RICE UNIVERSITY

CATALYTIC ALUMINA: AN ISOTOPIC TRACER
STUDY OF ACTIVE SITES FOR DEUTERIUM
EXCHANGE WITH BENZENE

by

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ABSTRACT

Catalytic Alumina: An Isotopic Tracer Study of Active Sites for Deuterium Exchange with Benzene

by Peter C. Saunders

Catalytic exchange of deuterium with benzene was used as a test reaction to investigate both the number and chemical nature of active sites on alumina. Previous work has involved deuterium exchange with paraffins and olefins on alumina. The results of this work are similar to those reported for the earlier studies.

In comparison with hydrogen exchange with perdeuteriobenzene, a primary kinetic isotope effect of 1.8 was found at 20°. However, redistribution of "hydrogen" atoms among the benzene isotopes was much faster than either of the exchange reactions. The addition of a small amount of benzene reduced the rate of the usually fast hydrogen-deuterium exchange by 98%. The strong, dissociative adsorption of benzene to the exclusion of hydrogen is a possible explanation for these results.

After catalyst pretreatment at 530°, "titration" using carbon dioxide as a poison of catalytic activity indicated an active site density of about 15 x 10^{12}/cm^2 for both the exchange and redistribution reaction. This number is close to that necessary to poison hydrogen-deuterium exchange, which indicates that all three reactions occur on the same or on closely related sites. Because Cl^14O_2
poisoning demonstrated that other sites besides those active for exchange also adsorb carbon dioxide, the above active site density is only an upper bound.

Poisoning with other materials had only a slight effect, which again may indicate that benzene was so strongly adsorbed that it excluded other molecules from the catalyst surface. The similarity of the exchange reaction over a deuterated catalyst ruled out the possibility of exchange with a majority of catalyst hydroxyl groups.
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<td>cm</td>
<td>Centimeters</td>
</tr>
<tr>
<td>cc</td>
<td>Cubic centimeters</td>
</tr>
<tr>
<td>cm²</td>
<td>square centimeters</td>
</tr>
<tr>
<td>ev</td>
<td>electrol volts</td>
</tr>
<tr>
<td>ft.</td>
<td>feet</td>
</tr>
<tr>
<td>g</td>
<td>grams</td>
</tr>
<tr>
<td>in.</td>
<td>inches</td>
</tr>
<tr>
<td>I.D.</td>
<td>inside diameter</td>
</tr>
<tr>
<td>kcal</td>
<td>kilocalories</td>
</tr>
<tr>
<td>c</td>
<td>micro-curieles</td>
</tr>
<tr>
<td>min.</td>
<td>minute</td>
</tr>
<tr>
<td>mm</td>
<td>millimeters</td>
</tr>
<tr>
<td>mole</td>
<td>gram molecular weight</td>
</tr>
<tr>
<td>m²</td>
<td>square meters</td>
</tr>
<tr>
<td>°</td>
<td>degrees Centigrade</td>
</tr>
<tr>
<td>sec.</td>
<td>seconds</td>
</tr>
<tr>
<td>$</td>
<td>standard taper</td>
</tr>
<tr>
<td>T</td>
<td>temperature, degrees Kelvin</td>
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<td>v</td>
<td>volts</td>
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<td>$C_n^H_m$</td>
<td>hydrocarbon molecule with $n$ carbon atoms and $m$ hydrogen atoms</td>
</tr>
<tr>
<td>$d_i$</td>
<td>fraction of the total hydrocarbon present as the isotopic species containing $i$ deuterium atoms</td>
</tr>
<tr>
<td>$d_0$</td>
<td>fraction of the total hydrocarbon present as the isotopic species containing zero deuterium atoms</td>
</tr>
<tr>
<td>$\frac{d}{dt}$</td>
<td>derivative with respect to time</td>
</tr>
<tr>
<td>$F_{HD}$</td>
<td>fraction of HD molecules in a $H_2$-$D_2$ mixture</td>
</tr>
<tr>
<td>$F_{HD}$</td>
<td>equilibrium value of $F_{HD}$</td>
</tr>
<tr>
<td>$F_{HD}$</td>
<td>initial value of $F_{HD}$</td>
</tr>
<tr>
<td>$i$</td>
<td>number of deuterium atoms in a hydrocarbon molecule</td>
</tr>
<tr>
<td>$k_i$</td>
<td>equilibrium constant for redistribution</td>
</tr>
<tr>
<td>$k_o$</td>
<td>rate constant equivalent to the initial rate of disappearance of the light hydrocarbon</td>
</tr>
<tr>
<td>$k_\phi$</td>
<td>rate constant for $D_2$-hydrocarbon exchange equivalent to the fraction of deuterium atoms entering a molecule per minute.</td>
</tr>
<tr>
<td>$k_\phi'$</td>
<td>rate constant for $H_2$-perdeuteriohydrocarbon exchange equivalent to the fraction of hydrogen atoms entering a molecule per minute</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>$k_u$</td>
<td>rate constant for redistribution per minute in arbitrary concentration units</td>
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<td>$k_{HD}$</td>
<td>rate constant for H$_2$-D$_2$ exchange per minute in arbitrary concentration units</td>
</tr>
<tr>
<td>$k_H$</td>
<td>represents rate constant for D$_2$-hydrocarbon exchange</td>
</tr>
<tr>
<td>$k_D$</td>
<td>represents rate constant for H$_2$-perdeuterio-hydrocarbon exchange</td>
</tr>
<tr>
<td>$\ln$</td>
<td>logarithm to the base $e$</td>
</tr>
<tr>
<td>$m$</td>
<td>number of hydrogen atoms in an undeuterated hydrocarbon molecule</td>
</tr>
<tr>
<td>$m/e$</td>
<td>mass number: ion mass (atomic mass units)/ion charge (electrons removed or added)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>reaction multiplicity $k_\phi/k_0$</td>
</tr>
<tr>
<td>$N$</td>
<td>total number of &quot;hydrogen&quot; atoms in a hydrocarbon molecule</td>
</tr>
<tr>
<td>$n$</td>
<td>number of carbon atoms in a hydrocarbon molecule</td>
</tr>
<tr>
<td>$t$</td>
<td>time, minutes</td>
</tr>
<tr>
<td>torr</td>
<td>millimeters of mercury</td>
</tr>
<tr>
<td>$u$</td>
<td>function for redistribution reactions (of the same nature as $\phi = \sum_{i=0}^{6} (6-i)d_4$)</td>
</tr>
<tr>
<td>$u_\infty$</td>
<td>equilibrium value of $u$</td>
</tr>
<tr>
<td>$u_0$</td>
<td>initial value of $u$</td>
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$\xi$
GREEK ALPHABET

$\phi$  total amount of deuterium in the hydrocarbon

$$= \sum_{i=0}^{i=N} id_i$$

$\phi_\infty$  equilibrium value of $\phi$

$\phi_0$  initial value of $\phi$

$\phi'$  total amount of hydrogen in the perdeuterio-

hydrocarbon  $$= \sum_{i=0}^{i=N} (N-i)d_i$$

$\phi'_\infty$  equilibrium value of $\phi'$

$\phi'_0$  initial value of $\phi'$

$c$  mean deuterium fraction $= \phi/N$
I. INTRODUCTION

By definition, catalysts are employed to modify the rate and direction of chemical reactions and because of this they have proven useful in many industrial applications. A number of investigations have been undertaken to provide some knowledge of how catalysts work. This work on catalytic aluminas is an extension of these investigations.

Heterogeneous catalysts, particularly solids, have the advantage of being a separable phase, and are widely used. For example, aluminas are among the most common dehydration catalysts and noble metals supported on alumina are used extensively for saturation of hydrocarbons. The catalytic activity of the solids can be attributed, in part, to their extremely large surface areas. It is desirable, therefore, to have some knowledge of the active sites on the surface of the catalyst, and of how these sites are formed. To this end, an investigation of the number and chemical nature of the active sites on alumina is the goal of this work.

Exchange reactions are useful in kinetic studies because the reaction which occurs only effects the isotopic distribution in the reaction mixture; the partial pressure of the exchange reactant always remains the same. Previous investigations on alumina have included exchange reactions employing paraffins and olefins. Therefore, the use of aromatic compounds is a logical extension.

Because deuterium exchange with benzene is one of the simpler systems to study, it is useful, as a test reaction, for this investigation. Together with hydrogen-perdeuterio-benzene exchange and benzene-
perdeuteriobenzene redistribution, the test reaction provided information about the chemical nature of the active sites. Poisoning of the catalyst with carbon dioxide as reflected in the benzene test reaction allowed "titration" of the number of active sites. Thus, through the use of these reactions along with a few related experiments, the goals of this work were achieved.
II. PREVIOUS WORK

Exchange reactions with deuterium have been used by a number of investigators. This section is a review of their work leading up to the present investigation using deuterium exchange with benzene.

II-1 Exchange Reactions

Deuterium exchange with benzene is a specific example of catalytic exchange of deuterium with a hydrocarbon. For the general case, consider a typical hydrocarbon, \( C_nH_m \), and deuterium, \( D_2 \). The reaction of these two species yields:

\[
C_nH_m + D_2 \rightarrow C_{n-1}H_mD + C_{n-2}H_mD_2 + \ldots + C_mH_mD_{n-1} + C_mD_n
\]

For this reaction two kinds of equilibria exist. The first is the equilibrium established between the total amount of deuterium in the "hydrogen" and in the hydrocarbon. In the example, the "hydrogen" consists of that portion of the gas phase containing \( D_2 \) (and \( H_2 \) and \( HD \)) molecules; however, the deuterating agent does not have to be molecular hydrogen. The second kind of equilibrium is established between the relative amounts of the different isotopic species of hydrocarbon.

These redistribution equilibria result from the following reaction scheme:

\[
\begin{align*}
C_nH_m + C_nH_{m-2}D_2 & \rightarrow 2C_{n-1}H_mD_2 & k_1 \\
C_{n-1}H_mD + C_nH_mD_3 & \rightarrow 2C_{n-2}H_mD_2 & k_2 \\
C_{n-2}H_mD_2 & \rightarrow 2C_{n}HD_{m-1} & k_{m-1}
\end{align*}
\]

\[ (1) \]
The equilibrium constants, $k_i$, calculated by classical theory are given by the equation

$$ k_i = \binom{i}{m} \quad \binom{i-1}{m} \binom{i+1}{m} $$

(2)

where $\binom{i}{m}$ represents the number of ways of selecting $i$ objects from a group of $m$ identical objects. These constants represent a binomial distribution of deuterium over the hydrocarbon molecules. Where the equilibrium constants have been measured for reactions of the above type, the values obtained were fairly close to the binomial distribution(1).

Two types of processes occur in exchange reactions, leading to two types of isotopic distribution. Both processes, however, must eventually yield the same equilibrium distribution.

One type of process is stepwise exchange in which only one hydrogen atom of a hydrocarbon molecule is replaced by a deuterium atom with each reaction on the surface of a catalyst. Stepwise exchange is characterized by a distribution of the isotopic species of the hydrocarbon which is binomial at each instant of the reaction. However, this is based on the assumption that each of the isotopic species of the reactant are in equilibrium and, that all of the hydrogen atoms are equally susceptible to exchange.

On the other hand, multiple exchange is that type of reaction in which more than one deuterium atom may be introduced into the hydrocarbon molecule with each interaction on the catalyst surface. In this case, the isotopic distribution is not binomial, although a binomial distribution is reached at equilibrium.
Several mechanisms have been proposed to explain the reactions. For stepwise exchange three possibilities exist. The hydrocarbon might not be chemisorbed except during the actual reaction with a chemisorbed deuterium. Or, the hydrocarbon might be dissociatively adsorbed producing radicles of the type, \( C_nH_{m-1} \). Or finally, the process might be associative producing species of the type, \( C_nH_{m+1} \). Experimental evidence suggests the second mechanism applies to saturated hydrocarbons while the third applies to unsaturated hydrocarbons (1).

Multiple exchange must, necessarily, be more complicated than stepwise. However, similar processes can be proposed. One is a reaction in which the hydrocarbon undergoes chemisorption only during its reaction with two or more chemisorbed deuterium atoms. Or, the formation of a single type of either a dissociated or associated species occurs through the loss or gain of at least two hydrogens. And lastly, it is possible to have the formation of several types of adsorbed species of different states of hydrogenation with exchange resulting from interconversion of these on the surface of the catalyst.

II-2 Methods of Study

Hydrogen isotopes are extremely useful in catalytic studies. Exchange reactions of hydrocarbons with deuterium can be analyzed using various methods of detecting the difference between hydrogen and deuterium. Early techniques employed, infrared spectroscopy, measurement of the dilution of deuterium by hydrogen using thermal
conductivity and the determination by combustion of the total deuterium in the hydrocarbon.

With the development of the mass spectrometer as a tool to follow exchange reactions, the relative amounts of the different isotopic species could be calculated. Also, for the first time it could be determined whether only one or more than one deuterium entered a hydrocarbon with each reaction on the catalyst surface. The technique has been expanded by using reactions involving undeuterated hydrocarbons, perdeuterio-hydrocarbons, or mixtures of the two.

The use of radioactive carbon-14 tracers allows the study of the reaction from the point of view of the carbon atom. This is more important, though, when isomerization or saturation is also occurring with exchange.

Considerable work has been done using direct methods of study of the catalyst surface. These methods include infrared, ESR, and others.

II-3 Summary of Previous Work

Some of the earlier work in catalysis involving exchange reactions was concerned with catalysis on metals in the form of films or of metal atoms on a support. Kemball (1) presented a review of much of this work in his paper on catalytic exchange of deuterium with hydrocarbons. He also discussed several unstable surface intermediates which may form during the exchange.
For example, the interconversion of monoadsorbed ethane and 1,2 diadsorbed ethane can explain the exchange of ethane on several metals (2). This type of exchange is referred to as the $\alpha\beta$-process (attachment on adjacent carbon atoms). $\alpha\beta$-exchange is also important in reactions of larger hydrocarbons such as propane and isobutane on rhodium films (3) or propane on several supported catalysts (4). At a higher temperature than that necessary for the $\alpha\beta$-process, $\alpha\sigma$-exchange (two point attachment on one carbon atom) can explain the exchange of methane (5) and neopentane (6) on several metals. Neopentane exchange on rhodium films (6) demonstrates that an $\alpha\gamma$-process (1,3 disorbed species) is also possible.

Anderson and Kemball (7) found that all of the hydrogens of cyclopentane and cyclohexane were able to exchange initially with deuterium on several metals. Burwell, Shim, and Rowlinson (8) found that optically active (+) 3 methylhexane racemized during the exchange process on several metals. Neither of these two reactions can be explained solely on the basis of the $\alpha\beta$-process. However, Gault, Rooney, and Kemball (9) presented evidence to show that a $\pi$-bonded intermediate could be a possible explanation for these and other exchange reactions. This intermediate would involve attachments at more than two consecutive carbon atoms. If a change to $sp^2$ hybridization occurred, carbon-hydrogen and carbon-carbon bonds would become planar with $p$ orbitals perpendicular to the surface forming $\pi$-bonds. Geometrical considerations indicate the bonding involves only one surface atom.
The possibility that isomerization of olefins could occur through a \( \Pi \)-bonded intermediate was also suggested by Gault et al. Results given by Crawford and Kemball (10) support their hypothesis that benzene can be \( \Pi \)-bonded to nickel surfaces in catalytic reactions.

Harper, Siegal, and Kemball (11) studied alkylbenzene exchange with deuterium on metal films. They emphasized the difference between the mechanisms of heterogeneous metal-catalyzed exchange and homogeneous acid-catalyzed exchange, and did not mention the concept of \( \Pi \)-bonding. They also pointed out the difference in the ease of exchange of various groups of hydrogen atoms on the ring and side chains.

Hightower and Kemball (12) used the reactions of p-xylene with deuterium to examine the role which supports play in determining the catalytic properties of platinum. In comparing their results for supported platinum with those for platinum films, they found that both types of catalysts exhibited similar rates at 100° for exchange of ring hydrogen. However, the films were much more active for exchange of the methyl hydrogen atoms and for deuteration.

They observed a difference in the reaction rates as the support was changed from gamma alumina to alpha alumina or silica. Some exchange activity of the gamma alumina alone was also found. But, they excluded direct catalysis of the exchange of the ring hydrogen atoms by the supports.

Larson and Hall (13) studied the exchange of CD\(_4\) (CH\(_4\)) with the OH (OD) groups of silica alumina and alumina catalysts. Based on their results, they suggested that the exchange reaction on alumina was
catalyzed by a small number \((3 \times 10^{12}/\text{cm}^2)\) of active sites and involved exchange with only about \(1\%\) \((3 \text{ to } 4 \times 10^{12}/\text{cm}^2)\) of the catalyst hydroxyl groups. The exchangeable hydrogen appeared to be located on specific sites.

\(\text{CH}_4\) and \(\text{CD}_4\) equilibrated rapidly at room temperature over the alumina catalyst. Carbon dioxide was found to poison this reaction. By desorbing various amounts of \(\text{CO}_2\) and then observing the poisoned reaction rate, the number of active sites was determined. And, because \(\text{CD}_4\) and \(\text{H}_2\) exchanged at the same rate as the \(\text{CD}_4\)-\(\text{CH}_4\) equilibration, it was suggested that the rate controlling step was probably the rupture of the \(\text{C-D}\) bond in \(\text{CD}_4\). The exchange of \(\text{D}_2\) with \(\text{CH}_4\) proceeded about \(1.8\) times faster than the \(\text{H}_2\)-\(\text{CD}_4\) exchange reaction.

Larson and Hall proposed that the small amount of hydrogen which exchanges on alumina between room temperature and \(135^\circ\) was located at sites where methane was dissociatively adsorbed. This adsorption was assumed to occur on an exposed metal ion resulting in an \(\text{Al-CH}_3\) species and an adjacent adsorbed \(\text{OH}\). Exchange took place if an \(\text{OD}\) group was also adjacent to the adsorbed pair (three-center mechanism).

More recent work in these areas has raised some doubt about the hydroxyl groups of alumina being sources of hydrogen. The exchange of surface hydroxyl groups of alumina with deuterium has been reported by several investigators. Temperatures of \(50-100^\circ\) or higher were needed to cause the replacement of surface hydrogen \((14, 15)\). Van Cauwelaert and Hall \((16)\) recently examined the exchange by circulating \(\text{D}_2\) over an alumina catalyst at various temperatures. No
exchange was detected at 0° and 65° even though an amount of hydrogen equivalent to 1% of the sites active for H₂-D₂ exchange could have been seen. The exchange became measurable at 100° and 150°. In contrast to this, H₂-D₂ exchange takes place readily at low temperatures (16, 17, 18) and is much faster than the D₂ exchange with the surface hydroxyl groups.

Van Cauwelaert and Hall measured the rates of H₂-D₂ exchange on alumina with a portion of the sites selectively poisoned with carbon dioxide. Only a small fraction of the alumina surface was active for the exchange reaction, which occurred on the sites selectively chemisorbing CO₂. For a pretreatment temperature of 500° and a reaction temperature of 0°, 16 x 10¹²CO₂/cm² were needed to completely poison the catalyst.

McCosh and Kemball (19) studied the exchange of benzene, toluene, and m-xylene with deuterium over an alumina catalyst, finding that hydrogen atoms in the ring positions of all three hydrocarbons reacted at the same rate. There were no appreciable directing effects due to the side groups, and their exchange was much less than ring exchange.

The activation energies for these reactions were constant at 6.0 kcal/mole and close to that for CH₄ exchange with D₂ (5.7kcal/mole) (13) and cyclopentene exchange with D₂ (5.9kcal/mole) (20). Because of this, McCosh and Kemball suggested that the exchange with hydrocarbons takes place with deuterium atoms which are present in the form of OD groups at special sites, and that the rate determining step is the conversion of OH to OD at these sites. Van Cauwelaert and Hall point
out that this suggestion does not explain the appreciable isotope effect found in the hydrocarbon exchange reactions \([k_H/k_D = 1.8\) for methane (13) and 2.8 for cyclopentene (20)], and that no exchange between catalyst OH groups and D\(_2\) could be detected below 65°. Also, because the CH\(_4\)–CD\(_4\) equilibration reaction and the H\(_2\)–D\(_2\) exchange reaction occur at room temperature and below, where less than 1% of the sites contain exchangeable hydroxyls, it appears unlikely that the three-center mechanism involving a hydroxyl proposed by Larson and Hall (13) accurately describes the reaction process.

Larson, Hightower, and Hall (21) demonstrated that hydrogen atoms in non-cyclic olefins and cyclopropane could be replaced at room temperature with deuterium by exchange with D\(_2\) over a "neutral" alumina catalyst. Neither saturation nor skeletal rearrangements occurred to an appreciable extent below 200°, although both double bond migration and cis-trans rotation did accompany the exchange.

Continuing in this area, Hightower and Hall found that only the vinyl hydrogen atoms in non-cyclic mono-olefins underwent exchange with D\(_2\) over alumina at temperatures below 100°. Furthermore, the vinyl hydrogen atoms in the terminal positions were more susceptible to exchange. Isomerization of the various butenes used as reactants did not involve exchange with D\(_2\). Hightower and Hall suggested that the process was not associative, but rather dissociative, involving the cleavage of a C–H or a C–D bond.

Hightower and Hall (20) extended their deuterium tracer studies to include cyclic olefins and found the same general reaction character-
istics as for non-cyclic olefins. In addition, the rigid configuration of the cyclic olefins allowed some of the geometric aspects of the reactions to be studied.

Again, only those hydrogen atoms which were originally vinyl, or could become vinyl by isomerization, underwent exchange. The predominant catalyst chemisorption evidently involved attraction of the double bond to the catalyst surface. Exchange occurred without isomerization, since nearly pure cyclopentene-\(d_2\) could be prepared; isomerization would have led to greater exchange, as was observed at higher temperatures.

As previously noted, the exchange seemed to occur by a dissociative process, probably involving "strained" Al-O-Al linkages (23) which could dissociate vinyl C-H bonds to form adsorbed olefinic species and OH groups (20, 22).

Poisoning experiments with carbon dioxide revealed only a small fraction of the total surface was active for the exchange between hydrocarbons and D\(_2\). \(14 \times 10^{12}\)CO\(_2\)/cm\(^2\) completely poisoned the exchange for an alumina catalyst pretreated at 530°. This figure can be compared with about \(2 \times 10^{15}\) lattice sites/cm\(^2\) and \(4 \times 10^{14}\)OH groups/cm\(^2\) (14).

The vinyl hydrogen atoms in cyclic olefins exchanged among the olefins themselves much more rapidly than they did with D\(_2\). Since olefins possibly exclude D\(_2\) from the catalyst surface (20) (as determined by poisoning), a simple interpretation is that sites effective for exchange hold several molecules either an olefin and D\(_2\) or two olefin molecules.
An interesting aspect of the work (20) resulted from the isomerization experiments. For reactions below 100° no double bond migration occurred unless the olefin contained a chain of three carbon atoms, including the double bond which appeared concave when viewed from outside the molecule. This indicated that the molecule may have to be "draped" over some surface atom. Although exchange and double bond migration are independent processes both may involve the same sites and have a common intermediate.
III. THE PRESENT INVESTIGATION

III-1 Alumina Catalysts

Of the several transition forms of alumina the high-surface area aluminas are the most interesting catalytically. Eta (η) and gamma (γ) alumina are the most common of these forms.

These transition aluminas are formed from the thermal decomposition of alumina hydrates. Eta alumina is one of the decomposition forms of Bayerite (beta-alumina trihydrate: Al₂O₃·3H₂O) and gamma alumina is one of the forms of Gibbsite (alpha-alumina trihydrate) (24). Both trihydrates lose water at low temperatures with the resulting formation of Böhmite (alpha-monohydrate). From the dehydration of the monohydrate, two different series of transition forms result, depending on the original trihydrate, with the eventual product being Alpha-alumina (corundum: Al₂O₃) (25). The transition aluminas are a nearly anhydrous form of Al₂O₃.

X-ray powder defraction measurements are used to identify the phases. However, it is difficult to distinguish between the eta and gamma forms; both are thought to have similar tetragonally deformed spinel lattices.

Observations have shown that the two aluminas vary in physical appearance and texture. More important, however, is the fact that gamma alumina was found by McIver, Tobin, and Barth (26) to contain 7 wt% water and eta alumina 4.5 wt% after removal of physically adsorbed water by evacuation at 25°. Assuming a cubic close packing
of oxide ions, they calculated that the water content of eta alumina could be accounted for in terms of surface hydroxyl groups. However, only 3.8% water could possibly be attributed to surface hydroxyl groups on gamma alumina. The excess water may exist as molecular water strongly bonded to the surface (26, 27).

As the aluminas are raised to high temperatures, dehydration occurs primarily through the condensation of surface hydroxyl groups (27). The development of surface acidity as measured by ammonia adsorption accompanies this dehydration. McIver et al. found the total acidity of both aluminas to be approximately the same, although the average strength of the acid sites of eta alumina was greater than that of gamma alumina. While the acidity of eta alumina increased continuously up to a dehydration temperature of 500°, gamma alumina did not develop appreciable acidity until 200-300°, corresponding to the elimination of the "excess" water. Also, for both aluminas, the total acidity reached a maximum and then decreased as additional water was lost. And as the dehydration temperature was increased the acid strength distribution of the two aluminas, relative to each other, changed.

Thus, the surface chemistry as well as the appearance of eta and gamma alumina is different. As reported by McIver et al., B. C. Lippins has described the surface of the eta alumina as being formed mainly by the 111 plane of the spinel while the surface of gamma alumina is formed by the 100 plane.
As suggested by some investigators (23), strain exists at a crystal surface. To minimize surface energy, metal oxide ions characteristically chemisorb water, usually to form hydroxyl ions. Upon dehydration of chemisorbed water, oxide ions, being more polarizable than metal cations, are preferentially exposed, forming a strained oxide surface which is abnormally reactive. On gamma alumina, the strain is concentrated at relatively few sites. Some of the surface hydroxyl groups are very difficult to remove, and it is apparently their removal which creates the strain sites (28).

To help explain these characteristics of the alumina surface, Peri developed a model for gamma alumina (29). His proposed surface included the two outer layers of an ionic crystal. For "ideal" dry alumina, the top layer contained only oxide ions regularly arranged over aluminum ions in octahedral sites of the next lower layer. This lower layer, representing the (100) plane of a cubic close-packed, oxide lattice (with aluminum ions located in all interstices), contained twice as many oxide ions as the top layer. Completely hydrolyzing the surface converts the top layer to a square lattice of hydroxyl ions located directly over the aluminum ions in the next lower layer.

Dehydration of the surface results in the combination of adjacent hydroxyl ions to form water which is desorbed. For each molecule of water formed, one oxide ion is left in the top layer and one aluminum ion is left in an incomplete octahedral site in the next lower layer.
Dehydration of the surface results in the combination of adjacent hydroxyl ions to form water which is desorbed. For each molecule of water formed, one oxide ion is left in the top layer and one aluminum ion is left in an incomplete octahedral site in the next lower layer.

To reduce the disorder which would result from a purely random process, Peri made the assumption that water must initially be removed in such a way that two (or more) oxide ions are not left on immediately adjacent sites and two (or more) immediately adjacent sites are not left vacant (i.e., local order must be preserved). The extent of this dehydration (67%) resulted in two domains in the oxide surface lattice (termed odd or even as determined from the numbering system).

Removal of the local order restriction allowed further dehydration leaving five types of isolated hydroxyl ions, differing in nearest neighbor configuration and covering about 10% of the surface. This dehydration created many oxide and vacancy defects (i.e., two or more oxide ions, or two or more vacancies on immediately adjoining sites), which lay in the boundaries between oxide domains. Allowing for surface mobility, further dehydration above 650° reduced the hydroxyl content below 9.6% and permitted the reduction of the number of defects.

Before any migration was allowed, five types of isolated hydroxyl groups were apparent. These had from zero to four nearest oxide neighbors. Peri, in an earlier paper (28), reported finding five
isolated hydroxyl bands in the infrared spectra of dry alumina and tentatively assigned these to the five types of hydroxyl sites.

On the basis of his model, Peri proposed (29) that the defect sites created in the boundaries between oxide domains could be high energy "strain" sites which are catalytically active. For example, triplet vacancies provide unusual exposure of aluminum ions in the layer below and should constitute strong "acid" sites. The vacancies characteristically adjoin pair or triplet oxide defects or B-site hydroxyl ions (approximately neutral hydroxyl ions with two oxide nearest neighbors).

To further examine the nature of the alumina surface, Peri studied the adsorption of carbon dioxide, hydrogen chloride, and ammonia. Ammonia reacted with the surface in several ways (30). At lower temperatures (50°), most ammonia was strongly adsorbed as such; however, some chemisorbed as NH$_2^-$ and hydroxyl ions. On heating, the molecular ammonia was either desorbed or reacted with the surface to form the hydroxyl and amide ions. The sites on which this occurred Peri called "acid-base" or "ion-pair" sites.

Chemisorption of carbon dioxide on silica alumina produced an infrared band in the 2360-2380cm$^{-1}$ region. Peri labeled the sites responsible for this band α-sites and identified them either as Al O$_2^-$-Al or Al O$^-$-Si, most probably the Al O$_2^-$-Al. These sites held hydrogen chloride more selectively than ammonia and formed OH groups with the chemisorption of the HCl, indicating a reactive oxide ion.
Strong adsorption of butene, benzene, and ammonia showed that the site contained an exposed metal ion.

Carbon dioxide adsorbed on gamma alumina in a manner similar to silica alumina, producing a $\alpha$-site band at 2370 cm$^{-1}$. A related band occurred near 1800 to 1870 cm$^{-1}$. The CO$_2$ on these sites remained linear, although it was no longer free to rotate. Peri suggested (32) that the adsorption energy resulted from ion-quadrupole interaction. This form of CO$_2$ could be removed easily by evacuation at 100° or by displacement with butene at room temperature. Peri estimated that from 5 to $8 \times 10^{12}$/cm$^2$ of these sites were present on his alumina surface and associated them with the isomerization of butene (31, 33).

A second type of CO$_2$ adsorption on alumina produced an infrared band at 3610 cm$^{-1}$, which apparently reflected strong interaction (probably bicarbonate formation) with a surface OH ion, and bands at 1350 and 1750 cm$^{-1}$ indicating carboxylate or carbonate structures (32). Because of the bicarbonate formation, it is evident that a substantial fraction of the sites have an adjacent hydroxyl ion. Lower site density involved in the H$_2$-D$_2$ exchange for alumina pretreated at 800° compared to alumina pretreated at 500° with its higher hydroxyl content conforms to this picture (16).

The independence of the various CO$_2$ adsorption sites on alumina was demonstrated by butene displacement of CO$_2$ (32). The bicarbonate OH band remained unaffected after displacement with butene of CO$_2$. 
on α-sites. Carbon dioxide poisoning of exchange reactions over alumina (13, 16) also presents evidence showing that several kinds of chemisorbed CO₂ exist.

Ammonia titrations have demonstrated that the α-sites represent only a fraction of a larger group of sites which are virtually equivalent for adsorption of NH₃. All of these have generally been termed "acid-base" sites. Although the α-sites are active for the chemisorption and polymerization of butene, they are not essential for catalytic activity (16, 20, 32).

III-2 Benzene Reaction

Several of the methods for the study of catalysts were discussed earlier (Section II-2). The exchange reaction of deuterium with benzene was used as a tool for the present work on the alumina catalyst. Other investigators have used catalytic exchange reactions of alkylbenzenes with deuterium on metal films (10, 11), supported platinum (12), chromium oxide gel (34), titania (35) and silica alumina and alumina (19). Because of the different types of carbon-hydrogen bonds present in the alkyl-benzenes, these compounds provide a useful reaction for study.

Benzene was chosen because of the simplicity of its exchange with deuterium, and because the D₂-benzene reaction was sufficient to provide the information about the alumina catalyst for which this study was undertaken. The reaction also formed a product
differing only in hydrogen-deuterium content, with no polymerization or other type of structural change occurring. The reaction products did not poison the catalyst for further reaction, and were easily analyzed without any fragmentation in the mass spectrometer.

Several different benzene exchange reactions were utilized.

One was the exchange of deuterium with benzene:

\[
D_2 + C_6H_6 \rightarrow C_6H_5D + C_6H_4D_2 + C_6H_3D_3 + C_6H_2D_4 + C_6HD_5 + C_6D_6
\]

A second was the "opposite" of the first, involving hydrogen exchange with perdeuteriobenzene (C_6D_6). A third was the redistribution reaction involving benzene and perdeuteriobenzene with no outside source of hydrogen or deuterium:

\[
C_6H_6 + C_6D_6 \rightarrow C_6H_5D + C_6H_4D_2 + C_6H_3D_3 + C_6H_2D_4 + C_6HD_5
\]

III-3 Methods of Study

The use of hydrogen isotopes allowed the benzene reaction products to be analyzed using a mass spectrometer. From the data produced by the mass spectrometer, the relative amount of each of the benzene isotopes in a sample was determined. By exchanging H_2 with C_6D_6 and comparing this with D_2C_6H_6 exchange, the isotope effect was examined. Benzene-perdeuteriobenzene redistribution afforded even more insight into the relation of the catalyst surface with the reactants.

In conjunction with the exchange reactions, poisoning of the catalyst surface with various amounts of CO_2, H_2O, NH_3, CO and NO was
used to gain some knowledge of the number and types of active sites. The reaction was allowed to continue long enough to establish an initial rate; then a measured amount of poison was injected into the reaction stream and a new rate determined. A capillary leak from the gas circulation stream to the mass spectrometer allowed continuous analysis of the reaction mixture. The adsorption of the poison on the catalyst was followed with radioactive carbon-14 tracers in the form of $^{14}C^0_2$.

In addition, hydrogen-deuterium exchange reactions were used to examine the interaction of the other exchange reactant, the hydrogen, with the alumina.

III-4 Treatment of the Data

The course of an exchange reaction of any molecule having $N$ equally exchangeable hydrogen atoms, provided that the influence of isotopes on the rate is ignored, is given by the first order equation:

$$\frac{d\phi}{dt} = k_{\phi} \left(1 - \frac{\phi}{\phi_\infty}\right)$$

(3)

where $\phi = \frac{N}{x_i \sum_i d_i}$ and $d_i$ is the fraction of the total hydrocarbon present as the isotopic species $C_{n-i}H_{m-i}D_i$ at time $t$. $k_{\phi}$ is a rate constant, equivalent to the number of deuterium atoms entering one molecule of the hydrocarbon in unit time at the start of the reaction, and $\phi_\infty$ is the equilibrium value of $\phi$. The integrated form of equation (3) is:

$$\ln(\phi_\infty - \phi) = \ln(\phi_\infty - \phi_0) - \frac{k_{\phi}t}{\phi_\infty}$$

(4)
These equations, developed by Kemball (1), are obeyed in a great variety of exchange reactions. A plot of $\ln(\phi_0 - \phi)$ versus time gives a straight line, providing that there is no time dependent poisoning and that all the $N$ hydrogen atoms are equally exchangeable.

The initial rate of disappearance, $k_0$, of the light hydrocarbon, $C_nH_m$, in fraction of molecules per unit time may be obtained from the equation:

$$\ln \left( d_0 \cdot d_0 \right) = \ln \left( 1 - d_0 \right) + \frac{k_0 t}{1 - d_0}$$

The ratio of the two rate constants, $M = \frac{k}{k_0}$, is the reaction "multiplicity" or mean number of hydrogen atoms replaced during a single residence of each molecule on the catalyst surface in the initial stages of the reaction. The mean deuterium fraction, $\sigma$, of the hydrocarbon at any stage in the reaction is given by:

$$\sigma = \frac{\phi}{N} = \frac{1}{N} \sum_{i=0}^{N} i d_i$$

These equations can be derived in several ways; however, the development of Bolder, Dallinga, and Kloosterziel (36) is straightforward and useful in helping to understand the reactions. Section A-1 of the Appendix contains a discussion of the development of these equations which take the following forms for the various aspects of this investigation:

Deuterium exchange with benzene:

$$\phi = \frac{6}{\sum_{i=0}^{2} i d_i}$$

$$\ln (\phi_\infty - \phi) = \ln (\phi_\infty - \phi_0) - \frac{k\phi t}{\phi_\infty}$$
Hydrogen exchange with perdeuteriobenzene:

\[ \phi' = \sum_{i=0}^{6} (6-i)d_{i} \]  

(8)

\[ \ln \left( \phi' - \phi' \right) = \ln \left( \phi' - \phi' \right) - \frac{k\phi't}{\phi'_{\infty}} \]  

(9)

Benzene-Perdeuteriobenzene redistribution:

\[ U = \sum_{i=0}^{4} id_{i} + \sum_{i=4}^{6} (6-i)d_{i} \]  

(10)

\[ \ln \left( U_{\infty} - U \right) = \ln \left( U_{\infty} - U_{0} \right) - k_{u}t \]  

(11)

Hydrogen-Deuterium exchange:

\[ \text{FHD} = \text{fraction of HD in the gas} \]

\[ \ln \left( \text{FHD}_{\infty} - \text{FHD} \right) = \ln \left( \text{FHD}_{\infty} - \text{FHD}_{0} \right) - 2k_{\text{HD}}t \]  

(12)

Section A-2 of the Appendix contains a complete discussion of the mathematical computations involved in the use of these equations.
IV. EXPERIMENTAL APPARATUS AND MATERIAL

IV-1 Experimental Apparatus

A. Vacuum System

All experiments were carried out in the circulation and vacuum system shown diagramatically in Figure 1. The circulation system itself consisted of a vertical catalyst and reaction tube (a), a mixing chamber (b), a small trap (c), an all-glass circulation pump (d), a provision for removing samples (e), a capillary leak into the mass spectrometer and a bypass (f), and a poison injection system (g). Also included in the total vacuum system were four, 5-liter, gas storage bulbs (h), a purification trap (i), a McLeod gauge (j), a manometer (k), and a 5-liter bulb for making large preparations of material (l).

The stopcocks used throughout the system were 2 and 4 mm vacuum bulb stopcocks, except where pressures greater than one atmosphere might be used. In this case, 2 and 4 mm high-vacuum spring loaded stopcocks were used. A minimal amount of Dow Corning high-vacuum silicon stopcock grease was used on all of the stopcocks.

A mercury diffusion pump was used with a Welch Duo-seal 1204 mechanical vacuum pump as the low vacuum source. The McLeod gauge employed, in direct comparison with a calibrated McLeod gauge, was found to measure a vacuum better than \(10^{-6}\) torr in noncondensables. "Sticking vacuum" is defined as that vacuum at which the mercury adheres briefly to the top of the closed capillary of the McLeod
Figure 1: Key

(a) Reaction Tube
(b) Mixing Chamber
(c) Small Trap (for freezing)
(d) All-glass Circulation Pump
(e) Stopcock for Removing Samples
(f) Capillary Leak to the Mass Spectrometer
(g) Poison Injection System
(h) 5-liter Storage Bulbs
(i) Inlet and Purification Trap
(j) McLeod Gauge
(k) Manometer (800 mm)
(l) 5-liter Bulb for Large Preparations
(m) Diffusion Pump (mercury)
(n) Storage Bulb Manometers
(o) Manifold with Trap for Freezing
Figure 1: Circulation and Vacuum System

(note: arrows show direction of circulation)

$\rightarrow$ indicates mercury
gauge as the mercury level is slowly lowered. The term will be used to mean a vacuum better than $10^{-6}$ torr. No attempt was made to keep mercury vapor out of any part of the system, including the reaction tube.

The reaction tube itself (shown enlarged in Figure 2) was made from a four-way oblique and straight bore spring loaded stopcock with two 10/30 $\frac{\$}{3}$ male fittings. Connected to the opposite side of the stopcock were two lengths of 4 mm capillary tubing, 10 in. long. The bottom of one was expanded into an 8 mm by 20 mm chamber, which contained the catalyst and glass wool packing. The other capillary entered the catalyst chamber below the catalyst, and acted as a preheater for the reaction mixture. The furnace consisted of a 1.5 in. I.D. cylinder made of Norton Company Alundum refractory material and wrapped with Nichrome heating wire and insulation. The furnace, rated at approximately 500 watts, was 10 in. long and fit closely around the reaction tube; the bottom 6 in. of the reaction tube were heated.

Temperature control of better than 0.5° was provided by an API Instrument Company Model 713 Temptendor. A water bath was used for temperatures less than 40°. An iron-constantan thermocouple with 0° cold junctions and a Leeds and Northrup millivolt potentiometer were used for monitoring the temperature. For all experiments the thermocouple was located adjacent to the catalyst chamber.
Figure 2: Reaction and Catalyst Tube
The all-glass circulation pump, 5 in. long, was made from two close-fitting Pyrex tubes. The inner tube, forming the piston, was sealed at one end with a small, round glass check valve in a ground glass seat. This valve allowed gas to flow through the piston in one direction only. An iron nail sealed in glass was located in the interior of the piston. The piston itself rested on a ground glass seat in the larger tube above another small glass check valve. A solenoid surrounding the entire pump activated the piston.

The solenoid was energized by the circuitry shown in Figure 4. A synchronous motor activated a microswitch which alternated between a high voltage (15 volts) and a low voltage (4 volts). The two voltages and the microswitch could be adjusted to change the amplitude of the piston movement and the period each voltage was applied. The pump was used with an amplitude of approximately 0.5 in. at 120 strokes per minute. This pumping rate was sufficient to circulate gas around the circulation loop in between 20 and 30 seconds.

Four bypass units were used in the system, one each at the 5-liter bulb, capillary leak, poison doser, and the reaction tube. These consisted of two, three-way stopcocks arranged so that there were two passages between them. Proper manipulation of the stopcocks would allow circulating gas to flow through one or the other of the two passages. The stopcocks were connected as closely as possible.

The capillary leak was made by drawing out a piece of 2 mm capillary tubing to a length of 2 ft. In this way the bore was uniformly constricted into a very small passage. The capillary
Figure 3: All-Glass Circulation Pump
Figure 4: Circulation Pump Control Circuitry

- Ohmite 60Ω, 50 watt Resistor
- Output to 3-Amp, 50 watt Power Resistor
- Solenoid Activating The Circulation Pump (15 V or 4 V)
- 4-A, 50 watt Power Resistor
- Hurst Synchronous Motor, 15 RPM, 115 V, with Cam To Activate Microswitch
- Attenuated Voltage Supplied From the Variac: To Go Through The Resistance or Be Shorted To The Solenoid (-24 V)
- On-Off Switch
- 115 Volts To Solenoid
- Cooling Fan
- 115 Volts To Variac
- Microswitch
leak was then sealed into a larger Pyrex tube approximately 3 ft. long. This, in turn, was sealed into the system with the large end of the capillary leak located at one of the bypass units, as shown in Figure 1. Thus, the gas stream could either be circulated across the opening to the leak or bypassed around it. The other end of the large tube was sealed into the mass spectrometer.

At one atmosphere pressure the leak rate of the capillary into a vacuum was about 1 torr per minute. However, in the circulation system at 108 torr, the leak rate into the mass spectrometer at $2 \times 10^{-6}$ torr was such that only 0.34% of the material was lost per hour. This provided sufficient pressure ($2 \times 10^{-6}$ torr) in the mass spectrometer for analysis.

The poison injection system, shown enlarged in Figure 5, consisted of another bypass unit located immediately before the reaction tube. One passage of the bypass unit was connected through a stopcock to the high vacuum system, a 200 mm closed end mercury manometer, and a 12/30 $\frac{\text{F}}{\text{F}}$ female fitting. The volume of the part enclosed by the two stopcocks of the bypass unit and the one stopcock isolating the rest of the injection system was labeled the "doser" (shown in Figure 5). This volume, measured by mercury before installation, was 1.973 cc.

The mercury manometer associated with the poison injection system was used to measure the pressure of all the gases used in the experiments. The manometer was sealed into the circulation system before filling with triple-distilled mercury, which had also
Figure 5: Poison Injection System
been sealed into the system. In this way both the manometer and the mercury were outgassed to a sticking vacuum. Filling was accomplished by slowing dropping the mercury, by means of the stopcock located immediately above the manometer, into the manometer; no gas was trapped in the manometer or mercury since the entire system was kept under a vacuum during this process. Formation of a "sticking vacuum" in the closed end of the manometer proved all gas had been excluded. Pressures could be read to the nearest 0.1 torr using the manometer.

The remaining two bypass units were used to isolate the 5-liter bulb and the reaction tube from the circulation system. Using stopcock (e) shown in Figure 1, sample tubes could be attached to the system, evacuated, and then connected to the circulation system providing a means for extracting samples. The rest of the system, shown in Figure 1, is self-explanatory.

The volume of the circulation system, measured approximately using a known volume of gas, was found to be 354 cc. Of this, the mixing chamber accounted for 85%.

B. Mass Spectrometer

Mass spectral analysis for deuterium content of the reaction mixture was made using a Consolidated Electrodynamics Corporation Type 21-104 mass spectrometer. As seen in Figure 1, sample introduction was continuous through a capillary leak entering the mass spectrometer just "upstream" from the ionizing region.
For the analysis of the benzene mixtures, a nominal voltage of 6 ev was used to avoid any detectable fragmentation. The repeller and focus controls were set almost to their maximum values providing for optimum resolution. Because of this, the voltage setting (6 ev) did not correspond to the actual voltage in the ionizing region. The ionization potential of benzene (37) is 9.24 ev and of perdeuterio-benzene is 9.25 ev (38). A correction based on a benzene sample before each experiment was made for naturally occurring Cl. The sensitivities of the various benzene isotopes appeared to be approximately equal.

C. Radioactivity Measurements

For the radioactive Cl4O2 analysis samples were expanded into the measuring system shown in Figure 6. This consisted of a 1/4 in. Swedgelok union cross, with metal Hoke valves on two ports isolating the high vacuum and sample inlet. The metal system was used to eliminate possible cross-contamination by material dissolved in stopcock grease. A third port of the cross led to a glass 200 mm closed-end manometer constructed in a manner similar to the one described for the poison injection system. The top port led to a small cylindrical chamber (0.5 in. by 1 in.) with a flat lip around the top. A thin (0.001 in.) sheet of mica was epoxied across the top forming a "window" for measuring radiation. A Geiger-Muller detector using a 99.05% helium-0.95% isobutane purge gas was positioned directly above the "window".
Figure 6: Radioactivity Measuring System
A Nuclear-Chicago Corporation Model 192A Ultrascalar counted the number of pulses received from the detector. An operating voltage of 1500 V was chosen using the plot of the plateau curve shown in Section A-3 of the Appendix. Also shown is a plot of counts per minute versus pressure for the measuring system.

IV-2 Materials

A. Alumina Catalyst

The alumina catalyst used in this work is the same GA-48 preparation used in several earlier studies (20, 22). It was prepared by the MK Research and Development Company of Pittsburgh, Pennsylvania, from the neutral hydrolysis of redistilled aluminum isopropoxide. X-ray measurements, made as the catalyst was dehydrated during the final stages of preparation, revealed that it was probably a mixture of eta (η) and gamma (γ) alumina. Spark spectral analysis showed that the metallic impurity level was less than 50 ppm. The catalyst surface area was 158 m²/g.

A 0.10 g sample was sealed into the reaction tube described in Section IV-1-A. No attempt was made to shield the alumina from the atmosphere.

The surface area of a 0.40 g sample of the GA-48 alumina which had been used extensively in previous work (20, 22) was redetermined by a B. E. T. measurement using nitrogen (See Section A-4 of the Appendix).
This determination showed the surface area to be $141 \, m^2/g$, a decrease of 11% with use.

A standard pretreatment was performed before each experiment. This included slow heating, under vacuum, from room temperature to $530^\circ$ for a period of 45 minutes. When the temperature reached $530^\circ$, the catalyst was isolated (using the bypass) and 150 torr of oxygen were admitted to the circulation system. Previously, the oxygen had been passed through a trap ([m] in Figure 1) filled with glass beads and thermostated at $-195^\circ$.

Next the oxygen was circulated over the catalyst at $530^\circ$ for one hour. During this time, the small trap in the circulation system was kept at $-195^\circ$. At the end of the hour the catalyst was again isolated, and the oxygen evacuated; the trap was heated rapidly with a heat gun during this evacuation. After several minutes, the catalyst was opened to the vacuum and evacuated to a sticking vacuum at $530^\circ$ for two hours. The catalyst was isolated at the end of the two hours, and preparations for the reaction were begun immediately.

B. Benzene

Benzene

The benzene ($C_6H_6$) was new, Fisher Scientific Company B-414 benzene, 99 mole % pure. For purposes of drying and purification about 10 ml were placed in a small sample tube with a 5 Å molecular sieves, which had been dried under vacuum at 300°. The sample tube
was made from a 5 in. length of 1/2 in. Pyrex tubing with one end closed. A 4 mm stopcock and 12/30 $^\text{g}$ male fitting were attached to the other end. All other sample tubes mentioned in this work are of the same description.

The sample tube containing the molecular sieves was evacuated, and the benzene was "expanded" into it without allowing the introduction of air. The benzene was then outgassed several times by freezing at $-195^\circ$, pumping, and thawing. Several millimeters of the dried benzene were evaporated under vacuum at room temperature, and several more were transferred in the vacuum system to another sample tube at $-195^\circ$. The latter was outgassed before each use by freezing at $-195^\circ$ and pumping to a sticking vacuum.

Perdeuteriobenzene

Deuterated benzene (C$_6$D$_6$) from Merck, Sharp, and Dohme of Canada, Ltd. was transferred from its sealed vessel to an evacuated sample tube by "expanding" it in such a manner as to exclude air. This was degassed several times in a freeze/pump/thaw cycle. Mass spectral analysis showed that the sample consisted of 97.1% C$_6$D$_6$ and 2.9% C$_6$HD$_5$.

C. Deuterium, Hydrogen and Helium

These gasses were stored in the 5-liter storage bulbs shown in Figure 1. At all times the pressure of the gas was kept slightly above atmospheric to prevent any contamination from leakage.
Deuterium

Deuterium was prepared using the Elhygen-D₂ Electrolytic Ultra-Pure Deuterium Generator and transferred through the trap thermostated at -195° to a 5-liter storage bulb in the vacuum system. The cathode of the unit, composed of a bundle of palladium tubes, accounts for the purity of the deuterium. The deuterium oxide used in the generator was supplied by Chemical Samples Company, and was 99.7% D₂O. Because the generator was fairly new, there was still some hydrogen dissolved in the palladium and, therefore, the isotopic purity of the product was not as good as that of the D₂O.

The deuterium storage bulb was refilled several times, and after each filling the gas was analyzed in the mass spectrometer for D₂, HD, and H₂. Values of 1.1% and 2.1% were used as approximations for the D₂ and H₂ fragmentation (39). The average of these values, 1.6%, was used as an approximation for HD fragmentation.

Hydrogen

Hydrogen was transferred from a storage cylinder through the trap at -195° to one of the 5-liter storage bulbs. As a check on the purity of the hydrogen and its effect on the catalyst, several special experiments were run. First, a control experiment in which two successive mixtures of D₂-C₆H₆ were reacted over the catalyst without any intervening pretreatment. Next, two experiments in which the first of the two successive mixtures was H₂-C₆D₆ and the second was D₂-C₆H₆. The
second reaction of the control experiment indicated slight poisoning. The second reaction of the two experiments employing both $H_2$ and $D_2$ showed approximately the same poisoning. The results indicate that the $H_2$ gas in no way effected the catalyst, and that it was probably free of any large amount of contaminant. The data from these experiments are given in Section VI-3.

Helium

Helium was transferred from a large cylinder to one of the storage bulbs of the vacuum system through an Electron Technology, Inc. Helium Diffusion Furnace. No further purification was necessary.

D. Poisons

Several different materials were used as poisons in the experiments. All, except oxygen and water, were stored in a one liter bulb sealed with a vacuum bulb stopcock; the bulb could be connected into the vacuum system by means of a 12/30 $\frac{1}{4}$ male fitting on the stopcock. An elongation of the bulb made freezing of the materials possible.

Carbon Dioxide

Gaseous $CO_2$ was prepared from dry ice (solid $CO_2$). The dry ice was placed in a small tube, and attached by a standard taper joint to the vacuum system. The tube was evacuated for a short time at room temperature, and then to a sticking vacuum at $-195^\circ$. After this the
solid CO$_2$ was quickly brought to dry ice-acetone temperature (-78°) and half of it transferred in the vacuum system to the evacuated bulb at -195°.

The prepared CO$_2$ was outgassed at -195° and then redistilled from -78° to -195° twice. Chromatographic and mass spectral analysis showed no detectable impurities.

Carbon Monoxide

Carbon monoxide supplied by Matheson Company was transferred through the trap thermostated at -78° to the storage bulb. If the carbon monoxide had contained carbon dioxide as a contaminant, this would have been evident in the results of poisoning with CO (see Section VI-8).

Oxygen

Oxygen used for poisoning was the same as that used for pre-treating the catalyst and is described in Section IV-2-A.

Water

De-ionized water was placed by expansion into an evacuated sample tube. The water was frozen at -195° and pumped to a sticking vacuum twice. Between the two freezings, some of the water was evaporated under vacuum. Next the sample was evacuated at 0° (as ice), after which it was distilled in the vacuum system from room temperature to an evacuated sample tube at -195°.
Ammonia

Ammonia (anhydrous) from a Matheson Company lecture bottle was transferred to the storage bulb and outgassed at -195° several times in a freeze/pump/thaw cycle.

Nitric Oxide

Nitric oxide (technical grade) was transferred from a Matheson Company lecture bottle to the storage bulb through the trap at -78°.

E. Radioactive C^{14}O_2

Radioactive carbon dioxide was prepared from Mallinckrodt Nuclear Barium Carbonate-C-14. The barium carbonate (3.5 mg) was placed in the bottom of a 10 mm diameter tube of approximately 15 ml capacity. The tube was sealed with a stopcock which opened into a small reservoir, and was connected via a side arm to a circulation system, similar to the one described for this work. The circulation system had a provision for injecting samples into a chromatographic column capable of separating air and water from CO_2.

Nitric acid was admitted through the stopcock to the evacuated tube containing the barium carbonate. C^{14}O_2, air and water were frozen into the circulation system and injected, in several doses, into the chromatographic column. The C^{14}O_2 was trapped at -195°.
The C\textsuperscript{14}O\textsubscript{2} was transferred to a sample tube and distilled twice from -78° to -195°. Part of this was then transferred to a small storage bulb and diluted with CO\textsubscript{2}, in a ratio of 20:1 to reduce the radioactivity to the desired level.

IV-3 Safety

Precautions were taken during the construction and operation of the equipment to minimize the danger from broken glassware and electrical shock. In addition, the exhaust of the mechanical vacuum pump was connected to a manifold which was vented into an exhaust fan. The fan, with a capacity of 985 cubic feet per minute, was used when large amounts of gas were evacuated and during the C\textsuperscript{14}O\textsubscript{2} experiments. The maximum discharge concentration, 4 x 10\textsuperscript{-10} \textmu c/cc, vented to the atmosphere during the radioactivity experiments was well below the limits (1 x 10\textsuperscript{-6} \textmu c/cc) set by the Texas State Department of Health (40).
V. PROCEDURE

The D₂-exchange reaction with benzene was the most frequently used reaction in these experiments. Because of this, a detailed description of the procedure followed for the D₂-benzene exchange experiments will be given. For the most part, the H₂-C₆D₆ exchange and the C₆D₆-C₆H₆ redistribution experiments were performed in the same manner as the D₂-benzene exchange experiments. The pretreatment of the catalyst has been described in Section IV-2-A.

V-1 Deuterium Exchange with Benzene

As soon as the catalyst was isolated after its pretreatment, the reaction procedure began. At this time the poison doser was bypassed (see the discussion of Section IV-1-A), and the benzene sample tube was connected to the inlet of the poison injection system. The capillary leak and the large preparation bulb had been bypassed previously. The entire circulation system, down to the stopcock of the benzene sample tube, was then evacuated to a sticking vacuum. The stopcocks of the poison doser bypass were switched, isolating the bypass part, and directing the circulation stream through the doser.

After isolating the circulation system from the vacuum, approximately 13 torr of benzene (previously outgassed) were admitted. This was frozen into the circulation system trap at -195°, outgassed to a sticking vacuum, and then revaporized. The pressure of the benzene was
corrected to exactly 10.0 torr, after which the stopcock on the poison
doser was closed, separating the circulation system from the poison
injection system manometer. At this point, the benzene contained in
the circulation loop only was refrozen into the trap, while the benzene
left in the manometer was pumped away.

After the circulation system, with the benzene still frozen in
the trap, had been completely evacuated again, 100.0 torr of D₂ gas
were admitted. The benzene and the D₂, in the circulation loop only,
were then well mixed using the pump. Because of the ease and accuracy
of its use, the manometer of the poison injection system was used to
measure the gas pressures for all experiments.

At the end of the catalyst pretreatment, the furnace was removed
and the catalyst allowed to equilibrate with the room temperature.
The reaction temperature was then set, using either a water bath in a
large Dewar or another furnace. This procedure, as well as the prepa-
ration of the mass spectrometer, was performed simultaneously with
the preparation of the reaction mixture.

After sufficient mixing of the gas, the poison doser was bypassed
(by switching the stopcocks to the previously evacuated side) and the
circulation stream was switched to flow past the capillary leak. The
benzene spectra was scanned several times to check the operation of the
mass spectrometer and capillary leak, and to get a "blank" from which
13C corrections could be calculated.

The reaction was begun by changing the stopcocks of the reaction
tube bypass. The strip chart recorder of the mass spectrometer, with
a speed of 1 in. per minute, was allowed to run continuously during the reaction to provide a time scale. Generally, 45 minutes elapsed from the time the pretreatment was concluded until the time the reaction was started.

V-2 Hydrogen Exchange with Perdeuteriobenzene

The preparation for these experiments proceeded in the same manner as for D₂-benzene exchange. However, two reactions were run during each experiment. The first reaction was stopped by evacuating the reaction mixture from the system and catalyst for about 5 minutes. Then a second reaction mixture was prepared and the second reaction run. The reasons for this are explained in Section IV-2-C.

V-3 Benzene-Perdeuteriobenzene Redistribution

The reaction mixture for the redistribution experiments was prepared in essentially the same manner as for the D₂-benzene exchange. Only 5 torr of each benzene were used, but their total was still 10 torr.

After the correct amount of the first benzene was added to the system, it was frozen into an evacuated tube connected to stopcock (e) of Figure 1. This was frozen back into the circulation system after the addition of the second benzene and before the addition of the helium, which was used to bring the pressure up to the 110 torr used in the exchange reactions.
V-4 Arrhenius Activation Energy of the D₂-Benzene Exchange

The procedure for these experiments was similar to the one described in Section V-1. The difference lay in the range of the reaction temperatures (from 0° to 67°).

V-5 Carbon Dioxide Poisoning

Preparation for poisoning experiments was the same as described in Sections V-1 and V-3. The initial reaction was allowed to continue until the unpoisoned rate had been established. At a suitable time, the poison, which had been isolated in the doser, was injected into the circulation stream by reversing the stopcocks from the bypass position. This injection caused a discontinuity in the reaction profile (relative amounts of isotopic species plotted against time). Therefore, the time of injection was chosen in order to introduce the least possible error into the results. For the D₂-benzene exchange, poison was injected at 24 minutes after the start, and for C₆H₆-C₆D₆ redistribution, at 8 minutes after the start.

While the "blank" benzene scans were being made, and during the first part of the reaction, the poison dose was prepared. As soon as the doser had been bypassed (Section V-1), it, and the poison injection system, were evacuated to a sticking vacuum. The CO₂ storage bulb was also attached and the CO₂ outgassed at -195°. The desired pressure of CO₂ was admitted to the injection system and allowed to equilibrate for as long as possible. Its pressure and the room temperature were noted; then the stopcock isolating the doser from the rest of the system was closed, the dose was ready for injection.
V-6 Other Poisons

The procedure used to inject all other poisons was the same as the procedure for carbon dioxide.

V-7 Radioactive Carbon Dioxide Poisoning

For the experiment in which radioactive $^{14}$CO$_2$ was used as a poison, the reaction mixture was prepared in the same manner as described in Section V-1. The first dose of $^{14}$CO$_2$ was prepared and injected at 24 minutes as described in Section V-5. The amount was approximately enough to completely poison the catalyst. At 31 minutes the doser was bypassed and evacuated and another identical dose of $^{14}$CO$_2$ prepared. After isolating the reaction tube at 42 minutes, the $^{14}$CO$_2$ was injected into the gas stream. Since it was assumed that the first dose would be completely absorbed, the purpose of the second dose was to allow measurement of the specific activity of a single dose of $^{14}$CO$_2$ in the gas stream. At 57 minutes the gas stream was again directed over the catalyst. At 83 minutes the catalyst temperature was suddenly raised to 96° using a heated water bath. A furnace set at 220° was placed around the catalyst tube at 101.5 minutes and the temperature rose from 96° to 222° in 8 minutes. The set point was raised to 400° at 144 minutes and the temperature reached 400° at 152 minutes.

During each of the steps of this experiment at least two samples for radioactivity analysis were taken by expansion at stopcock (e) into an evacuated tube. A mass spectral scan was made approximately every two minutes and before and after each sample or event in the
experiment. Figure 22 shows the various samples and events on the same time scale. Approximately 2.7% of the volume of the reaction mixture was removed with each sample.

Immediately prior to the experiment, an operating voltage plateau curve (see Section A-3 of the Appendix) was determined and an operating voltage of 1500 v chosen. Each sample, as it was taken from the reaction mixture, was expanded into the measuring system (Figure 5) and its pressure and activity (counts min.\(^{-1}\)) recorded. Since each previous sample seemed to leave a small absorbed residue, a background count was also taken each time.

V-8 Hydrogen-Deuterium Exchange

Several experiments were run in order to observe \(\text{H}_2\)-\(\text{D}_2\) exchange over the alumina catalyst. The pretreatment was the same as that used in other experiments. After the pretreatment, the catalyst was bypassed and the desired amount of \(\text{D}_2\) (55 torr -- measured with the poison injection system manometer) was admitted to the circulation system. The manifold, connected to the poison injection system and the gas storage bulbs, was then filled to a pressure of about one atmosphere with \(\text{H}_2\). With this large pressure differential, the \(\text{H}_2\) was admitted to the circulation system bringing the total pressure to 110 torr. After circulation, in order to insure mixing, the bypass around the capillary leak was switched to admit the mixture to the mass spectrometer. Peak heights of the "blank" sample were recorded and
exchange reaction including some runs during the "aging" process. A typical reaction profile showing the relative amounts of each benzene isotope plotted against time is pictured in Figure 7 and the corresponding \( \ln(\Phi_\infty - \Phi) \) versus time plot in Figure 8.

A reaction rate averaging very close to \( 5.32\%/(\text{min. 0.1g}) \) was found for the first seven experiments, after which the rate suddenly dropped to a value of \( 5.07\%/(\text{min. 0.1g}) \) decreasing slightly thereafter. The final experiments did begin to show a small upward trend. The lower set of rate constants averaged \( 4.94\%/(\text{min. 0.1g}) \) with the overall average being \( 5.05\%/(\text{min. 0.1g}) \). Table I is arranged with the experiments in chronological order.

The exchange multiplicity (M value) for these experiments is also given in Table I. These values ranged from 1.02 to 1.12, averaging 1.09. Using the overall average rate and the number of sites per cm\(^2\) on the catalyst determined in this investigation (Section VI-5) the "turnover number" for the reactions is \( 0.042 \) \( \text{D atoms exchanged} / (\text{sec. site}) \).

VI-2 Hydrogen Exchange With Perdeuteriobenzene

Several experiments involved exchange of \( \text{H}_2 \) with the deuterated benzene to find the back exchange rate. These experiments employed the same mixture ratio of 10:100 torr benzene:hydrogen and the same temperature, 20°, as the \( \text{D}_2 \)-benzene exchange. Figures 9 and 10 contain a typical reaction profile and rate plot and Table II presents the data.
## Table I: Deuterium Exchange with Benzene Rate Constants

<table>
<thead>
<tr>
<th>Experiment(1)</th>
<th>$k_0$ [%(min.0.1g)]</th>
<th>± Error</th>
<th>M Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-1</td>
<td>7.42</td>
<td>0.05</td>
<td>1.087</td>
</tr>
<tr>
<td>0-2</td>
<td>6.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-3</td>
<td>6.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-4</td>
<td>6.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6A-1</td>
<td>5.32</td>
<td>0.05</td>
<td>1.087</td>
</tr>
<tr>
<td>6A-2</td>
<td>5.36</td>
<td>0.09</td>
<td>1.064</td>
</tr>
<tr>
<td>6A-3</td>
<td>5.69</td>
<td>0.07</td>
<td>1.119</td>
</tr>
<tr>
<td>6A-4</td>
<td>5.23</td>
<td>0.05</td>
<td>1.019</td>
</tr>
<tr>
<td>6A-5</td>
<td>5.27</td>
<td>0.05</td>
<td>1.088</td>
</tr>
<tr>
<td>6A-6</td>
<td>5.34</td>
<td>0.02</td>
<td>1.124</td>
</tr>
<tr>
<td>6A-7</td>
<td>5.42</td>
<td>0.03</td>
<td>1.097</td>
</tr>
<tr>
<td>6A-8</td>
<td>5.07</td>
<td>0.02</td>
<td>1.100</td>
</tr>
<tr>
<td>6A-9</td>
<td>5.03</td>
<td>0.02</td>
<td>1.080</td>
</tr>
<tr>
<td>6A-10</td>
<td>4.99</td>
<td>0.03</td>
<td>1.094</td>
</tr>
<tr>
<td>6A-11</td>
<td>5.03</td>
<td>0.07</td>
<td>1.092</td>
</tr>
<tr>
<td>2-1</td>
<td>5.01</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>5-1</td>
<td>2.10</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>5-2</td>
<td>6.57</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>5-3</td>
<td>9.13</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>5-4</td>
<td>3.53</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>5-5</td>
<td>13.90</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>8-1</td>
<td>4.98</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>8-2</td>
<td>4.76</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>8-3</td>
<td>4.76</td>
<td>0.07</td>
<td></td>
</tr>
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<td>8-4</td>
<td>4.94</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>8-5</td>
<td>4.74</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>8-6</td>
<td>4.96</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>8-7</td>
<td>5.03</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>8-8</td>
<td>5.16</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>7-1</td>
<td>4.70</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>11-1(3)</td>
<td>5.51</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>9-1(5)</td>
<td>5.01</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

Average $D_2$-Benzene Exchange Rate: 5.05%/min.0.1g

Notes:
1. Experiment numbers refer to the individual discussion sections in Section VI (Results), and to the individual experiments.
2. Experiment numbers 0-1 to 0-4 refer to "aging" reactions.
3. Experiments with long pretreatment times. Percent change from previous experiment: Exp. 6A-3: 4.3%, Exp. 11-1: 6.7%.
4. Greatest change between two consecutive experiments: 7%. Average change: 2.5%.
5. Experiment with deuterated catalyst
Figure 8: D₂ Exchange with Benzene, Experiment 0-2
Figure 9: H₂ Exchange with Perdeuterobenzene
Experiment 2-3A Reaction Profile
Figure 10: H₂ Exchange with Perdeuteriobenzene, Experiment 2-3A
The exchange rate of the perdeuteriobenzene, 2.74 %/(min. 0.1g ), was somewhat slower than the D₂-benzene exchange. Using an average rate of 5.03 %/(min. 0.1g ) from the five D₂-benzene exchange reactions preceding the H₂-perdeuteriobenzene experiments, a primary isotope effect, \( K_H/K_D \), of 1.83 ± 0.06 was calculated. Excluding other considerations, this indicates the rate limiting step of the exchange is probably the cleavage of a C-D bond.

VI-3 Poisoning Effect of the Exchange Reaction

As a consequence of testing the hydrogen gas for contamination, several exchange experiments were run using consecutive reactions without intervening pretreatment. In this way the poisoning effect of the reaction could be determined by comparing the first with the second. The results in Table III show at most a decrease in activity of 8.4% for two D₂-C₆H₆ reactions and a decrease of 7.6% for an H₂-C₆D₆,D₂-C₆H₆ set.

VI-4 Benzene-Perdeuteriobenzene Redistribution

Redistribution experiments were performed using an equal amount of each benzene. The 5:5:100 torr mixture of C₆H₆:C₆D₆:helium approximated the conditions of the exchange reactions as closely as possible; the reaction temperature was 20°.
Table II: Hydrogen Exchange with Perdeuteriobenzene

<table>
<thead>
<tr>
<th>Experiment</th>
<th>( k_\phi' ) ( \pm \text{Error} ) [%/ (min.0.1g)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-2A</td>
<td>2.73 ( \pm ) 0.10</td>
</tr>
<tr>
<td>2-3A</td>
<td>2.75 ( \pm ) 0.02</td>
</tr>
</tbody>
</table>

Average \( H_2 \)-Perdeuteriobenzene Exchange Rate:

\[ 2.74 \pm 0.08 \text{%/}(\text{min.0.1g}) \]

Isotope Effect:

\[ \frac{k_H}{k_D} = \frac{5.03 \pm 0.03}{2.74 \pm 0.08} = 1.83 \pm 0.06 \]

Using the average \( D_2 \)-benzene exchange rate constant for the five preceding reactions (Exp. 6A-8 through Exp. 2-1A of Table I): \( 5.03 \pm 0.03 \text{%/}(\text{min.0.1g}) \)

Table III: Poisoning Effect of One Exchange Reaction on Another

<table>
<thead>
<tr>
<th>Experiment</th>
<th>( k_\phi ) ( \pm \text{Error} ) [%/ (min.0.1g)]</th>
<th>( k_\phi' ) ( \pm \text{Error} ) [%/ (min.0.1g)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1A</td>
<td>5.01 ( \pm ) 0.03</td>
<td></td>
</tr>
<tr>
<td>2-1B</td>
<td>4.59 ( \pm ) 0.05</td>
<td></td>
</tr>
<tr>
<td>2-2A</td>
<td>4.63 ( \pm ) 0.05</td>
<td>2.73 ( \pm ) 0.10</td>
</tr>
<tr>
<td>2-2B</td>
<td>4.85 ( \pm ) 0.05</td>
<td>2.75 ( \pm ) 0.02</td>
</tr>
</tbody>
</table>

Percent Decrease of the Second Reaction (\( D_2 \)-Benzene Exchange) With Respect to the Average \( D_2 \)-Benzene Exchange Rate:

\[ \begin{align*}
\text{Exp. 2-1} & \quad 8.38\% \\
\text{Exp. 2-2} & \quad 7.58\% \\
\text{Exp. 2-3} & \quad 3.19\%
\end{align*} \]

Notes: \( k_\phi = D_2 \)-Benzene Exchange Rate; \( k_\phi' = H_2 \)-Perdeuteriobenzene Exchange Rate
A refers to the first reaction of an experiment and B refers to the second reaction run without intervening catalyst pretreatment.
Since the initial benzene ratio was 50:50, it was assumed that the equilibrium mixture would be a binary distribution. With this assumption equations (10) and (11) were used to plot the data. Figures 11 and 12 show a redistribution reaction profile and rate plot. It can be seen from Figure 11 that the equilibrium mixture is not exactly binary. This is because of the 2.9% C6HD5 impurity in the perdeuteriobenzene. In spite of this, the rate plot (Figure 12) is a straight line. Although linearity is not a sensitive function of the \( U_\infty \) (and similarly \( \Phi_\infty \)) value during initial stages at low conversion, these values become critical as equilibrium is approached.

Because of the methods of analysis, a direct comparison of the rate constants of exchange and redistribution gives no meaningful data. However, a comparison of the reaction profiles (Figures 8 and 11) does show that redistribution is many times faster than exchange. Redistribution essentially reached equilibrium after 25 minutes, while the exchange reaction was still far from equilibrium (even at 67° the exchange was still far from equilibrium at 25 minutes).

One interesting feature of Figure 11 is that \( \text{C}_6\text{H}_6 \) and \( \text{C}_6\text{D}_6 \) disappear at the same rate while the other corresponding benzene isotope pairs, \( \text{C}_6\text{H}_5\text{D}-\text{C}_6\text{HD}_5 \) and \( \text{C}_6\text{H}_4\text{D}_2-\text{C}_6\text{H}_2\text{D}_4 \), are formed at the same rate.

VI-5 Deuterium-Benzene Exchange Activation Energy

An Arrhenius plot of \( \ln (k\phi) \) versus \( 1/T \) for the \( \text{D}_2-\text{benzene} \) exchange reaction between 10° and 67° is shown in Figure 13 and the
Figure 11: Benzene-Perdeuteriobenzene Redistribution
Experiment 6B-1 Reaction Profile
Figure 12: Benzene-Perdeuteriobenzene Redistribution: Experiment 6B-1
Table IV: Arrhenius Activation Energy for Deuterium Exchange with Benzene

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (°K)</th>
<th>k_0 [%/ (min. 0.1g)]</th>
<th>± Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>6A-11</td>
<td>293</td>
<td>5.03</td>
<td>0.02</td>
</tr>
<tr>
<td>5-1</td>
<td>307</td>
<td>6.57</td>
<td>0.05</td>
</tr>
<tr>
<td>5-2</td>
<td>323</td>
<td>9.13</td>
<td>0.05</td>
</tr>
<tr>
<td>5-3</td>
<td>283</td>
<td>3.53</td>
<td>0.11</td>
</tr>
<tr>
<td>5-4</td>
<td>340.6</td>
<td>13.90</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Activation Energy: 4.3 ± 0.3 kcal/mole

Table VIII: Hydrogen-Deuterium Exchange

<table>
<thead>
<tr>
<th>Reaction</th>
<th>k_{HD} (arbitrary conc. units/min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_1: Initial Exchange</td>
<td>0.408</td>
</tr>
<tr>
<td>k_2: Exchange with Poisoning from first reaction</td>
<td>0.171</td>
</tr>
<tr>
<td>k_3: Exchange with Poisoning from Benzene</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Percent of Exchange Activity Remaining After Poisoning:

- \( k_2/k_1 \): 41.9%
- \( k_3/k_1 \): 2.2%
- \( k_3/k_2 \): 5.3%
Figure 13: Arrhenius Activation Energy for D₂ Exchange with Benzene
data is given in Table IV. From the plot, an activation energy of 4.3 ± 0.3 kcal/mole was calculated. This can be compared with 6.0 kcal/mole reported by McCosh and Kemball (19) for benzene over their alumina catalyst.

VI-6 Carbon Dioxide Poisoning

A. Deuterium Exchange with Benzene

After the initial rate of the D₂-benzene reaction had been established, measured amounts of CO₂ were injected into the circulation stream using the poison doser. The effect of the CO₂ was immediate in all the reactions, causing a decrease in the rate of exchange. Figures 14 and 15 are reaction profile plots for two experiments representing high and low degrees of poisoning. Figures 16 and 17 are the corresponding rate plots. In both cases, sharp changes in the slopes (Figures 16 and 17) occur within 45 seconds after the injection of the CO₂; this corresponds closely to the circulation time (30 seconds) around the system. This behavior is typical of all the poisoning experiments, with the rate curve remaining linear after poisoning.

In agreement with results reported elsewhere (13, 20), CO₂ acted as a total poison for the reaction, with the addition of various amounts making it possible to "titrate" the number of active sites. The fraction of exchange activity not poisoned, \( \frac{k_P}{k_\Phi} \) (\( k_\Phi \) and \( k_P \) represent exchange rates before and after poisoning), is plotted
Table V: Carbon Dioxide Poisoning

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$k_\phi$ $\pm$ Error</th>
<th>$k_\phi^P$ $\pm$ Error</th>
<th>$k_\phi^P/k_\phi$ $\pm$ Error</th>
<th>$#CO_2/cm^2 \times 10^{-12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6A-1</td>
<td>5.32 0.05</td>
<td>2.81 0.05</td>
<td>0.53 0.02</td>
<td>4.17</td>
</tr>
<tr>
<td>6A-2</td>
<td>5.36 0.09</td>
<td>3.56 0.04</td>
<td>0.66 0.02</td>
<td>2.63</td>
</tr>
<tr>
<td>6A-3</td>
<td>5.69 0.07</td>
<td>2.48 0.02</td>
<td>0.44 0.01</td>
<td>5.51</td>
</tr>
<tr>
<td>6A-4</td>
<td>5.23 0.05</td>
<td>1.67 0.09</td>
<td>0.32 0.02</td>
<td>7.05</td>
</tr>
<tr>
<td>6A-5</td>
<td>5.27 0.05</td>
<td>4.26 0.09</td>
<td>0.81 0.02</td>
<td>1.46</td>
</tr>
<tr>
<td>6A-6</td>
<td>5.34 0.02</td>
<td>1.27 0.05</td>
<td>0.24 0.01</td>
<td>8.10</td>
</tr>
<tr>
<td>6A-7</td>
<td>5.42 0.03</td>
<td>0.97 0.05</td>
<td>0.18 0.01</td>
<td>9.15</td>
</tr>
<tr>
<td>6A-8</td>
<td>5.07 0.02</td>
<td>2.22 0.02</td>
<td>0.44 0.01</td>
<td>5.52</td>
</tr>
<tr>
<td>6A-9</td>
<td>5.03 0.02</td>
<td>0.29 0.03</td>
<td>0.49 0.01</td>
<td>11.99</td>
</tr>
<tr>
<td>6A-10</td>
<td>4.99 0.03</td>
<td>1.80 0.04</td>
<td>0.36 0.01</td>
<td>6.40</td>
</tr>
<tr>
<td>6A-11</td>
<td>5.03 0.07</td>
<td>0.15 0.02</td>
<td>0.03 0.01</td>
<td>13.20</td>
</tr>
</tbody>
</table>

B. Benzene-Perdeuteriobenzene Redistribution

<table>
<thead>
<tr>
<th>(k_u)</th>
<th>(k_u^P)</th>
<th>(k_u^P/k_u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6B-1</td>
<td>0.2360 0.0010</td>
<td>0.129 0.013</td>
</tr>
<tr>
<td>6B-2</td>
<td>0.2004 0.0002</td>
<td>0.0259 0.0025</td>
</tr>
<tr>
<td>6B-3</td>
<td>0.2274 0.0010</td>
<td>0.0151 0.0001</td>
</tr>
<tr>
<td>6B-4</td>
<td>0.2175 0.0009</td>
<td>0.0896 0.0020</td>
</tr>
</tbody>
</table>

Notes: Redistribution rate constants in arbitrary units per min.
$k_\phi$ ($k_u$) is the unpoisoned rate constant and $k_\phi^P$ ($k_u^P$) is the poisoned rate constant for D_2-Benzene Exchange (Redistribution).
Figure 14: CO₂ Poisoning of D₂ Exchange with Benzene (high degree)
Experiment 5-9 Reaction Profile
Figure 15: CO₂ Poisoning of D₂ Exchange with Benzene (low degree)
Experiment 5-2 Reaction Profile
Figure 16: CO₂ Poisoning of D₂ Exchange with Benzene (high degree)

Experiment 5-9
Figure 17: CO₂ Poisoning of D₂ Exchange with Benzene (low degree)
Experiment 5-2

Time (min.)
against the specific CO\textsubscript{2} adsorption in Figure 18. The intercept on the abscissa, indicating the number of molecules necessary to completely poison the reaction, shows 14.5 \times 10^{12} \text{CO}_2/\text{cm}^2.

B. Benzene-Perdeuteriobenzene Redistribution

CO\textsubscript{2} poisoning of the redistribution reaction was carried out in the same manner as for exchange. Because of the fast rate of redistribution, the dose of CO\textsubscript{2} was injected at 8 minutes, instead of 24 as in exchange poisoning. Figures 19 and 20 show a typical reaction profile and rate plot for redistribution poisoning. Again, the effect was immediate and comparison of Figure 19 with Figure 11 points out the abruptness.

Figure 21 is a "poisoning" curve similar to Figure 18 for exchange. It indicates that about 15.5 \times 10^{12} \text{CO}_2/\text{cm}^2 are necessary to completely poison the redistribution reaction. The closeness of this figure to that for exchange, and the similarity of the shape of the curves indicates that exchange and redistribution apparently occur on the same, or related, sites.

VI-7 Radioactivity C\textsuperscript{14}O\textsubscript{2} Poisoning

Although it has been established that CO\textsubscript{2} completely poisons the exchange reaction, it could not be accurately determined whether all of the CO\textsubscript{2} was adsorbed or not. To accomplish this, radioactive C\textsuperscript{14}O\textsubscript{2} was used as the poison in a manner similar to the regular poisoning experiments with one exception being the addition of a second dose of C\textsuperscript{14}O\textsubscript{2}.
Figure 18: Carbon Dioxide Poisoning Curve for Deuterium Exchange with Benzene; Fraction of Exchange not Poisoned per Number of Carbon Dioxide Molecules
Figure 19: CO$_2$ Poisoning of Benzene-Perdeuteriobenzene Redistribution Experiment 6B-2 Reaction Profile
Figure 20: Benzene-Perdeuteriobenzene Redistribution: Experiment 6B-3 with CO₂ Poisoning
Figure 21: Carbon Dioxide Poisoning Curve for Redistribution; Fraction of Redistribution Reaction not Poisoned per Number of Carbon Dioxide Molecules
Figure 22 shows the rate plot and the specific activity of the gas phase on the same time axis. The specific activity of the reaction mixture was tested before and after injection of a dose of C\textsuperscript{14}O\textsubscript{2} just sufficient to completely poison the catalyst. No residual activity was found, although at 25 minutes some slight activity existed. The reaction rate had been altered to its poisoned value before this activity disappeared.

At 42 minutes the catalyst was bypassed and an identical dose of C\textsuperscript{14}O\textsubscript{2} was admitted to the system. A specific activity of 13.8 units (counts per minute per torr) was measured in the gas. This is the same as would have been detected after the first dose of C\textsuperscript{14}O\textsubscript{2}, if none had been adsorbed.

When the gas was again passed over the catalyst, the specific activity immediately decreased to about 9.4 units, demonstrating that the capacity of the catalyst to adsorb CO\textsubscript{2} was greater than that necessary to poison the exchange. The temperature was raised to 96° with the subsequent desorption of an amount of C\textsuperscript{14}O\textsubscript{2} slightly larger (15 units) than the second dose. No exchange activity was observed, possibly indicating that some C\textsuperscript{14}O\textsubscript{2} from the first dose was desorbed from weaker sites not participating in the reaction. The excess (1.2 units) corresponded approximately to the amount initially observed in the gas after the first dose of C\textsuperscript{14}O\textsubscript{2} was injected.

After the temperature was increased to 220°, part of the first dose definitely was desorbed and the exchange reaction was initiated.
Table VI: Radioactive Carbon Dioxide Poisoning Deuterium Exchange with Benzene

Experiment 7-1
Unpoisoned rate: \(4.70 \pm 0.05 \%/(\text{min.}0.1g)\)

Poisoned rate after the first CO\(_2\) dose: \(0.13 \pm 0.05 \%/(\text{min.}0.1g)\)

Poisoned rate after the second CO\(_2\) dose: \(0.0 \%/(\text{min.}0.1g)\)

\#CO\(_2\)/cm\(^2\) in each dose: \(14.52 \times 10^{12}\)

Radioactivity Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (min.)</th>
<th>Specific Activity (Counts per min.)</th>
<th>Counting Error per torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>First dose of CO(_2)</td>
<td>1.8</td>
</tr>
<tr>
<td>4</td>
<td>26</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>5</td>
<td>37</td>
<td>Bypassed Catalyst, Added second</td>
<td>13.6</td>
</tr>
<tr>
<td>6</td>
<td>42</td>
<td>dose of CO(_2)</td>
<td>0.9</td>
</tr>
<tr>
<td>7</td>
<td>48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>57</td>
<td>Opened Catalyst to circulation</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>59</td>
<td>stream</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>65</td>
<td>Temperature increased to 96(^o)</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>72</td>
<td>15.3</td>
<td>0.9</td>
</tr>
<tr>
<td>13</td>
<td>80</td>
<td>9.3</td>
<td>0.8</td>
</tr>
<tr>
<td>14</td>
<td>83</td>
<td>9.5</td>
<td>0.8</td>
</tr>
<tr>
<td>15</td>
<td>85</td>
<td>Temperature increased to 222(^o)</td>
<td>15.3</td>
</tr>
<tr>
<td>16</td>
<td>90</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>17</td>
<td>97</td>
<td>15.7</td>
<td>1.1</td>
</tr>
<tr>
<td>18</td>
<td>101.5</td>
<td>Temperature increased to 400(^o)</td>
<td>15.7</td>
</tr>
<tr>
<td>19</td>
<td>106</td>
<td>21.2</td>
<td>1.1</td>
</tr>
<tr>
<td>20</td>
<td>110</td>
<td>23.2</td>
<td>1.2</td>
</tr>
<tr>
<td>21</td>
<td>118</td>
<td>21.2</td>
<td>1.3</td>
</tr>
<tr>
<td>22</td>
<td>129</td>
<td>21.8</td>
<td>1.2</td>
</tr>
<tr>
<td>23</td>
<td>139</td>
<td>21.8</td>
<td>1.2</td>
</tr>
<tr>
<td>24</td>
<td>144</td>
<td>Temperature increased to 400(^o)</td>
<td>21.8</td>
</tr>
<tr>
<td>25</td>
<td>148</td>
<td>27.7</td>
<td>1.3</td>
</tr>
<tr>
<td>26</td>
<td>158</td>
<td>29.2</td>
<td>1.4</td>
</tr>
<tr>
<td>27</td>
<td>170</td>
<td>27.2</td>
<td>1.5</td>
</tr>
<tr>
<td>28</td>
<td>182</td>
<td>29.4</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Figure 22: Radioactive Carbon Dioxide Poisoning of $D_2$ Exchange with Benzene: Showing both the Rate Curve and Specific Activity of the Reaction (note: The radioactive carbon dioxide was a 20:1 mixture of $CO_2:C^{14}O_2$)
again (at a higher rate than at 20°). A final temperature increase to 400° caused still more $^{14}$O$_2$ desorption. The final activity of the gas 28.4 units, was approximately double that of one dose, 13.8, showing that all the CO$_2$ could eventually be reclaimed.

VI-8 Other Poisons

Several other materials were used in an attempt to poison the D$_2$-benzene exchange. These, along with the data, are listed in Table VII. The procedure used for each was the same as for CO$_2$ poisoning although only two experiments were performed with each and no "poisoning" plots were made. In all cases, except O$_2$ and H$_2$O, the dose sizes were (1) an amount equal to that of CO$_2$ necessary to just poison the catalyst and (2) an amount three times larger than this.

Oxygen appeared to have no effect at all on the reaction rate. The amount of water added (vapor pressure, 24 torr, at 25°) acted only as a slight poison reducing the activity not poisoned to 80.3% of its initial value.

The first dose of carbon monoxide had approximately the same effect as the water (79.4% activity not poisoned); a three-fold increase in the amount of CO only reduced the activity to 73% of the original.

Nitric oxide had the least effect of all reducing the activity to 89.9% and 85.9% of the original for the two dose sizes.
Table VII: Other Poisons

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$k_\phi$ [%/(min.0.1g)] ± Error</th>
<th>$k_\phi^P$ [%/(min.0.1g)] ± Error</th>
<th>$k_\phi^P/k_\phi$ ± Error</th>
<th>#CO$_2$/cm$^2$ x 10$^{-12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen: O$_2$ 8-1</td>
<td>4.98 ± 0.05</td>
<td>4.94 ± 0.13</td>
<td>0.992 ± 0.036</td>
<td>14.37</td>
</tr>
<tr>
<td>Water: H$_2$O 8-2</td>
<td>4.76 ± 0.02</td>
<td>3.82 ± 0.07</td>
<td>0.803 ± 0.019</td>
<td>9.02</td>
</tr>
<tr>
<td>Carbon Monoxide: CO 8-3</td>
<td>4.76 ± 0.07</td>
<td>3.78 ± 0.05</td>
<td>0.794 ± 0.023</td>
<td>14.77</td>
</tr>
<tr>
<td>8-4</td>
<td>4.96 ± 0.07</td>
<td>3.62 ± 0.11</td>
<td>0.730 ± 0.033</td>
<td>48.92</td>
</tr>
<tr>
<td>Ammonia: NH$_3$ 8-5</td>
<td>4.74 ± 0.04</td>
<td>4.19 ± 0.07</td>
<td>0.884 ± 0.022</td>
<td>14.40</td>
</tr>
<tr>
<td>8-6</td>
<td>4.96 ± 0.09</td>
<td>3.07 ± 0.05</td>
<td>0.619 ± 0.022</td>
<td>48.32</td>
</tr>
<tr>
<td>Nitric Oxide: NO 8-7</td>
<td>5.03 ± 0.03</td>
<td>4.52 ± 0.05</td>
<td>0.899 ± 0.016</td>
<td>14.56</td>
</tr>
<tr>
<td>8-8</td>
<td>5.16 ± 0.02</td>
<td>4.43 ± 0.05</td>
<td>0.859 ± 0.013</td>
<td>48.64</td>
</tr>
</tbody>
</table>

Notes: $k_\phi$ is the unpoisoned rate constant and $k_\phi^P$ is the poisoned rate constant for D$_2$-Benzene exchange.
The effect of the small dose of ammonia (88.4%) was similar to the effect of NO; however, the large amount of ammonia caused considerably more reduction (to 61.9%) in activity than any of the other gases. It was not determined whether D₂ was exchanging with NH₃.

The CO and NO were observed in the gas phase using the mass spectrometer. For less than complete poisoning, no CO₂ was ever observed; however, after both the large and small doses, NO and CO were seen. Although the amounts were too small to afford accurate analysis, it appeared that the amount of each material in the gas (determined from peak heights) increased in the same proportion as the amount in the dose. Within the error of the determination, this indicated that a three-fold increase in the amount of CO and NO in the gas caused very little increased adsorption.

VI-9 Deuterium Exchange with Benzene over a Deuterated Catalyst

The D₂-benzene exchange reaction under the usual conditions was run on the alumina catalyst which had been deuterated in circulating D₂ at 500°. Approximately 99.8% of exchangeable hydroxyls should have been deuterated. The results presented in Table I are identical with all other D₂-benzene exchange reactions and show no exchange of the catalyst hydroxyl hydrogen with the benzene.
VI-10 Hydrogen-Deuterium Exchange

Although the details of $\text{H}_2$-$\text{D}_2$ exchange on alumina (16) are well established, several experiments were performed to get some idea of the effect of benzene on the reaction.

Catalyst pretreatment was performed in the same way as in all other experiments, and the reaction temperature was $20^\circ$. One experiment was run with two successive mixtures of 55:55 torr $\text{H}_2$:$\text{D}_2$, with no intervening pretreatment. A reduction in the rate of the second reaction was evident.

After reactivation of the catalyst, a second experiment was performed in which the second reaction mixture contained approximately 1 torr benzene. This resulted in slightly more molecules of benzene in the gas than the number of $\text{CO}_2$ molecules necessary to completely poison the catalyst. Figure 23 shows the reaction profile of both reactions of the second experiment. The plots of $\ln (\text{HD}_\infty - \text{HD})$ versus time according to equation (12) are shown in Figure 24. The curve for the second reaction shows both the effect of poisoning from the first reaction, and the sudden result of benzene chemisorption.

In agreement with the first experiment, the $\text{H}_2$-$\text{D}_2$ exchange seemed to poison the catalyst for further exchange. This poisoning reduced the activity to 41.9% of the original value before the benzene appeared to have any effect. The effect of the benzene became apparent 2 minutes from the start of the reaction as evidenced by the sharp break in the rate plot of the second reaction. The result was the reduction of the activity to 5.3% of the original value.
Figure 23: Hydrogen-Deuterium Exchange: Reaction Profile Showing Exchange with and without Benzene in the Reaction Mixture
Figure 24: Hydrogen-Deuterium Exchange: Showing Exchange With and Without Benzene in The Reaction Mixture
Figure 25: Carbon Dioxide Poisoning Curve for Hydrogen-Deuterium Exchange; Fraction of Exchange not Poisoned Per Number of Carbon Dioxide molecules [data from Van Cauwelaert and Hall(16)]
of the second reaction or to 2.2% of that of the first.

A third experiment was performed in which four times the amount of benzene of the second experiment was used. Qualitatively, it showed that the \( \text{H}_2-\text{D}_2 \) exchange was not completely halted even though more than four times the number of molecules of benzene were available than the number of sites found by CO\(_2\) poisoning.

VI-11 Catalyst Pretreatment Time

Catalyst pretreatment is one of the big factors in catalyst activity (16). To minimize this as a source of error the pretreatment for every reaction was kept as nearly the same as possible.

To conserve time, a procedure was chosen which utilized a fairly short oxygen treatment and dehydration time. Treatment in oxygen (530\(^\circ\)) is mainly for removing residual hydrocarbons from the surface. However, dehydration time and temperature, as discussed in Section III-1, have considerable effect on the catalyst activity.

To check the effect of the short dehydration time (2 hours), two experiments (shown in Table I) were run with dehydration times of 8 and 12 hours. For both the activity of the catalyst increased less than 6.5% compared to the previously run experiment. Overall, the largest variation in activity from one experiment to another was 7% with the average being 2.5%. 
VII. DISCUSSION

The results of this work conform in almost all respects (except activation energy) to those reported in several of the investigations discussed in Sections II-3 and III-1.

Comparison of the rates of D₂ exchange with benzene and H₂ exchange with deuterated benzene shows a large primary isotope effect, $K_H/K_D = 18$. This agrees with similar results for olefins (20) and methane (13). H₂-D₂ exchange is much faster than either of the benzene exchange reactions, essentially reaching equilibrium in only 8 minutes, which seems to indicate that cleavage of a C-H or C-D bond is involved in the rate-limiting step of the exchange.

McCosh and Kemball (19), on the basis of similar activation energies for exchange of several different compounds with D₂, proposed that exchange takes place with deuterium atoms present in special OD groups on the catalyst and that the rate-limiting step is the conversion of OH to OD at these sites. As pointed out previously, more recent evidence concerning hydrogen exchange with the OH groups shows this to be an unlikely explanation. The experiment performed in this work, showing no difference in activity for a deuterated or an undeuterated catalyst does not support McCosh and Kemball's proposal.

The one area where results of this investigation fail to agree with those previously published is in the activation energy determination. McCosh and Kemball reported an activation energy of
6.0 ± 0.5 kcal/mole for D$_2$-benzene exchange over their alumina catalyst. In addition, several molecules mentioned in Section II-3 have energies close to 6.0 kcal/mole. In this work a value of 4.3 ± 0.3 kcal/mole was found. No explanation is apparent for this discrepancy. McCosh and Kemball also reported a rate constant of 1%//(min.0.1g) at 27° as compared to the value of 5.05%//(min.0.1g) at 20° found in this investigation.

Because of the nature of this work, one of the concepts for comparing catalytic activity takes on added importance. With the number of active sites known, a "turnover number" defined as the number of D atoms exchanged per second per site can be calculated. The usefulness of this type of calculation is usually limited by the fact that an estimation of the number of sites is necessary. The number determined from the D$_2$-benzene exchange data, 0.042 D atoms exchanged/(sec. site), indicates that the "residence" time of the hydrocarbon on an active site is 24 seconds before an exchange is completed.

As a result of the H$_2$-D$_2$ exchange experiments it seems evident that chemisorption of hydrogen is blocked, to a large extent, by benzene on some of the active sites. Redistribution of hydrogen and deuterium atoms among the benzene isotopes occurred much faster than exchange with hydrogen or deuterium from the gas. Similar characteristics were exhibited by olefin exchange and redistribution on alumina (20). Thus, if hydrogen is eliminated from the stronger
sites by the benzene, scrambling can occur much faster than exchange, since the chance of having two benzene molecules in close proximity on the surface is greater than having a benzene and hydrogen.

The fast redistribution reaction invalidates any conclusions about reaction mechanism derived from the reaction multiplicity, M. A value of M = 1 theoretically implies that the exchange is stepwise. Regardless of how many deuterium atoms from the gas are exchanged into the benzene for each interaction with the surface, the redistribution among benzene isotopes is so much faster that an equilibrium distribution is maintained. The M value is always equal to one in this situation.

In contrast to the aromatic and olefinic systems, Larson and Hall (13) reported that the CD₄-CH₄ redistribution rate was the same as H₂-CD₄ exchange. Also olefins poisoned these reactions. McCosh and Kemball found ring exchange of alkyl-benzenes to be much greater than side-group exchange, so it appears that olefinic and aromatic species are very strongly chemisorbed on the active sites, possibly in a dissociative manner, to the exclusion of paraffins and hydrogen. The blocking of hydrogen exchange by methane adsorption is not so great as with benzene, since the methane redistribution and exchange occur at the same rate.

Only the vinyl hydrogen atoms of olefins were able to undergo exchange below 100° in the reactions investigated by Hightower and Hall (20, 22). A dissociative mechanism was most likely, probably
taking place on an "acid-base" site. Peri (30) found these types of sites react dissociatively with NH\textsubscript{3} to form Al-NH\textsubscript{2} and Al-OH surface species. If a benzene molecule were dissociatively chemisorbed in this manner, it could return to the gas phase by recombining with its own hydrogen or with a hydrogen on a nearby site.

It appears that any exchangeable hydrogen on the surface must be held on a special site. In redistribution reactions this H atom, probably held as an Al-OH species, can only come from another chemisorbed benzene, since there is no exchange with the catalyst hydroxyls. The fact that corresponding species (C\textsubscript{6}H\textsubscript{6}-C\textsubscript{6}D\textsubscript{6}, etc. :See Section VI-4) disappear or are formed at the same rate for redistribution, while exchange exhibits a strong isotope effect, is another indication of the lack of an "outside" source of hydrogen. For example, suppose hydrogen or deuterium from catalyst hydroxyls had exchanged with the benzene. The C\textsubscript{6}H\textsubscript{6} species would have disappeared faster than the C\textsubscript{6}D\textsubscript{6} and the corresponding C\textsubscript{6}H\textsubscript{5}D would have appeared at a faster rate than the C\textsubscript{6}D\textsubscript{5}H due to the isotope effect. If, instead, the C\textsubscript{6}D\textsubscript{6} could only get a hydrogen by exchange with C\textsubscript{6}H\textsubscript{6}, the rate of disappearance of both would be the same.

For poisoning both the D\textsubscript{2}-benzene exchange and the redistribution reaction, the number of CO\textsubscript{2} molecules necessary (14.5 and 15.5 \times 10^{12}\text{CO}_2/\text{cm}^2) is approximately the same. Moreover, the number is only slightly larger than the number (14 \times 10^{12}\text{CO}_2/\text{cm}^2), reported by Hightower and Hall (20), necessary to poison the D\textsubscript{2}-cyclopentene
exchange on a similarly pretreated alumina catalyst. Figure 25 is a "poisoning" plot derived from data of Van Cauwelaert and Hall (16) for CO\textsubscript{2} poisoning of H\textsubscript{2}-D\textsubscript{2} exchange over an alumina catalyst pretreated at 500°. Its shape and intercept correspond closely to the plots of this investigation. In addition to the other factors already mentioned, the almost exact correspondence of the exchange and redistribution plots and the similarity of the H\textsubscript{2}-D\textsubscript{2} exchange curve indicates that the same or closely related sites are active for all three reactions.

The curvature of the poisoning plots suggests a heterogeneous distribution of sites with the initial steepest slope caused by chemisorption on the strong sites. CO\textsubscript{2} desorption curves of Van Cauwelaert and Hall (16) support this contention. As the activity of the catalysts is increasingly poisoned, the decided flattening of the curves is probably caused by adsorption of CO\textsubscript{2} on sites which do not enter into the reaction. Therefore, it must be understood that the number of CO\textsubscript{2} molecules calculated to be necessary to poison the catalyst is only an upper bound.

Carbon dioxide chemisorbs in several different ways. Weak adsorption sites, the α-sites, (Van Cauwelaert and Hall found 10 to 15 x 10\textsuperscript{12} α-sites/cm\textsuperscript{2} on their alumina catalysts) lose CO\textsubscript{2} through evacuation at 100° and can be removed more readily than other forms of chemisorbed CO\textsubscript{2}. It was actually necessary to do this prior to removing other forms of CO\textsubscript{2} poisoning the H\textsubscript{2}-D\textsubscript{2} exchange (16). These α-sites apparently are not necessary for exchange of benzene.
A second type of more strongly chemisorbed CO₂ has been investigated by Peri (32) and others (41) using infrared techniques. The bands produced were attributed to surface bicarbonate or stable carboxylate and carbonate structures. The bicarbonate structure and the subsequent shifting of the bands characterizing it when OH groups are changed to OD on the catalyst surface indicate a hydroxyl associated with this type of site. These are probably the sites measured in the CO₂ poisoning experiments.

The radioactive C¹⁴O₂ study confirmed the existence of several types of sites. After the catalyst had adsorbed just enough C¹⁴O₂ to poison its activity, it was still capable of adsorbing more. In addition, it was necessary to desorb this latter C¹⁴O₂ before any of the poisoned active sites could be uncovered.

The other poisons listed in Section VI-8 seemed to have only a small effect on the catalyst activity, even when the amount used was three times the amount of CO₂ necessary for complete poisoning. Moreover, they all seemed to have about the same effect (except for O₂, which had none) and incomplete adsorption, even when small amounts were used, was observed for NO and CO.

Either these materials did not chemisorb in the same manner as CO₂ or else they were prevented from adsorbing. Nitric oxide poisoned the CD₄-CH₄ redistribution reaction of Larson and Hall to the same extent as CO₂. And recently Parkyns (42) reported that carbon monoxide adsorbed instantly on alumina at room temperature followed by the slow development of the bicarbonate surface structure (as
shown by developing infrared bands). He suggested this oxidation occurred on the "acid-base" sites. And although Peri (30) stated that ammonia was desorbed at room temperature mainly as molecular ammonia, it has been used to measure the number of acid sites on alumina. So it appears that these materials are capable of chemisorbing on the types of sites proposed for the exchange reactions, but are possibly prevented from doing so by the more strongly adsorbed benzene.

The sparcity and strength of the CO$_2$ chemisorption (compared to $2 \times 10^{15}$ lattice sites/cm$^2$ and $4 \times 10^{16}$OH/cm$^2$) suggests that a rather special surface configuration is a requirement of the sites involved - for example, a triplet vacancy or a doublet vacancy with an adjacent hydroxyl group. The formation of a bicarbonate species upon chemisorption of CO$_2$ implies that a substantial fraction of the measured sites has an adjacent hydroxyl. Parkyns (41) used the following scheme to account for most of the reactions he observed when CO$_2$ was added to the alumina.

```
\begin{center}
\begin{tikzpicture}
    \node (a) at (0,0) {OH};
    \node (b) at (-1,0) {Al};
    \node (c) at (1,0) {Al};
    \node (d) at (2,0) {Al};
    \node (e) at (3,0) {OH};
    \node (f) at (2.5,-0.5) {Al};
    \node (g) at (2.5,0.5) {Al};
    \node (h) at (2.5,1.5) {Al};
    \draw (a) -- (b);
    \draw (a) -- (c);
    \draw (a) -- (d);
    \draw (b) -- (0.5,0);
    \draw (c) -- (1.5,0);
    \draw (d) -- (2.5,0);
    \draw (e) -- (2.5,-1);
    \draw (f) -- (2.5,-2);
    \draw (g) -- (2.5,-3);
    \draw (h) -- (2.5,-4);
    \node (i) at (5,0) {CO$_2$};
    \node (j) at (6,0) {OH};
    \node (k) at (6.5,0) {Al};
    \node (l) at (7.5,0) {Al};
    \node (m) at (8.5,0) {Al};
    \node (n) at (8.5,1) {OH};
    \node (o) at (7.5,1.5) {Al};
    \node (p) at (7.5,2.5) {Al};
    \node (q) at (7.5,3.5) {Al};
    \node (r) at (7.5,4.5) {Al};
    \draw (i) -- (j);
    \draw (i) -- (k);
    \draw (i) -- (l);
    \draw (j) -- (6.5,0.5);
    \draw (k) -- (7.5,0.5);
    \draw (l) -- (8.5,0.5);
    \draw (m) -- (8.5,1);\draw (n) -- (8.5,1.5);
    \draw (o) -- (8.5,2.5);
    \draw (p) -- (8.5,3.5);
    \draw (q) -- (8.5,4.5);
\end{tikzpicture}
\end{center}
```
If this mechanism is correct, then the reactive OH groups are likely to be adjacent to sites where CO$_2$ is initially adsorbed. These sites appear to be vacant sites (exposed aluminum ions). The development and existence of these "high energy" sites on alumina is discussed in connection with Peri's work in Section III-1.

It seems most likely that the benzene molecule is adsorbed in a dissociative process on the "acid-base" sites forming an adsorbed phenyl (Al-\(\bigcirc\)) and an Al-OH. These sites are probably "strained" Al-O-Al linkages or else exposed aluminum ions with adjacent Al species. The H is then free to recombine with the parent molecule or with another close by.

CO$_2$ studies have shown that OH groups are likely to be adjacent to the active site. In view of the possibilities, it would appear that the high energy "strain" sites formed during dehydration of the catalyst are active in the dissociative adsorption of benzene and therefore are the catalytic agents in the reaction.
VIII. SUMMARY AND SUGGESTIONS

In agreement with Hightower and Hall (20), $14.5 \times 10^{12} \text{CO}_2/\text{cm}^2$ were necessary to completely poison the exchange reaction. Moreover, this investigation has expanded the knowledge in this area of study of the alumina catalysts by showing that $15.5 \times 10^{12} \text{CO}_2/\text{cm}^2$ were necessary to poison the $\text{C}_6\text{H}_6-\text{C}_6\text{D}_6$ redistribution reaction and, that the same sites were probably active for both reactions. Radioactive $\text{C}^{14}_2\text{O}_2$ poisoning emphasized the heterogeneous nature of the sites, showing that more sites chemisorb $\text{CO}_2$ than are necessary for reaction. Results with other poisons were inconclusive for direct study of the active sites.

$\text{D}_2$-benzene exchange was 1.8 times as fast as corresponding $\text{H}_2$-perdeuteriobenzene exchange; however, when the two isotopes were reacted together without any source of outside hydrogen the resulting equilibration among the species was many times faster than either of the exchange reactions. This, together with the fact that benzene poisons the $\text{H}_2-\text{D}_2$ exchange reaction, is a possible indication that benzene is more strongly adsorbed than hydrogen.

As discussed, the lack of a large effect from the poisons other than $\text{CO}_2$ on the exchange could possibly be a result of their being excluded from the surface by the benzene. From the current knowledge, a ranking of materials by strength of adsorption can be proposed: $\text{CO}_2 >$ aromatics and olefins $> \text{NO,CO,NH}_3 >$ paraffins.
There are several areas in which this work could be continued. The mathematical analysis was simplified and unsatisfactory because it did not allow a way of directly comparing exchange and redistribution reactions. The theory has been developed (36) which relates stepwise, multiple exchange, and redistribution reactions. Because of the actual mechanism of reaction and conditions, this theory cannot readily be applied to the redistribution reactions. Although some attempt was made to do this, no satisfactory results were achieved. However, with more time, the reaction and equations could be adjusted in order to directly compare the data.

A continuation of the poisoning study using ammonia might prove interesting. If indeed, this molecule is being excluded from the surface by the benzene, it still might be able to adsorb slightly, as in the case of the H₂-D₂ exchange. A D₂ exchange reaction with ammonia might occur in this case.

The activation energies of the reactions deserves further study, especially in view of the contradiction between McCosh and Kemball's theory of catalyst hydroxyl exchange being the limiting step, and the existence of an isotope effect.

Employing the concept of "turnover number" another area of study could be explored. For example, pressure dependency studies could be made by varying the partial pressure of the benzene in the exchange reactions. The effect of this on the rate and "turnover number" could be used to help determine the order of the reaction.

Finally, there are many variations of reactants, reaction condition, and pretreatment which might prove useful.
APPENDIX

A-1 Development of Mathematical Equations
A-2 Mathematical Computation
A-3 Radioactive Carbon Dioxide Measurements
A-4 Alumina Catalyst Surface Area
A-l Development of the Mathematical Equations

Section III-4 gives a summary of the equations used for the analysis of data in this investigation. Although these can be derived in several ways, the development of Bolder, Dallinga, and Kloosterziel (36) will be given.

If $\text{AH}_{N-i} \text{D}_i$ is a hydrocarbon molecule, the reaction system for stepwise exchange can be written

$$\text{AH}_{N-i} \text{D}_i + \text{D}_i \rightarrow \text{AH}_{N-i-1} \text{D}_{i-1} + \text{H}_1,$$  \hspace{1cm} i = 0, 1, \ldots, N-1 \ (A1)

Provided that there is no kinetic isotope effect, the corresponding rate equations are

$$\frac{d}{dt} d_i = k \frac{[\text{(N-i-1)}d_{i-1}s - (N-1)d_is - id_1r + (i+1)d_{i+1}r]}{N} \hspace{1cm} i = 0, 1, \ldots, N \ (A2)$$

Terms with indices beyond the range of $i$ must be discarded.

The following definitions are used:

(a) $d_i$ is the fraction of molecules having $i$ deuterium atoms

(b) $\sigma$, the mean deuterium fraction of the hydrocarbon,

$$\sigma = \frac{1}{N} \sum_{i=0}^{N} id_i$$

(c) $a = \text{the total number of "hydrogen" atoms in the hydrocarbon}$

divided by the total number of "hydrogen" atoms in the deuterating agent

(d) $s = \text{the fraction of deuterium in the total "hydrogen" of the}$

deuterating agent

(e) $s + a\sigma = \text{constant}$
(f) $k =$ rate constant per hydrocarbon molecule in arbitrary concentration units

(g) $r = 1 - s$

Defining a new time scale
$$\tau = \int_{t'=0}^{t} \frac{k(t')}{N} \, dt'$$  \hspace{1cm} \text{(A3)}$$

equation (A2) becomes
$$\frac{d}{d\tau} d_{i} = (N-i-1)s d_{i-1} - [(N-i)s + i r] d_{i} + (i + 1) r d_{i+1}$$
$$i = 1, 2, \ldots, N$$  \hspace{1cm} \text{(A4)}$$

Putting this into matrix form gives
$$\frac{d}{d\tau} D = FD$$  \hspace{1cm} \text{(A5)}$$

where
$$D = \begin{pmatrix} d_0 \\ d_1 \\ \vdots \\ d_N \end{pmatrix}$$  \hspace{1cm} \text{(A6)}$$

and
$$F_{i,i-1} = (N-i-1)s$$
$$F_{i,i} = -(N-i)s - ir$$  \hspace{1cm} \text{(A7)}$$
$$F_{i,i+1} = (i+1)r$$

Equation (A5) along with the equation
$$s + a \sigma = \text{constant} = s(0) + a \sigma(0) = S(\infty) + a \sigma(\infty)$$  \hspace{1cm} \text{(A8)}$$
forms a complete set of equations.

Using the transformation
$$U = P \, D$$  \hspace{1cm} \text{(A9)}$$

where
$$P_{i,j} = (-1)^{j-i} \frac{j!}{i!(j-i)!}$$  \hspace{1cm} \text{(A10)}$$
the rate equation in \( U \) becomes
\[
\frac{d}{dT} (U_i) + iU_i = -(N-i-1)sU_{i-1}
\] (A11)

since \( U_0 = \sum_{i=0}^{N} d_i = 1 \) and \( U = -\sum_{i=0}^{N} id_i = -N\sigma \)

then \( \frac{d}{dT} (U_0) = 0 \) and \( \frac{d}{dT} (U_1) + U_1 = -N \)

or \( \frac{d}{dT} \sigma + \sigma = s \)

Using equation (A8) this becomes
\[
\frac{d}{dT} (s - \sigma) = -(1 + a)(s - \sigma)
\]

which can be integrated to give
\[
s - \sigma = [s(0) - \sigma(0)] \exp[-(1+a)T] \] (A12)

Thus, the difference between the deuterium fraction in the hydrocarbon and in the deuterating agent changes exponentially with time and so
\[ s(\infty) = \sigma(\infty). \]

Substitution into equation (A12) gives
\[
\sigma - \sigma(\infty) = [\sigma(0) - \sigma(\infty)] \exp[-(1+a)T] \] (A13)

If the rate constant, \( k \), does not vary with time then \( \tau = kt/N \) and equation (A13) is the same as equation (4) of Section III-4.

The equation \( s - s(\infty) = [s(0) - s(\infty)] \exp[-(1+a)T] \) (A14)

also results and the knowledge of \( s \) as a function of time allows
the integration of equation (A11) in the form
\[
\frac{d}{dT} U_i + iU_i = f(T) \] (A15)

Using the special initial condition, \( d_0(0) = 1 \) (i.e., no deuterium initially in the hydrocarbon), the integration gives, after some manipulation
\[ d_1 = \binom{N}{i} \sigma^i (1 - \sigma)^{N-i} \quad i = 1, \ldots, N \quad (A16) \]

where \( \sigma = 1 - \sigma^* \). This equation describes the stepwise deuteration reaction for each instant of time and represents a binomial distribution of deuterium over the hydrocarbon.

Bolder et al. extended their development to include the multiple exchange reaction and redistribution reaction. Because the multiple exchange equations do not apply in the benzene situation, they will not be discussed.

In redistribution reactions (equilibration between the isotopic species), there is no source of outside deuterium and so

\[ s = \sigma = \sigma(0) = \frac{1}{N} \sum_{i=0}^{N} i \ d_1 \quad (A17) \]

Therefore, equation (A13) does not hold.

However, a rate law for redistribution can be developed (a special case of multiple exchange equations) resulting in the form

\[ u_2 - u_2(\infty) = [u_2(0) - u_4(\infty)] \exp[-m_2 \tau] \quad (A18) \]

where

\[ u_2 = \sum_{i=2}^{N} \frac{i!}{2(i-2)!} \ d_1 \quad (A19) \]

and

\[ u_2(\infty) = \binom{N}{2} s^2 \quad (A20) \]

This is not as general as equation (A13); it may be affected both by the mechanism and the initial conditions of the reaction.

If equation (A18) does not hold for \( u_2 \), there is always some other \( u \) (but not \( u_2 \) as defined by equation (A19)) that varies
exponentially (36). For the benzene redistribution reaction \( u_2 \)
equation (A19) did not satisfy equation (A18), but the function
\[
u = \sum_{i=0}^{3} i d_i + \sum_{i=4}^{6} (6 - i) d_i \quad (A21)
\]
did.

From the comparison of equations (4) and (A13) it can be seen that \( \phi_\infty = \frac{N}{(1 - a)} \) and since \( a \) is defined as the ratio of exchangeable "hydrogen" atoms (H) in the hydrocarbon to the exchangeable "hydrogen" atoms (D) in the deuterating agent, \( \phi_\infty = \frac{N}{H + D} \).

Plots of \( \ln(\phi_\infty - \phi) \) for \( \phi \) and \( \phi' \) and \( \ln (u_\infty - u) \) for the \( u \) of equation (A21) versus time should be linear and from the slope, the rate constants can be calculated. The equations presented use "fraction of the total hydrocarbon" instead of "percent" (as Kemball does) to represent the isotopic distribution, and therefore, the rate constants differ by a factor of 100. Rates expressed as \( \%/(\text{min} \times 0.1 \text{g}) \) are convenient for comparing catalyst activity, and so all values presented as data will be the rate constant, calculated from the equations presented in Section III-4, multiplied by 100.

Hydrogen-deuterium exchange is a special case of the redistribution reaction for which \( N = 2 \) and \( u_2 = d_2 \) (from equation (A19): \( d_2 = \) fraction of \( D_2 \) in the mixture). Since \( d_0 \) (fraction of \( H_2 \)) and \( d_1 \) (fraction of HD) are linearly related by the material balance, they also follow exponential kinetics. In fact the equation
\[
[FHD] - [FHD]_\infty = ([FHD]_0 - [FHD]_\infty) \exp(-2kt) \quad (A22)
\]
which has been used in other investigations (18, 20) is the same as equation (A18). Equation (A22) was used to analyze \( H_2-D_2 \) exchange
data with either experimental equilibrium data or equation (A20) used to calculate $[\text{FHD}]_\infty$. 
Mathematical Computations

A. Benzene Reactions

A Fortran IV computer program was used as an aid in the computation necessary to reduce the data to a usable form. In Section III-4, the equations which should be satisfied by the exchange data are discussed.

The peak heights of each benzene isotope were measured from recorded scans across the m/e range of 78 to 84. Since the strip chart recorder had been allowed to run continuously during each experiment, the time of each isotope peak could be determined from its position on the chart. Plots of the peak heights against time were made, from which the peak height of each isotope at the same point in time was measured. These measurements were entered as data in the computer. The interval between measurements was generally three minutes, except at the beginning of the reaction and at other critical points.

From the values of the parent peak height and first $^{13}C$ isotope peak determined for the "blank" sample before each experiment, the $^{13}C$ isotope correction was calculated by the program. This correction was generally the average of four scans, and for all the experiments averaged 6.36%. The $^{13}C$ correction was then applied to each of the isotope peaks in turn, and the true peak heights were calculated. From these true peak heights the fraction of each benzene isotope in the sample was determined. Using the fraction of each isotope, the various $r$'s defined in Section III-4 were calculated.

From this point on, the program diverged, with the calculations depending on the type of reaction being analyzed. The calculation will be discussed in the following parts.
Deuterium Exchange with Benzene

For the $D_2$-benzene exchange, the value for $\ln(\phi_\infty - \phi)$ was calculated by the program using $\phi = \sum_{i=0}^{6} d_i$. In order to do this, an expression for $\phi_\infty$ was needed. First, consider the following definitions:

Press "H": The pressure of the deuterium or hydrogen gas used in the exchange

Press "HC": The pressure of the benzene used in the exchange

$PD_2$: The fraction of the deuterium or hydrogen gas which is $D_2$

$FH_2$: The fraction of the deuterium or hydrogen gas which is $H_2$

$FHD$: The fraction of the deuterium or hydrogen gas which is HD

$PD$: An artificial pressure equivalent to the number of exchangeable $D$ atoms in the reaction mixture. The expression for this is $PD = \text{Press } "H"(2PD_2 + FHD)$.

$PH$: An artificial pressure equivalent to the number of exchangeable $H$ atoms. This also includes the $H$ atoms of the benzene, and is $PH = \text{Press } "H"(2FH_2 + FHD) + 6 \times \text{Press } "HC"$.

Using these definitions, the expression for $\phi_\infty$ is $\frac{6 \times PD}{PH + PD}$.

This is equivalent to the expression given in Section A-1 of the Appendix.

Hydrogen Exchange with Perdeuteriobenzene

$H_2-C_6D_6$ is just the reverse of the $D_2$ benzene reaction. If the $H$'s and the $D$'s of all the expressions just given were switched, the
expressions would apply to \(H_2C_6D_6\) exchange (i.e., the hydrogen takes the place of the deuterium in this reaction). However, using

\[
\phi' = \sum_{i=0}^{6} (6-i) d_i
\]

accomplishes this without any switch. This is the expression the computer program used in calculating \(\ln (\phi'_\infty - \phi)\).

To determine \(O'_\infty\) it was necessary to make the switch. The composition of the deuterated benzene was also taken into account, since both H and D atoms are present in it. (See Section IV-2-B.)

\[\text{C}_6\text{D}_6 - \text{C}_6\text{H}_6 \text{ Redistribution}\]

\[\ln (u_\infty - u) \text{ using } u = \sum_{i=0}^{3} i d_{1} + \sum_{i=4}^{6} (6-i)d_{1}\]

was calculated by the program for the redistribution reaction. To calculate \(u_\infty\) it was assumed that the equilibrium mixture would be a binary distribution from which all the \(d_{1}\)'s could be determined. Although the initial mixture was 50:50 in the benzenes, this assumption is only approximate because of the isotopic impurity of the deuterated benzene sample.

Plotting the values of \(\ln(\phi_\infty - \phi)\) and \(\ln(u_\infty - u)\) against time resulted in straight lines for all of the experiments. From the slopes of the plots for the exchange reactions the rate constant, \(k\phi = -\text{slope} \times (100\ \phi_\infty)\), was calculated. The rate constant for the redistribution reaction was calculated using the same expression, however the manner of plotting the data for redistribution did not allow for the direct comparison with the exchange rate constant.

The initial rate of disappearance of the benzene, \(k_0\), in the exchange reactions was determined using equation (5); \(d_o\) was the
fraction of unsubstituted benzene calculated by the computer program for each sample. From ko and the rate constant, kφ, the M value for the initial exchange of each experiment was determined.

B. Activation Energy of the D2-Benzene Exchange

Activation energy was calculated using the Arrhenius' law:

\[ k = k_0 e^{-\frac{E}{RT}} \]

A plot of \( \ln k \) versus \( 1/T \) should give a straight line. From the slope and the relation, \( E = -\text{slope} \cdot R \), the activation energy, \( E \), was determined.

C. Carbon Dioxide Poisoning

Poisoning experiment data was handled in the same manner as that for the unpoisoned reactions. Reaction profiles for poisoning experiments were continuous showing a break only at the time of poisoning. The plots of \( \ln(\phi_\infty - \phi) \) and \( \ln(U_\infty - U) \) showed a sharp break from one straight line section to the other.

The ratio of the poisoned reaction rate to the unpoisoned rate, \( k^p_\phi/k_\phi \), giving the fraction of activity not poisoned for an experiment, was plotted against the number of CO2 molecules per cm^2 of the catalyst. The number of CO2 molecules was calculated from the known volume of the doser and the temperature and pressure of each dose. The intercept on the abscissa gave the number of molecules necessary to completely poison the catalyst.
D. Radioactive Carbon Dioxide Poisoning

The rate constants for the radioactive Cl4O2 poisoning experiment were calculated in the same manner as described above. The more difficult part of the analysis was the determination of the true specific activity of each sample. After the first dose of Cl4O2 had been adsorbed, the catalyst was bypassed and another similar dose of Cl4O2 was admitted to the circulation stream. Since sampling reduced the amount of material in this stream, without reducing correspondingly the amount of Cl4O2 on the isolated catalyst, the specific activity of the gas phase later in the experiment, when the Cl4O2 was desorbed, was erroneously high. In order to correct for this, the following calculation procedure was followed.

First, the specific activity (counts per minute per torr) of each sample was calculated. The statistical counting error was also determined. Second, the average activity of one dose of Cl4O2 in the gas phase was found from the measured activity of the second dose admitted. When part of the initially adsorbed Cl4O2 (and consequently unreduced by previous sampling) was desorbed at 96°, the average gas phase activity was subtracted from the total amount of activity. The remaining activity resulted from the desorbed Cl4O2 and it was therefore, necessary to correct this figure for the volume reduction which had taken place. The average reduction was 2.74% per sample and so the specific activity of the desorbed Cl4O2 was reduced 2.74% for each of the four samples taken prior to the desorption. Combining this corrected value
with the gas phase value originally subtracted gave the corrected specific activity of the reaction mixture at 96°. Similar corrections were made each time the temperature was raised. The results attest to the applicability of this calculation.

E. Hydrogen-Deuterium Exchange

To plot the H\textsubscript{2}-D\textsubscript{2} exchange rate, equation (12) was used. The necessary fragmentation corrections have been discussed in Section IV-2-C. H\textsubscript{2}-D\textsubscript{2} exchange was extremely rapid at 20° and the equilibrium values were estimated from the data. Since benzene slowed the reaction to the extent that equilibrium was not reached, the value of \( \text{FHD}_\infty \) found by this method was also used in the calculations for the second part of the experiment.
A-3 Radioactive $^{14}_{\text{Cl}}O_2$

Figure A-3-1: Operating voltage plateau curve

Figure A-e-2: Pressure dependency curve of the detection system
Figure A-3-1: Operating Voltage Plateau Curve

Nuclear-Chicago Ultrascalar; Geiger-Muller Detector
Figure A-3-2: Pressure Dependency Curve of the Radioactive Detection System

(Using a Butadiene-$^{14}C$, Butene Mixture)
The surface area of new GA-48 alumina is 158 m²/g. It was felt that it would be instructive to redetermine the surface area for a sample which had been used extensively in other investigations (20,22). The following two figures show the results for a 0.4 g sample of previously used alumina.

Figure A-4-1: Nitrogen adsorption isotherm at -195°

Figure A-4-2: B.E.T. surface area measurement with nitrogen
Figure A-4-1: N\textsubscript{2} Adsorption Isotherm at -195\degree C:

0.4 g GA-48 Alumina

\( P_0 = 775.5 \) torr
Figure A-4-2: B.E.T. Surface Area Determination:
0.4 g GA-48 Alumina

\[ P = \frac{P_o (P_o - P)}{V_a} \times 10^2 \]

\[ P_o = 775.5 \text{ torr} \quad \text{S.A.} = 141.05 \text{ m}^2/\text{g} \]
LITERATURE CITED


20. Hightower, J. W. and Hall, W. K., (to be Published)


