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Comparison of the Behavior of Platinum and Nickel in Some Catalytic Reactions of Cyclohexane

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The exchange reaction between cyclohexane and deuterium gas and the reactions of dehydrogenation and hydrogenolysis in the presence of deuterium have been investigated over a wide range of temperature on platinum and nickel powder catalysts. The results are as follows:

i. In the temperature range 30–100°C only deuterium exchange takes place. The activation energies are the same for both catalysts although the rate of exchange is about one order of magnitude higher on Pt than on Ni.

ii. Between 100 and 200°C poisoning occurs due to extensive decomposition. This effect is characteristic of nickel and causes a decrease of two orders of magnitude in catalytic activity but leaves the activation energy unchanged.

iii. Above 200°C besides exchange other reactions commence and result in the formation of *n*-hexane, benzene and toluene on Ni and benzene on platinum. In this temperature range the deuterium appears in equilibrium distribution not only in the products but in the parent molecule.

It seems very likely that at high temperature the dissociative adsorption is not rate controlling and thus the exchange and the chemical transformation are controlled by the desorption and by the surface reaction, respectively.

INTRODUCTION

Deuterium exchange of C_1–C_3 hydrocarbons on platinum (*1*) and nickel (*2,3*) show no particular differences in kinetic parameters and deuterium distribution. However, at higher temperatures reactions like hydrogenolysis (*1,4,5*) proceed by different pathways depending on the type of metal catalyst. This phenomenon was explained by the predominance of strongly bonded intermediates, characteristic of nickel (*6*). On platinum, formation of these species is retarded leading to the formation of other products by a less strongly bonded pathway (*1*).

We decided to examine these phenomena by a study of the catalytic reactions of cyclohexane on both metals. The subject of the present work is to measure deuterium exchange in cyclohexane accompanied by other catalytic reactions such as dehydrogenation and hydrogenolysis in a wide temperature range.

EXPERIMENTAL METHODS

All experiments were carried out in a circulating apparatus (*7*). An AEI MS 10 C2 mass spectrometer was directly connected to this apparatus by a capillary leak and in this way the concentration of both deuterated species and reaction products could be continuously monitored during reaction. Corrections were made for naturally occurring carbon-13 and deuterium, fragmentation on a statistical basis, and time elapsed during the determination of different species. All calculations were carried out by using ICT 1905 and TPA/i computers.

The preparation of platinum black and nickel powder catalysts used has been given elsewhere (*1,4*). Surface areas for

nickel and platinum were 6.3 and 3.4 $m^2 g^{-1}$, respectively, as measured by the BET method. Deuterium gas was passed through a heated palladium thimble and chromatographic grade cyclohexane was supplied by Merck. Usually a 10:1 deuterium–cyclohexane mixture (total pressure 100 Torr) and 0.154 g Ni or 0.3 g Pt were used in the experiments. Deuterium exchange is characterized by light cyclohexane conversion. The term consumption is used for reaction of cyclohexane, regardless of whether it is a deuterated or light molecule, either by dehydrogenation or hydrogenolysis. Initial rates both for exchange and consumption were calculated and are denoted by w_0 (mol s^{-1} m^{-2}).

RESULTS

Preliminary experiments established that deactivation of a catalyst (as represented by the change in k_ϕ) is characterized by a decrease of the cyclohexane-d_{12} to cyclohexane-d_1 ratio (*8*). During an experimental run this ratio decreases to a lesser extent on platinum than on nickel, as shown in Fig. 1. In addition, fresh catalysts can be poisoned more quickly during the run than the used ones (see, e.g., Pt on which k_ϕ drops after a number of experiments at the same temperature due to deactivation).

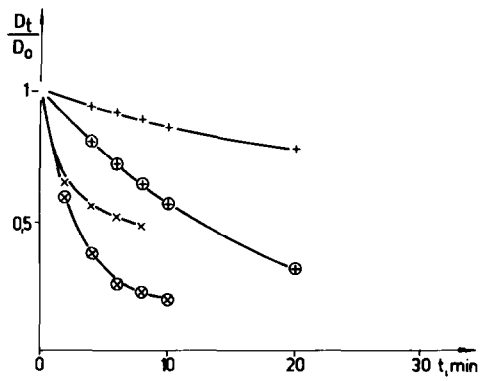


FIG. 1. Comparison of poisoning effect on Ni and Pt catalysts in cyclohexane exchange. Symbols: (+) Pt, $T = 105°C$, $k_\phi = 0.26$; (⊕) Ni, $T = 230°C$, $k_\phi = 0.18$; (×) Pt, $T = 105°C$, $k_\phi = 149$; (⊗) Ni, $T = 115°C$, $k_\phi = 8.3$; $D_t = ([d_{12}]/[d_1])_{t=t_i}$ and $D_0 = ([d_{12}]/[d_1])_{t=0}$.

In order to obtain consistent kinetic measurements all runs were carried out on a catalyst previously aged. In this way further self-poisoning between the runs disturbing the kinetic data were minimized.

Deuterium exchange was carried out in the temperature range of 30–315°C as shown in Fig. 2. The rate data suggest that the exchange reaction of cyclohexane can be divided into three distinctive temperature zones: 30–100°C, 100–200°C and above 200°C. In the latter case exchange is accompanied by consumption of cyclohexane. For the sake of simplicity these three parts are considered separately.

i. In the low temperature range the apparent activation energies of exchange on both catalysts are similar (i.e., 79.4 and 67 kJ mol^{-1} for Pt and Ni, respectively) which is in agreement with earlier results (*8,9*), but there is a difference of about one order of magnitude in the rate of exchange. In Fig. 3 (lower curves) the distributions determined on both catalysts in the low temperature range are compared. On nickel the distribution is shifted towards highly deuterated species in agreement with our earlier results (*2,3*). On platinum, however, cyclohexane-d_1 predominates and the formation of perdeuterated compounds occurs only at higher temperatures. No maximum was found at cyclohexane-d_6 even at low temperatures.

ii. In the temperature range between 100 and 200°C only deuterium exchange occurs. As shown in Fig. 2 exchange activity on nickel decreased by two orders of magnitude due to poisoning, whereas on platinum only a decrease in the apparent activation energy of exchange can be measured. On nickel the apparent energy of activation for deuterium exchange remained nearly as it was at lower tempera-

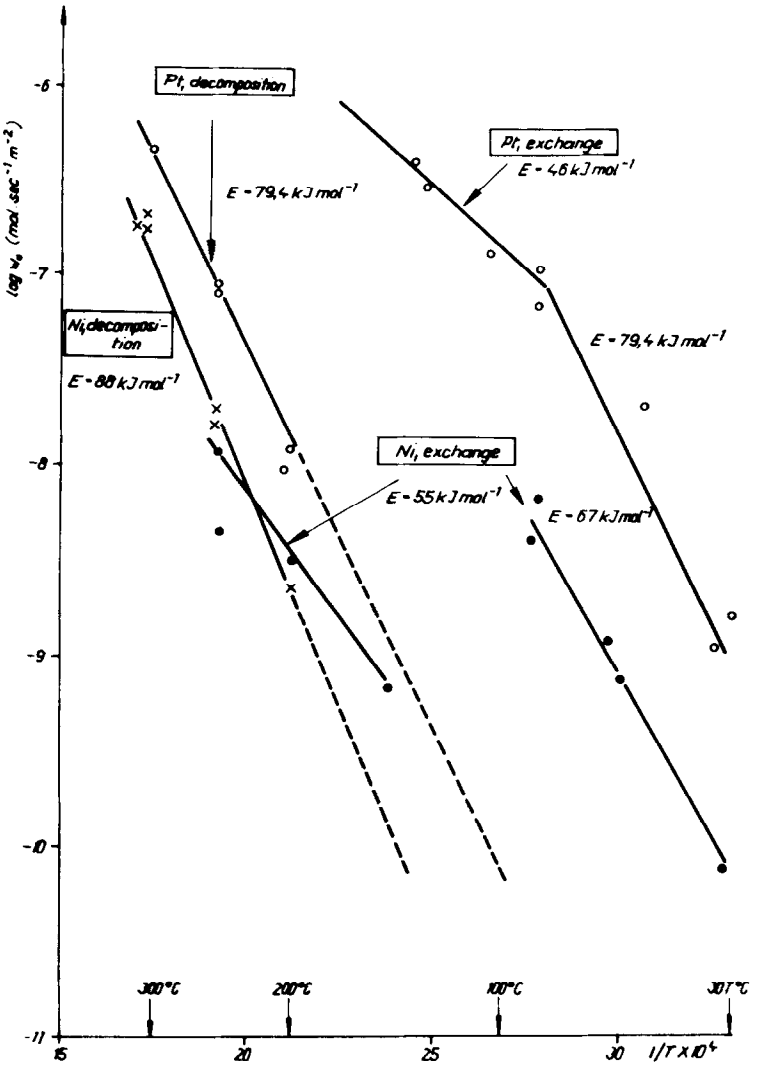


FIG. 2. Arrhenius plots for deuterium exchange and decomposition of cyclohexane.

ture. It is characteristic of this temperature range that the formation of perdeuterated compounds due to the relative contribution of multiple exchange is increased as shown in the upper part of Fig. 3.

iii. The temperature range above 200°C is the most interesting one. Figure 2 shows the consumption of cyclohexane in the presence of hydrogen on platinum and on nickel. Here the main reaction is the dehydrogenation of cyclohexane to benzene on both catalysts. The apparent energies of activation for consumption are nearly the same (79.4 and 88 kJ mol^{-1} on Pt and Ni, respectively) and the reaction is five times faster on platinum than on nickel.

Above 200°C the rate of exchange is very fast and its measurement becomes difficult. Still it seems interesting from the point of view of the mechanism to measure simultaneously the exchange and the consumption of cyclohexane. For this purpose

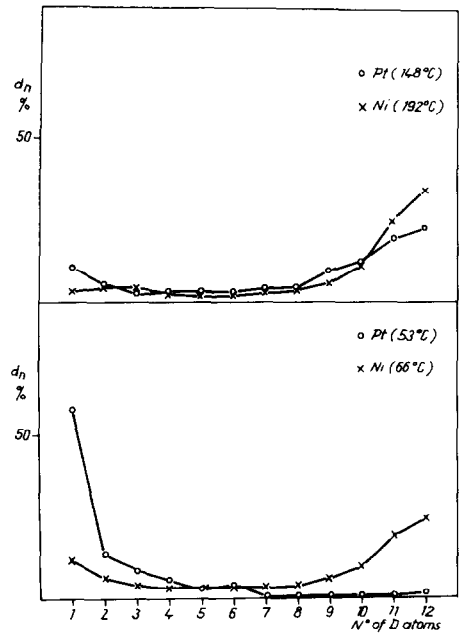


FIG. 3. Characteristic initial distribution of deuterated isomers.

the reaction was carried out in the presence of deuterium at 300°C. In Fig. 4 the uncorrected mass spectra observed are presented. On platinum peaks which are characteristic of deuterated benzene are obtained as a result of dehydrogenation. This is also true on nickel; however, peaks also appear in the mass range of $m/e =$ 96–100 owing to the formation of deuterated *n*-hexane.

After considering the pattern of deuterated peaks in cyclohexane we were tempted to assume that such a pattern was the result of desorption of cyclohexane species which had achieved a local equilibrium on the surface due to a fast exchange. The extent of equilibrium depends only on the parameters ϕ_{equ} as defined by the following equation:

$$\phi_{equ} = 1200 \times \frac{[D]_a}{[D]_a + 12 \times [CH]_a}, \qquad (1)$$

where $[D]_a$ and $[CH]_a$ are the surface concentrations of deuterium and cyclohexane, respectively.

Furthermore, if adsorbed cyclohexane species containing deuterium atoms in equilibrium quantity can be converted into benzene by losing six hydrogen atoms, then benzene must also contain deuterium atoms in equilibrium distribution. In this case ϕ_B is equal to $\phi_{CH}/2$ where ϕ is defined as $\Sigma_{x=1}^{n} x d_x$ (where x is the number of deuterium atoms in the molecule and d_x is the amount of the species containing x deuterium atoms).

Since $[D]_a$ and $[CH]_a$ are not known a semiempirical method was developed to separate the spectra of cyclohexane and benzene based on the above-mentioned assumption. This procedure is given in the Appendix. In Fig. 5 the experimental distributions of cyclohexane, benzene and *n*-hexane are compared to those calculated by using the pattern in paragraph (iii) of the Appendix and is referred to as the theoretical distribution.

The agreement for benzene is extremely good both for nickel and platinum. As far as the higher mass range is concerned the agreement on nickel is adequate. Here the formation of deuterated cyclohexane was omitted and only deuterated *n*-hexane was taken into account in the calculation.[1]

On platinum the agreement between the theoretical and experimental cyclohexane spectra is rather poor. For this range only the shape of the distribution of deuterated species and the benzene spectrum point to surface equilibrium.

In Fig. 5 it is clearly shown that large amounts of light cyclohexane as a parent molecule coexist with deuterated species. By considering this fact together with surface equilibrium it is obvious that at this

[1] Recently we have proven by using a GC-MS apparatus (*19*) that this assumption is valid since cyclohexane is not desorbed in highly deuterated form.

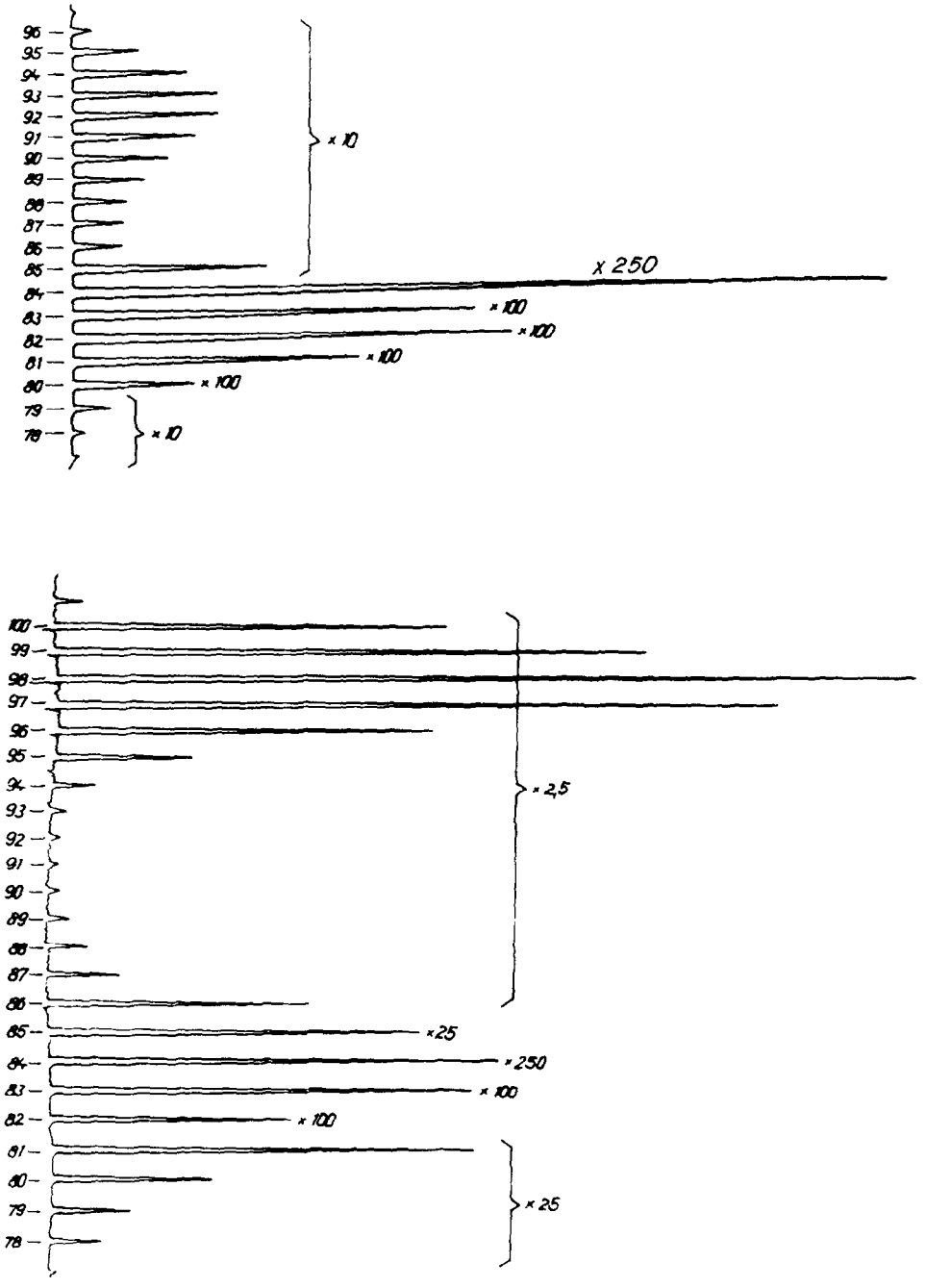


FIG. 4. Uncorrected spectra of deuterated cyclohexane at 300°C (upper spectrum, Pt; lower spectrum, Ni).

temperature adsorption–desorption equilibrium for the whole system does not occur. This statement is valid for the run as is illustrated in Fig. 6. Here the shape of distribution of benzene and cyclohexane remains unchanged during the run until the light cyclohexane has completely disappeared.

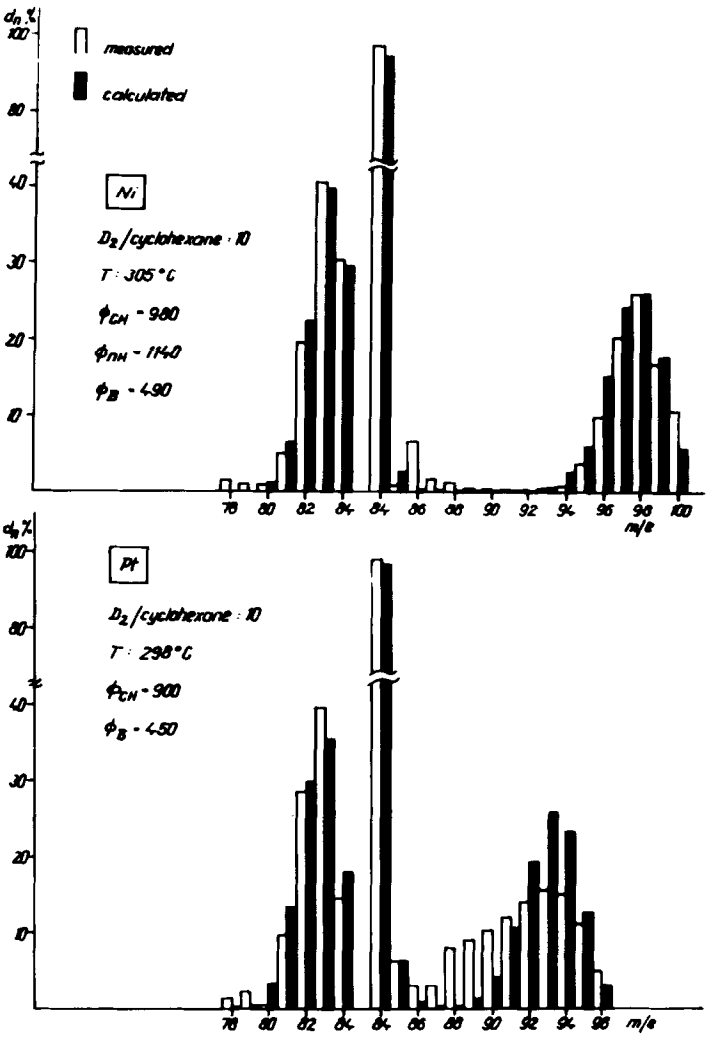
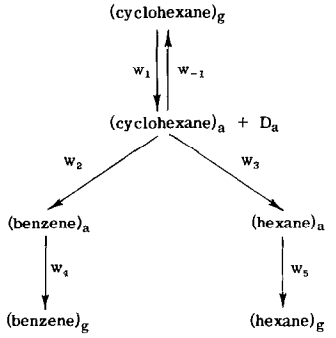


FIG. 5. Comparison of theoretical and measured spectra of deuterated cyclohexane and benzene.

DISCUSSION

The experimental results may be explained in the following way:



where the subscripts a and g refer to the species on the surface and in the gas phase, respectively.

Some explanation is needed to understand this scheme. First, due to competitive adsorption of hydrogen and hydrocarbon (*16*) a great part of the surface is covered by deuterium atoms. Second, cyclohexane is not adsorbed in molecular form but via dissociation, e.g., hydrogen content $(\text{cyclohexane})_g > (\text{cyclohexane})_a$, and the degree of dissociation depends upon the nature of the catalyst.

At low temperatures no particular dif-

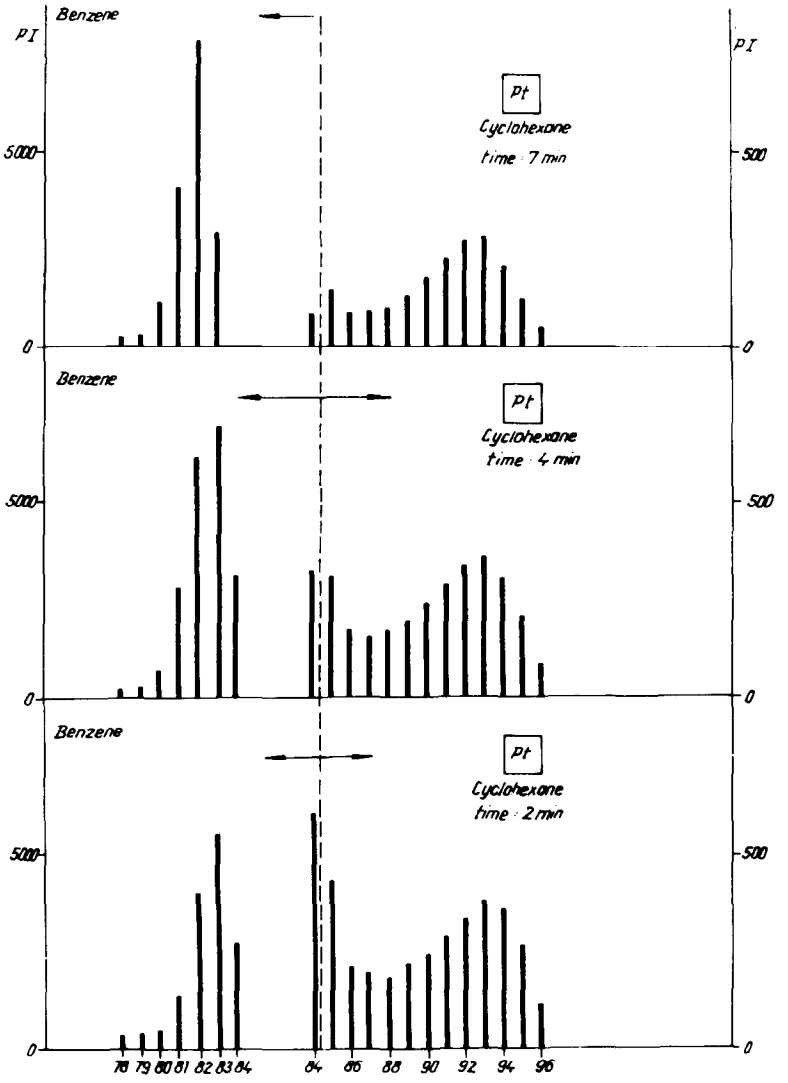


FIG. 6. The change of one measured distribution of deuterated cyclohexane and benzene as a function of time.

ferences can be seen compared to earlier investigations on films (*9*), powder (*8*) and supported metal catalysts (*10–14*). No maximum was found at cyclohexane-d_6 as in previous experiments (*8*) which means that this is not a main characteristic of the exchange.

In this temperature range $w_1 = w_{-1}$, w_2 and $w_3 = 0$ which means that adsorption–desorption equilibrium is maintained for cyclohexane. The difference in exchange activity between platinum and nickel may be due to the fact that even at low temperatures poisoning at the first exposure of the gas mixture to nickel destroys a part of the active centers. Further poisoning does not occur except at higher temperature. On platinum a treatment of higher temperature is needed for a considerable loss of activity, as was shown earlier (*1*).

At low temperature the rate of exchange is possibly controlled by the rate of cyclo-

hexane adsorption (w_1) similar to the mechanism of other hydrocarbons based on the kinetic isotope effect (*15,16*).

At higher temperature on platinum the deuterium exchange is still not poisoned and the decrease in the activation energy may be the result of a change in the reaction mechanism, such as a different rate controlling step. On nickel the decomposition of cyclohexane produces further blockage of the active sites resulting in a two order loss of exchange activity. The poisoning of exchange reactions on platinum and nickel at these temperatures is in excellent agreement with the data given by Kempling and Whan (*17*) for other hydrocarbons.

The most interesting temperature range lies above 200°C where we observe solely dehydrogenation on platinum, and dehydrogenation and hydrogenolysis on nickel. According to the literature (*11,12*) the rate of exchange on nickel decreases once dehydrogenation commences. On the basis of our experiments carried out in the presence of deuterium it can be established that this is indeed the case only if the exchange products are considered to be the deuterated cyclohexane molecules that return to the gas phase in their original form. However, the distributions of the deuterium atoms in cyclohexane and in benzene are similar on platinum and on nickel (in the latter case deuterated cyclohexane is not desorbed at all, but only as *n*-hexane) therefore all products should be considered as carriers for the cyclohexane exchanged.

The results at high temperature may therefore be explained in the following way. Both the adsorption of cyclohexane and surface exchange between $(\text{cyclohexane})_a$ and D_a are also fast. Isotope equilibrium for the deuterated cyclohexane species is therefore quickly attained on the surface.

Now, cyclohexane in isotope equilibrium leaves the surface either by slow desorption (w_{-1}) or as a consumption product also in a slow process (w_2 and w_3). w_1 is greater than each of the other steps represented by w_{-1}, w_2 and w_3. Since the adsorption and surface exchange are fast compared to the rates by which the deuterated species can be removed from the surface and since only a small part of the molecules in the gas phase can be accommodated on the surface, a considerable amount of light cyclohexane coexists with the deuterated cyclohexane in the gas phase. The light molecules can be further adsorbed on the surface only if sites are vacant. Slow desorption causes a long residence time for the adsorbed cyclohexane and therefore the exchange achieves equilibrium.

The difference between the platinum and nickel can be a consequence of surface intermediates. We have mentioned that nickel has an ability to convert adsorbed hydrocarbons into strongly bonded species, whereas on platinum the weak–strong transformation is hindered (*1*). Since strongly bonded species are responsible not only for poisoning but also hydrogenolysis it is not surprising that on nickel hydrogenolysis occurs simultaneously with exchange poisoning at higher temperatures. On platinum, however, the sole formation of benzene can be explained by the predominance of less dehydrogenated species on the surface as was proven earlier (*18*). These investigations give new support to our explanation of the different behavior of platinum and nickel.

APPENDIX

Peak separation of cyclohexane-d_0 and benzene-d_6 which appear at $m/e = 84$ can be carried out in the following way:

i. A correction for the naturally occurring carbon-13 in the range of m/e 78–96 is made.

ii. Fragmentation correction is applied for the range of m/e 96–85. ($f_{-1} = 0.06$).

iii. Since the mass spectrum at the high

mass range of deuterated cyclohexane is not disturbed by other compounds, the place of maximum as well as the ratio of the intensity of maximum to those one mass unit up and down is characteristic of the equilibrium distribution. By applying the relationship between ϕ_{equ} and the distribution of deuterated isomers (d_x) according to equation

$$d_x = \frac{n!}{x!(n-x)!} \cdot \left(\frac{\phi}{100\,n}\right)^x \cdot \left(1 - \frac{\phi}{100\,n}\right)^{n-x} \quad (1)$$

(where n is the number of hydrogen atoms in the molecules) one can find a ϕ_{CH} value at which the theoretical distribution adequately fits the experimental one.

iv. If hydrogen loss takes place in a statistical way then $\phi_B = \phi_{CH}/2$.

v. Since the peak at m/e 83 is effected only by cyclohexane-d_0 the following equation can be written:

$$I_{84}\,(\text{total}) = I_{84}\,(\text{benzene-}d_6) + I_{84}\,(\text{cyclohexane-}d_0), \quad (2)$$

$$I_{83}\,(\text{total}) = I_{83}\,(\text{benzene-}d_5) + f_{-1} \cdot I_{84}\,(\text{cyclohexane-}d_0). \quad (3)$$

Once ϕ_B is known the theoretical equilibrium distribution of deuterated benzene can be calculated by using Eq. (1) and the ratio of peak intensities of m/e 84 and 83 can be determined from the distribution.

Thus

$$R = \frac{I_{84}\,(\text{calc})}{I_{83}\,(\text{calc})} = \frac{I_{84}\,(\text{benzene-}d_6)}{I_{83}\,(\text{benzene-}d_5)}$$

by using the expressions from Eqs. (2) and (3)

$$I_{84}\,(\text{benzene-}d_6) = \frac{R \cdot [I_{83}\,(\text{total}) - f_{-1} \cdot I_{84}\,(\text{total})]}{1 - R \cdot f_{-1}}. \quad (4)$$

Once benzene-d_6 and benzene-d_5 are known, the fragmentation correction for deuterated benzene can be applied and thus the distribution of benzene isomers formed from cyclohexane can be calculated.

The procedure for Ni (on which n-hexane is formed) is similar but the distribution is calculated for n-hexane. From ϕ_{nH}, ϕ_{CH} is derived by multiplying by 12/14 which is the hydrogen ratio in the molecules.

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