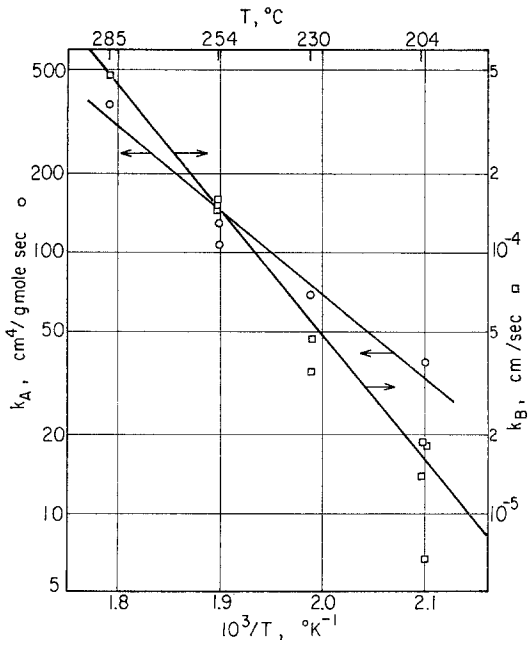


FIG. 6. Arrhenius plot for hydrogenation and dehydrogenation rate constants, k_A, k_B.

sure is raised by a factor of 500 to values close to 1 atm, both rate constants decrease by a factor of 2 to 8, a remarkably small change considering the magnitude of the hydrogen partial pressure change. The reason for this small change at high pressures of hydrogen was not investigated further.

At low hydrogen partial pressures benzene is the primary product. If no hydrogen is added initially, the dehydrogenation reaction will produce hydrogen and thus increase the rate of production of cyclohexane, thereby reducing the selectivity toward benzene. This can be seen graphically by Run 127 in Fig. 3. When benzene is the sought-after product, it would be desirable to remove the hydrogen as it is formed, in particular to reduce the concentration of hydrogen atoms on the surface.

This removal was attempted by the addition of oxygen. Oxygen was found to decrease markedly the production of cyclohexane, as Fig. 7 dramatically shows. When oxygen was added initially the selectivity was much higher than in the previous runs without oxygen and remained constant. Also, the rate of dehydrogenation was unchanged and the catalyst did not lose any of its activity at 203°C. Some hydrocarbon oxidation, however, occurred simultaneously. These oxidation products amounted to about 10% of the cyclohexene converted. A comparison of the extreme variation of selectivity possible on gold is shown below.

Selectivity S	Oxygen partial pressure	Hydrogen partial pressure	Temperature	Run
110	0.041 atm	—	203°C	131
0.032	—	0.74 atm	203°C	135

Identification of oxidation products was attempted by gas chromatographic scanning but was unsuccessful. Chromatograph conditions were chosen such that peaks with retention times from CO to and beyond cyclohexanone would have been noted. The

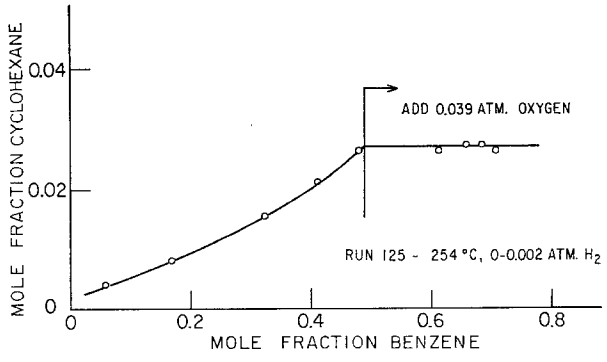


FIG. 7. Effect of oxygen on selectivity.

amount of hydrocarbon oxidized was determined by the difference between the loss of hydrocarbon in the presence of oxygen and the normal removal of hydrocarbon by sampling. Because the amount oxidized has to be back-calculated the accuracy is not very high, probable ±5% of the hydrocarbon. A similar material balance on oxygen indicates the average oxygen content of the oxidation products to be between one and four atoms per molecule.

At 254°C continuous deactivation, presumably by oxidation products, was observed, amounting to about 40% after 30% of the cyclohexene had reacted. At 230°C the amount of deactivation had declined to about 15% in the same interval, while at 203°C no deactivation was detectable.

Separate experiments were carried out to provide additional information. With only hydrogen and oxygen as reactants, the rate of water formation at 203°C, adjusted from 33 torr of hydrogen and 32 torr of oxygen to 1 and 4 torr, respectively, by assuming the rate to be first order in hydrogen and half-order in oxygen, was found to be 130 times faster than hydrogenation and 10 times faster than dehydrogenation at the same hydrogen partial pressure and 4 torr of hydrocarbon.

Small amounts of cyclohexadiene were detected in runs where hydrogen was not initially present and in runs with oxygen. In the former case at 254°C the diene concentration very rapidly rose to about 0.15% and slowly declined. With oxygen present the behavior was similar except the maximum amount was usually 0.4%. It is natural to believe that only small amounts appeared because cyclohexadiene was much more reactive than cyclohexene. Indeed, when 1,3-cyclohexadiene reacted in the absence of hydrogen, yielding approximately equal proportions of cyclohexene and benzene, the diene reacted immeasurably fast, reaching 99.4% conversion by the time the first sample was taken 4 min after the reaction had begun. This would imply the rate to be at least 170 times that of cyclohexene dehydrogenation.

Experiments with excess cyclohexane and benzene revealed no inhibition of either hydrogenation or dehydrogenation of cyclohexene, implying that fractional utilization of active sites by chemisorbed hydrocarbons is small.

A variety of experimental checks was made. At several occasions experiments were performed to determine whether significant amounts of irreversible poisons were contained in the purified liquid cyclohexene or were produced during the reaction. Figure 4, Run 127, shows the addition of cyclohexene in the middle of the run. Since the first order slope after cyclohexene addition is the same as that before, the absence of poisoning is evident.

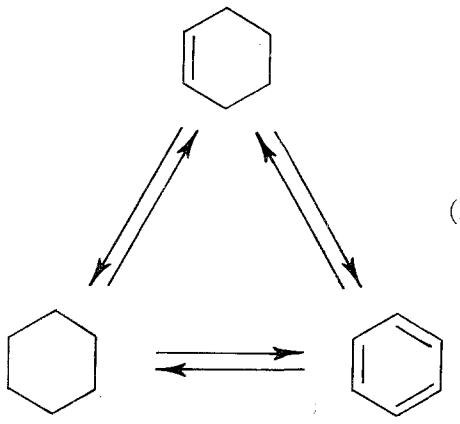
The hydrogen used was purified by liquefaction before filling the cylinders, but in general was not further purified. A number of early runs were made in which this hydrogen was further purified by diffusion through a heated Pd-Ag alloy thimble. No significant difference was found when operating with or without the palladium thimble.

Experiments where small amounts of air and water were added in the middle of a run showed that these contaminants did not poison the catalyst but increased its activity. It is believed this increase was due to incomplete activation in the early runs.

Different amounts of catalyst at identical conditions gave the same specific rate constant (Runs 20 and 21). In the absence of catalyst, no hydrogenation was observed in the presence of 0.30 atm of hydrogen at 325°C, nor any oxidation or dehydrogenation with 0.04 atm of oxygen at 254°C. Surface area determinations indicated the surface areas of fresh catalyst and two used catalysts (Runs 114 and 131), to be identical.

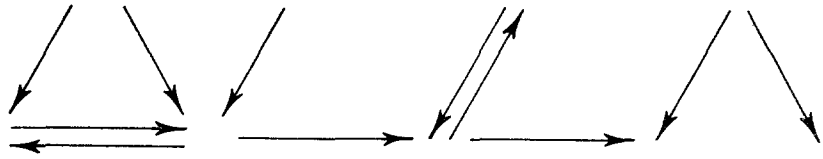
Discussion

The first objective of this study was to determine the form of the reaction network. In general, the reaction network for cyclohexene, benzene, and cyclohexane is made up of separate hydrogenation–dehydrogenation between each of the three, six in all, as sketched in Eq. (19). However, if some of the rate constnnts in Eq. (17) are much smaller than the others, their reactions are effectively eliminated. Therefore, without a



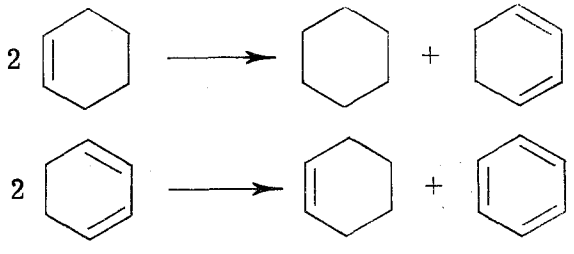
(17)

loss of generality, possible candidates for the reaction network of interest are



The correct form of the reaction network can be elucidated by a simple graphical procedure which we may call the method of characteristic patterns. The reaction paths are plotted in composition space, in this case on triangular coordinates. What results is a characteristic pattern or "fingerprint" of the reaction network. The characteristic patterns for various forms are quite different, as can be seen in Fig. 8. By recognizing the differences in these patterns, critical experiments can quickly delineate the proper form of the network. In this regard only three experiments were required to determine the form of the reaction network in this study.

In addition to the hydrogenation–dehydrogenation reactions shown in Eq. (17) there is the possibility of disproportionation or hydrogen transfer reactions. There has been considerable mention of these in the literature (*18–20*)



(18)

These may be eliminated from consideration in the present study as the selectivity varied quite markedly with hydrogen partial pressure, from almost quantitatively producing benzene in the absence of hydrogen to practically quantitative production of cyclohexane at a hydrogen partial pressure of 1 atm. Clearly these results indicate that disproportionation, if present, can be safely neglected.

The slow rate of hydrogenation as compared to dehydrogenation is apparently due to the small extent of hydrogen chemisorption on the surface. In that regard Mikovsky, Boudart, and Taylor (*4*) speculate that hydrogen chemisorption on copper, silver, and gold is related to the promotion of *d* electrons to the top of the *s* band creating vacant *d* orbitals which are then available for surface bond formation. The edge of the absorption band of gold in the visible indicates an internal photoelectric effect requiring a promotional energy of 2.3 eV, but the corresponding thermal energy might be substantially less, because of the Franck-Condon principle and the higher density of unsaturated valences on the surface than in the layers beneath. With this in mind, the slow but finite rate of hydrogenation above 200°C is not at variance with the undetectable chemisorption of hydrogen at room temperature (*1*), because the number of surface sites capable of chemisorbing hydrogen may increase with temperature, as a result of the promotional effect.

Comparing the rates of hydrogenation and dehydrogenation from this work with those of Kemball *et al.* (*15*), corrected from geo-

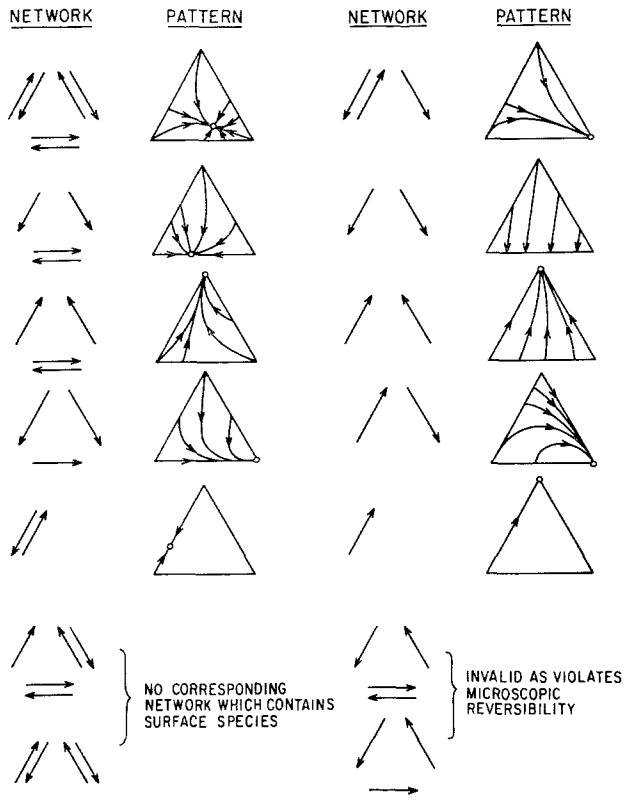


FIG. 8. Characteristic patterns for first order three-component networks.

metrical area to true surface area by the roughness factor of 1.4 reported by Sarakhov (*21*), at 254°C, 20 torr of hydrogen, and 2 torr of hydrocarbon, we find the rate of hydrogenation to be nearly identical, while dehydrogenation rates in this work differ by being only 20% lower. This close agreement is quite gratifying, indicating the gold powder activated by oxygen treatment (removal of adsorbed impurities by oxidation) is about as active as vacuum-evaporated films. In this regard Plumb and Thakkar (*22*) have noted that pure gold surfaces (with 10 ppm or less of impurities in the bulk material) will stay clean in the presence of oxygen, but that impure gold containing significant quantities of oxidizable impurities such as copper will form surface layers of the oxidized impurities. In addition to the primary evidence afforded by the agreement between rates on our gold powder and on evaporated films, the facts that the catalyst did not lose activity during dehydrogenation and that air did not poison the catalyst infer that the impurities present at the surface of the powder did not materially affect its catalytic activity.

It is interesting to compare gold with other catalysts. Comparing the rates of hydrogenation and dehydrogenation at 254°C and 20 torr of hydrogen with the frequency of collisions with the surface, we find that the probability of reaction per collision for the hydrocarbon is about 10^{-8}. Madden and Kemball (*23*), studying the hydrogenation of cyclohexene on evaporated nickel films, found a probability of 10^{-8} at -30°C and the same hydrogen partial pressure as above. If these results could be extrapolated to 254°C, the probability would be about 10^{-1}. On that basis, gold would be 10^{7} times less active than nickel in the hydrogenation of cyclohexene.

It is clear that the role of oxygen in increasing the selectivity toward benzene is to remove hydrogen. It is interesting to compare the results for the addition of oxygen to cyclohexene using gold with the

similar addition of air to cyclohexane using platinum, palladium, and other catalysts (*24*). Roughly optimal conditions were realized at 316°C and 0.37 atm of oxygen with a supported platinum catalyst, where 50% conversion of cyclohexane was attained. Of the cyclohexane converted, 75% went to form benzene, but 25% was completely oxidized to carbon dioxide. Without oxygen, at these temperatures, a negligible conversion to benzene was observed and the catalyst was apparently greatly deactivated by hydrocarbon fragments. Gold is definitely superior to platinum with respect to selectivity in the presence of oxygen or in the absence of hydrogen, no doubt because of the weak chemisorption of hydrocarbon and oxygen on its surface. Therefore we conclude that gold is an attractive catalyst for oxidative dehydrogenation.

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