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The Dehydrogenation of Cyclohexane Vapor on Silica-Supported Nickel Catalysts

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The dehydrogenation of cyclohexane vapor has been studied over nickel-on-silica catalysts in a flow system from 100° to 260° at atmospheric pressure. The fraction of cyclohexane converted to benzene (C) was extremely low (about 0.01) between 100° and 180°, while at 235°, C increased to a maximum value around 0.25 and then rapidly decreased with further rise in temperature. In the range 150–220°, the apparent activation energy was 30 ± 2 kcal/mole and the reaction rate dependence was zero order with respect to benzene, and first order with respect to cyclohexane and to the inverse of the hydrogen concentration.

It is suggested that the slowest step in the reaction involves the initial formation, from adsorbed cyclohexane, of adsorbed cyclohexene and hydrogen. The results are contrasted and compared with earlier findings on benzene hydrogenation.

INTRODUCTION

In the study of heterogeneous catalytic reactions it is often necessary to use extremely pure preparations in order to evaluate the possibility of a link between the catalyst activity and its physical and chemical properties. Hence most kinetic investigations are carried out with catalysts which in general, would show wide differences in surface and bulk properties when compared with the real catalysts normally employed in the laboratory or on an even larger scale. In the present series of experiments attention is focused on the study of heterogeneous reactions on real or "practical" catalysts.

In an earlier communication on the catalytic vapor phase hydrogenation of benzene (*1*), it was indicated that the nature of this reaction above 170° would be understood better by an examination of cyclohexane dehydrogenation on a similar surface at the same temperature. The latter study was the aim of the present experiments.

EXPERIMENTAL

Apparatus. This was essentially similar to that used and described earlier (*1*). Two metered gas channels were provided up to a vertical preheater preceding the catalyst chamber. In one channel, cylinder hydrogen was passed through a "Deoxo" unit, a drying tower, and then into a thermostatically controlled cyclohexane saturator. The other channel was used as a benzene or diluent stream, in which benzene could be introduced by bubbling nitrogen into a saturator through a sintered glass distributor. The saturator temperatures were controlled to ±0.01° and the delivery efficiencies, tested prior to each catalytic run, were not accepted unless better than 99.5%. All joints and stopcocks were lubricated, where necessary, with a 1/1 w/w glycerine/mannitol paste.

The products of catalysis were analyzed by refractive index measurement at 15° and the fraction of cyclohexane dehydrogenated found from a calibration graph of a series of known C_6H_6/C_6H_{12} mixtures.

Several product samples were analyzed by vapor phase chromatography using a 6 ft squalene column at 68°. Nitrogen was used as the carrier gas at 2.5 liter/hr with inlet and outlet pressures 536 mm and 237 mm, respectively. All mixtures so tested analyzed to within ± 0.1% of that found by refractive index and no products other than benzene and cyclohexane were detected.

Materials. "AnalaR" cyclohexane and "AnalaR" benzene were twice distilled and then stored over molecular sieves.

Nickel-on-silica catalysts were prepared as outlined previously (*1*, *2*). The finely powdered, nonpyrophoric catalyst was compacted into pellets 0.3 cm × 0.3 cm dia. and 0.15 cm × 0.15 cm dia. using 5% graphite as a binding agent.

Further experimental details are given below.

Results

Preliminary investigations were made with a closely packed bed of discs of fine mesh nickel gauze, 10 cm deep, held normal to the gas stream. These were pre-etched with 2 *M* potassium hydroxide and activated in flowing hydrogen at 200° for 1–2 hr. Within the range 100° to 260° the catalysis registered by this material was always $<2\%$.

(*i*) *The Effect of Carrier Gas Composition, Space Velocity, and Catalyst Pellet Size on the Fraction of Cyclohexane Dehydrogenated*

Experiments were carried out to find the effect of space velocity and pellet size on the observed conversion at constant cyclohexane (100 mm) and hydrogen (660 mm) partial pressures at 235°. Two series of runs were also completed with the same cyclohexane pressure and catalyst temperature using (a) nitrogen as the carrier gas and (b) a hydrogen/nitrogen mixture (2/3 v/v) as the carrier gas. The results are given in Table 1.

The results cover a ratio of individual pellet volumes from eight to one and show a constant difference of 0.005 in the fraction converted using hydrogen as the carrier gas. The larger pellets gave the slightly higher conversion at all space velocities. This is the reverse of that expected if the reaction was subjected to a pure restriction of molecular transport from the moving gas phase to the catalyst surface or conversely, transport of products in the opposite direction. Since, reaction rates governed by transport restrictions are functions of geometric, rather than adsorption, surface area (*3*). Again, if such rate-controlling conditions prevailed, the measured *C* values would not reflect constant differences throughout the wide range of space velocities studied. The small difference in these *C* values is more likely related to a minor variation in catalyst surface condition.

The other results in Table 1 show a progressive increase in *C* as the hydrogen carrier was partly, and then wholly replaced by nitrogen. This feature is discussed later but it does indicate that nitrogen has no surface poisoning effect.

(*ii*) *Variation of Fraction Dehydrogenated with Cyclohexane Partial Pressure*

In this series of runs the hydrogen partial pressure was maintained at 340 mm and the total flow rate at 50 ml/min (space velocity = 4.432 cc gas/cc cat/hour). The cyclohexane partial pressure was varied from 60 mm to 300 mm using nitrogen as diluent. Runs were carried out at catalyst temperatures of 215° and 235° and the results are given in Table 2.

The results indicate that the fraction of cyclohexane dehydrogenated is independent of the cyclohexane partial pressure. The reaction rate dependence is therefore first order with respect to cyclohexane concentration.

(*iii*) *The Effect of Benzene Partial Pressure*

In these experiments the catalyst temperature, hydrogen, and cyclohexane partial pressures were kept constant at 235°, 204 mm and 100 mm, respectively. Variation of the partial pressure of benzene was achieved by passing nitrogen through the benzene saturators at different steady temperatures while maintaining a steady overall flow rate of 50 ml/min. The results,

TABLE 1

Variation of the Fraction of Cyclohexane Dehydrogenated with Space Velocity, Pellet Size, and Carrier Gas Composition

10^4/Space velocity (cc gas/cc catalyst/hour)$^{-1}$	Mole fraction cyclohexane dehydrogenated (C)			
	Hydrogen carrier		Nitrogen carrier	Hydrogen/nitrogen carrier
	(Pellet size = 0.3 cm × 0.3 cm)	(Pellet size = 0.15 cm × 0.15 cm)	(Pellet size = 0.3 cm × 0.3 cm)	(Pellet size = 0.3 cm × 0.3 cm)
1.108	0.070	—	0.090	0.080
1.477	0.085	0.080	0.110	0.095
2.216	0.120	0.115	0.155	0.138
2.955	—	—	0.180	0.165
4.432	0.175	0.170	0.225	0.210
8.864	0.240	0.235	0.305	0.280
14.770	—	—	0.345	0.320

Table 3, indicate a zero order dehydrogenation rate dependence on benzene partial pressure. With the introduction of the higher amounts of benzene into the system, the reaction became fairly exothermic and runs had to be given an initial 30 min before a particular steady temperature was achieved.

TABLE 2

The Effect of Cyclohexane Partial Pressure on the Fraction of Cyclohexane Dehydrogenated

Catalyst temperature (°C)	Cyclohexane partial pressure (mm Hg)	C
235°	60	0.210
235°	80	0.214
235°	100	0.210
235°	120	0.205
235°	140	0.210
235°	180	0.210
235°	300	0.212
215°	60	0.190
215°	100	0.190
215°	140	0.194
215°	180	0.185
215°	220	0.186
215°	300	0.190

TABLE 3

The Effect of Benzene Partial Pressure on the Fraction of Cyclohexane Dehydrogenated[a]

Benzene partial pressure (mm Hg)	Nitrogen partial pressure (mm Hg)	C
100	356	0.290
150	306	0.295
200	256	0.290
250	206	0.290
300	156	0.285

[a] Catalyst temperature, 235°C.

(iv) *The Effect of Hydrogen Partial Pressure*

This parameter was examined at a constant cyclohexane partial pressure (300 mm) and catalyst temperature (235°). The hydrogen partial pressure was varied by mixing with nitrogen and the flow rate maintained at 50 ml/min.

The results are given in Table 4, while in Fig. 1 $\log_{10}$ (rate) is plotted as a function of $\log_{10}$ (total hydrogen pressure). This yields a straight line of slope = —1 which indicates a negative first order rate dependence on hydrogen.

TABLE 4

The Effect of Hydrogen Partial Pressure on Fraction of Cyclohexane Dehydrogenated

Hydrogen partial pressure added (mm Hg)	C
460	0.20
368	0.23
276	0.26
184	0.29
92	0.33
0	0.36

(v) *The Experimental Activation Energy*

The effect of temperature on C was obtained from a series of experiments with cyclohexane and hydrogen partial pressures respectively 100 mm and 660 mm at a flow rate of 50 ml/min and catalyst temperatures from 200° to 260°.

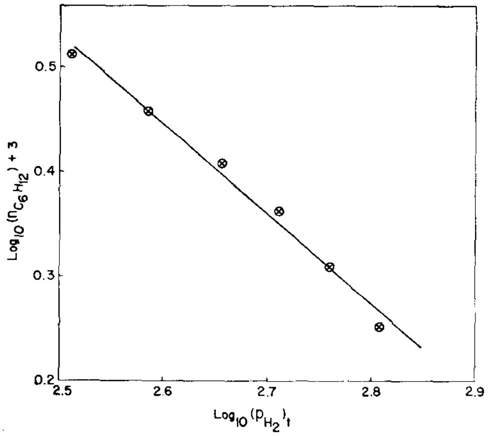

FIG. 1. Variation of $\log_{10}$ (number of moles cyclohexane dehydrogenated) with $\log_{10}$ (total hydrogen pressure) at 235° and $P_{C_6H_{12}} = 300$ mm Hg.

Using (a) hydrogen, (b) nitrogen, and (c) hydrogen/nitrogen (2:3 v/v) as carrier gases, no appreciable catalysis was observed below 150°. In Fig. 2 the results are plotted as C versus the catalyst temperature (°C). Each curve shows the same activity pattern which may be separated into three fairly well-defined sections. From 150° to 220°, there is a rapid rise in catalysis which starts to decline at the higher temperature and then almost remains steady for a further 20°. Finally from 240° to 280°, the fraction converted falls rapidly from values in the region of 0.2—the actual value depending on the carrier gas composition—to an indicated zero value.

The rate constant for the reaction between 150° and 220° was derived from the experimental kinetic expression:

$$r = k\,\frac{(n_{C_6H_{12}})^1(n_{C_6H_6})^0}{(n_{H_2})^1} \tag{1}$$

and setting the number of moles of hydrogen gained by the system per second of delivery as:

$$n' = \frac{3 \times p^i{}_{C_6H_{12}} \times F \times C}{22{,}400 \times P} \tag{2}$$

where $p^i{}_{C_6H_{12}}$ and P are the initial cyclohexane and total system pressures, respectively, F is the flow rate in ml/sec, and C is the mole fraction of cyclohexane dehydrogenated during the course of a run.

The experimental rate constant, k', then becomes:

$$k' = \frac{3(p^i{}_{C_6H_{12}}) \times F \times C \times X}{22{,}400 \times P \times S} \tag{3}$$

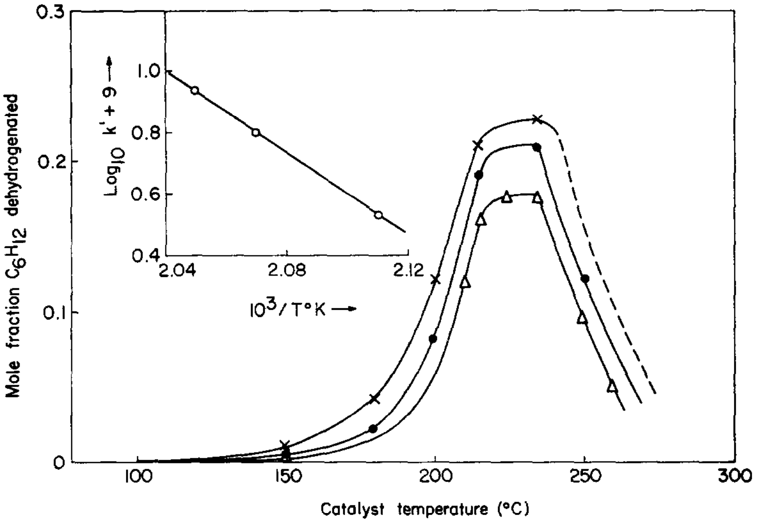

FIG. 2. Effect of temperature on fraction dehydrogenated. Carrier gas: x—nitrogen; ●—hydrogen/nitrogen (2/3 v/v); △—hydrogen. Inset: Arrhenius Ea plot.

where S is the total catalyst surface area (m^2) and X is an arbitrary factor introduced to allow for differences in gas residence time within the catalyst zone and is assumed proportional to reaction temperature/saturator temperature in °K. Equation (3) gives k' in $\sec^{-1}m^{-2}$.

In the usual manner, a plot of log k' versus $1/T$°K yields the activation energy from the slope of the line. This is shown, inset, in Fig. 2 and gives an experimental activation energy for cyclohexane dehydrogenation, from 150° to 220°, of 30 ± 2 kcals/mole.

DISCUSSION

Very few kinetic results are available for cyclohexane dehydrogenation. Bridges and Houghton (*4*) studied the flow dehydrogenation by a continuous temperature-rise method, with several catalysts, at 150–650° and found over-all zero or first order kinetics which appeared to be related to the catalyst used. In general, however, a zero order rate dependence on cyclohexane concentration is found (*5*).

In this work, the zero order rate dependence on benzene suggests that much of the active catalyst surface is covered with adsorbed benzene. At the same time, the fact that varying the concentration of benzene added to the reaction stream gives no alteration in the reaction product mixture, at constant cyclohexane and hydrogen partial pressures, indicates that surface equilibrium, as far as C_6H_6 is concerned, is not well established or is difficult to upset.

The catalyst used in these studies gave a peak activity of a factor of three times less than that for C_6H_6 hydrogenation (*1*), although the course of activity change with temperature was fairly similar to that for the latter reaction. The fairly rapid increase in the rate of catalysis from 150° to 230° in C_6H_{12} dehydrogenation may be compared to the fall in C from a value of 0.92 to around 0.10 in C_6H_6 hydrogenation in the same temperature range. Such evidence is most probably indicative of a reversibility of mechanism between these temperatures.

The thermodynamic equilibrium for the reaction:

$$C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2 \qquad (4)$$

moves increasingly to the right as the temperature is raised from 25° to 277°. This is evident from the free energy calculations of Janz (*6*) for benzene hydrogenation. Thus at 550°K, ΔG for hydrogenation has been calculated to be 0.0 kcal/mole. This value falls rapidly with decreasing temperature (—14.35 kcal/mole at 400°K and —23.4 kcal/mole at 298.16°K). Hence, if the present dehydrogenation rate was subjected purely to a controlling equilibrium involving C_6H_6 and C_6H_{12} directly, then a steady increase in the rate of catalysis would be expected over the temperature range studied. The results only show this trend up to 230°. Also, while the effect of increasing the hydrogen content of the carrier gas is such as to reduce the conversion (Fig. 2) it does so in a fashion which reflects an almost constant difference on C, irrespective of temperature. This could imply an absence of any over-all surface equilibria involving C_6H_6 and C_6H_{12} or, alternatively, that the equilibria are too slow in settling to have much influence on the catalytic mechanism.

The complete absence of cyclohexene and cyclohexadiene in the product fractions probably indicates that these species are dehydrogenated in fast consecutive steps or even that cyclohexene rapidly disproportionates to benzene with the simultaneous loss of two hydrogen molecules.

The above factors may well indicate that the dehydrogenation rate is controlled by a single slow step in a formal mechanistic scheme. This step may well be the initial formation, from adsorbed cyclohexane, of adsorbed cyclohexene and hydrogen, which would account for the experimental rate dependence on both hydrogen and cyclohexane concentrations.

At temperatures much above 250° the rate of catalysis rapidly falls away in a fashion that suggests a sharp decrease in active adsorption of reactants which disallows catalysis.

The experimental activation energy of

30 ± 2 kcal/mole for the active dehydrogenation stage is similar to the value of 26 kcal/mole found for nickel tungstate on alumina in a higher temperature range (*4*), but there is no basis of comparison with Balandin's dehydrogenation work with Re/charcoal (*5*) from 250–340°, which gave an E_A of 7.8 kcal/mole, since the main products in that case were methane and hydrogen, which indicates a difference in mechanism. However, for a catalyst of 26.8% Re on wood charcoal the same workers have reported (*8*) an activation energy of 25.2 kcal/mole from 280° to 380° for dehydrogenation to benzene. Relatively small amounts of cyclohexadiene and cyclohexene were present in their product fractions. At the same time the low dehydrogenation activity and high E_A found with the present catalyst (52% w/w of nickel) is consistent with the observations of other Russian workers (*7*) that supported nickel catalysts for C_6H_{12} dehydrogenation lose activity as the nickel content is raised much above 35% w/w.

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