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The Exchange with Deuterium of Two Cycloalkanes on Palladium Films.

π-Bonded Intermediates in Heterogeneous Catalysis

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The catalytic exchange of 1,1,3,3-tetramethylcyclohexane and 1,1-dimethylcyclobutane with deuterium on palladium films has been studied by means of a mass spectrometer.

The results for 1,1,3,3-tetramethylcyclohexane provide further evidence for the theory that π-bonded intermediates are important in various reactions of hydrocarbons on transition metal catalysts. Some improvements in the details of the mechanistic aspects of this theory, presented in a recent report, are also suggested.

Reasons are given for the anomalous behavior of 1,1-dimethylcyclobutane, which has little tendency to exchange by a multiple process in contrast to the other cycloalkanes previously investigated.

INTRODUCTION

The exchange of several polymethylcyclopentanes with deuterium on metal films (*1*, *2*) has provided evidence for the theory that catalytic activity of transition metals for many hydrocarbon reactions is due to intermediate formation and decomposition of π-bonded organometallic complexes. Mechanistic aspects of this theory have been developed in some detail (*2*) and can be summarized as follows.

Saturated hydrocarbons and olefins not only react by the interconversion of mono- and 1,2-diadsorbed σ-bonded intermediates ($\alpha\beta$ exchange process) but, if there is a chain of three or more carbon atoms none of which is quaternary or occupies a bridgehead position, an allylic species π-bonded to one metal atom can also form. If the number of carbon atoms permits the π-allyl intermediate can also interconvert with other similar species having more extensive π-electron systems. The $\alpha\beta$ process takes place by the addition and removal of one hydrogen atom at a time from and to the surface. On the other hand, the π-bonded species can also react with a hydrogen molecule with addition of one atom to the planar complex on the side away from the surface. Thus the outermost carbon atoms in the π-bonded species interchange between the sp^2 and sp^3 hybridized state and the two possible ways of adding and removing a hydrogen atom allow inversion of these carbon atoms. Aromatic hydrocarbons and conjugated diolefins are chemisorbed directly as π-bonded complexes and can react with hydrogen in the same way.

The exchange of various cycloalkanes with deuterium on metal films, especially those of palladium (*2*, *3*, *4*) clearly shows that two processes can operate in these reactions. The first process only allows initial exchange of hydrogen atoms on one side of the ring in these compounds and is the $\alpha\beta$ exchange process. The second allows initial exchange of hydrogen atoms on both sides of the ring and is believed to involve π-bonded intermediates. Direct conversion of σ-bonded diadsorbed species to the π-allyl intermediate was also thought to be possi-

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ble and to proceed via a transition state involving a π-bonded olefinic complex.

The compounds investigated in the present work were chosen because their structural features are highly suited for further testing of this theory. There is only one possible way in which a π-allyl intermediate could be formed in each case and the carbon atoms of interest are all part of the ring structure. Since *gem*-dimethyl groups block the propagation of exchange (*2*) initial replacement of hydrogen atoms is limited to those on these three carbon atoms. These hydrogen atoms are therefore divided into two groups of three with one group on each side of the ring. The initial exchange of the first group could be explained by the $\alpha\beta$ process but the π-allyl intermediate should only allow replacement of two hydrogen atoms in the second group. This prediction is based on the fact that the middle carbon atom of the π-allyl complex cannot revert to sp^3 hybridization while the other two are sp^2 hybridized and consequently there is no way in which the hydrogen atom on the upper side of the ring at this middle carbon atom can be easily replaced if the mechanism is correct.

EXPERIMENTAL

The apparatus and method of preparing palladium films have been described previously (*5, 6*). Palladium wire of "spectrographically standardized" quality was obtained from Johnson Matthey and deuterium was prepared by electrolysis of 99.5% heavy water and purified by diffusion through palladium.

The hydrocarbons which have not previously been recorded in the literature were synthesized by Mr. J. J. McCullough of this department and details will be published elsewhere. The compounds were purified to 100% purity by the method of preparative gas–liquid chromatography and their structure was confirmed by infrared analysis, and quantitative determination of carbon and hydrogen content. Their mass spectra also agreed with expectation. The reaction mixture consisted of partial pressures of 2 mm and 20 mm of Hg for hydrocarbon and deuterium, respectively, in each experiment and this corresponded to 1.4×10^{19} molecules of hydrocarbon in the reaction vessel.

Cycloalkanes with *gem*-dimethyl groups give extremely small parent peaks in the mass spectrometer and thus the pseudoparent peaks corresponding to the loss of a methyl group were used in analysis. The voltage for the ionizing electrons for 1,1,3,3-tetramethylcyclohexane was 18 volts and this was raised to 50 volts for 1,1-dimethylcyclobutane in order to increase the intensity of the pseudoparent peaks which were quite small as the molecule fragments mainly to C_2 and C_4 ions. In each case the usual corrections were made to allow for naturally occurring heavy carbon and deuterium and for formation of fragment ions involving the loss of hydrogen or deuterium atoms from the pseudoparent ion.

RESULTS

Initial distributions of products together with the corresponding mean deuterium numbers (M) for 1,1,3,3-tetramethylcyclohexane at four different temperatures are given in Table 1. The films employed at the two higher temperatures had previously been used once for the same reaction to cause partial poisoning in order that the rate of exchange should be sufficiently slow to allow the initial distributions to be determined.

TABLE 1

INITIAL DISTRIBUTION OF PRODUCTS FOR THE EXCHANGE OF 1,1,3,3-TETRAMETHYLCYCLOHEXANE (I) AND 1,1-DIMETHYLCYCLOBUTANE (II)

Compound	I	I	I	I	II
Temperature (°C)	42°	110°	196°	324°	68°
d_1	39.5	28.7	19.5	14.7	88.1
d_2	3.0	3.9	4.9	8.0	10.5
d_3	12.6	8.0	5.2	2.6	1.4
d_4	8.1	14.1	8.1	3.4	—
d_5	36.0	39.2	36.4	17.9	—
d_6	0.8	6.1	24.5	46.4	—
d_7	—	—	1.4	5.8	—
d_8	—	—	—	1.2	—
M	3.01	3.49	4.16	4.70	1.13

Five hydrogen atoms were readily exchanged initially with only a very small amount of the d_6 isomer being formed at 42°C. The initial distribution of products at this temperature had maxima in the d_3 and d_5 isomers, respectively. At higher temperatures the maximum in the d_3 isomer disappeared and initial replacement of the sixth hydrogen became important so that the maximum eventually shifted from the d_5 to the d_6 isomer. Small amounts of d_7 and d_8 isomers were also formed initially at elevated temperatures. A logarithmic plot of the ratio of the concentrations of the d_6 and d_5 isomers against the reciprocal of absolute temperature gave a straight line, shown in Fig. 1, and the derived activation energy was 6.2 kcal/mole.

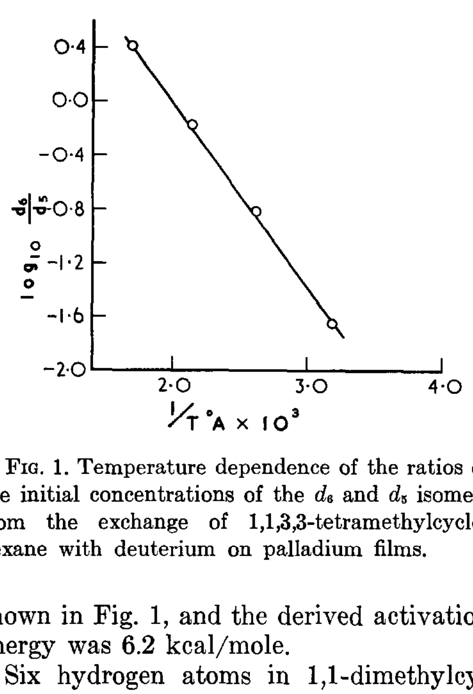

FIG. 1. Temperature dependence of the ratios of the initial concentrations of the d_6 and d_5 isomers from the exchange of 1,1,3,3-tetramethylcyclohexane with deuterium on palladium films.

Six hydrogen atoms in 1,1-dimethylcyclobutane were readily exchanged at 68°C but the initial replacement of only one hydrogen atom was predominant and the concentration of products in the initial distribution, which is given in the table, fell rapidly from the d_1 to the d_3 isomer.

After the reaction had proceeded for sufficient time to determine the initial distribution the temperature was raised and at 150°C the mass spectra of the products indicated that cracking had commenced. This reaction was allowed to proceed at 300°C until substantial conversion had occurred and analysis by gas–liquid chromatography showed that selective cracking to 2,2-dimethylbutane had taken place.

DISCUSSION

The initial replacement of hydrogen atoms on both sides of the ring in 1,1,3,3-tetramethylcyclohexane agrees with the behavior of 1,1,3,3,4-pentamethylcyclopentane (*2*) and contrasts with that of *nor*bornane (*4*) and 1,1,3,3-tetramethylcyclopentane (*2*) where initial exchange is limited to the hydrogen atoms on one side only of the rings on palladium catalysts. The results are therefore, further evidence that there is a distinction between the surface intermediates which are possible with a chain of three or more carbon atoms and a chain which is limited to two. Moreover, the maxima in the d_3 and d_5 isomers in the initial distributions of products at 42°C also show that two processes operate and that three intermediates must be involved. The difficulty of initially replacing the sixth hydrogen atom at lower temperatures is in full agreement with expectation and is very good evidence that the π-allyl intermediate is formed and can react with a deuterium molecule.

However, there is still some uncertainty about the nature of the diadsorbed intermediate. If this is σ-bonded to two metal atoms and is converted directly to the π-allyl intermediate then the transition state must involve the simultaneous breaking of a C–M bond, a change to sp^2 hybridization at two carbon atoms, and removal of a hydrogen atom from a third carbon atom. It is more likely that these changes occur in two steps and if this is true a π-bonded olefin must be regarded as an intermediate in the reaction and not merely as a transition state complex. The αβ exchange process is likely to be the interconversion of σ-bonded alkyl and π-bonded olefin with the latter only reacting readily with a surface deuterium atom in order to satisfy the condition that this process is limited to initial exchange of hydrogen atoms on one side only of the rings in cycloalkanes. The second process is the interconversion of a π-bonded olefin and a π-allyl intermediate. This modified mechanism has the advantage that all the intermediates are in turn ligands of the same metal atom so that the necessity of having two metal atoms conveniently spaced does not arise. Halpern (*7*) has concluded from studies of the hydrogenation of olefins homogeneously catalyzed by ruthenium chloride that interconversion of σ-bonded alkyl and π-bonded olefin is the mechanism of the $\alpha\beta$ process and Green and Nagy (*8*) have demonstrated that reversible formation of σ-bonded alkyl from π-bonded olefin is possible in some complexes of iron.

The process responsible for the initial production of the d_6 isomer must be one of some difficulty. This is shown by the apparent additional activation energy of 6.2 kcal/mole required over and above that necessary for the processes involved in the initial exchange of the first five hydrogen atoms. While the exact nature of this process is uncertain it is possible that the π-bonded olefin reacts with a deuterium molecule at higher temperatures in the same way as the π-allyl intermediate. Initial formation of d_7 and d_8 isomers at elevated temperatures can be attributed to exchange of hydrogen atoms in the *gem*-dimethyl groups while the molecule is held on the surface as a π-bonded complex.

The reluctance of 1,1-dimethylcyclobutane to undergo a multiple exchange process contrasts with the behavior of other cycloalkanes on palladium catalysts. Since only slightly more than one hydrogen atom is replaced during each sojourn of the molecule on the surface there must be a barrier to the formation of a 1,2-diadsorbed intermediate. If the latter is a π-bonded olefin then the difficulty involved in its formation is due to the unstable nature of cyclobutene in comparison with cycloalkenes containing larger rings. There is even less chance of forming a π-allyl intermediate because of the strain this would necessitate in a cyclobutane ring. The selective cracking to 2,2-dimethylbutane is of interest because it shows that only bonds between carbon atoms which have one or more hydrogen atoms attached are easily ruptured. Thus a 1,2-diadsorbed intermediate seems to be at least required in order to crack a carbon–carbon bond on palladium metal.

General Aspects

The mechanistic advantages of the theory of π-bonded intermediates are well illustrated by its application to various reactions of the six-membered cyclic hydrocar-

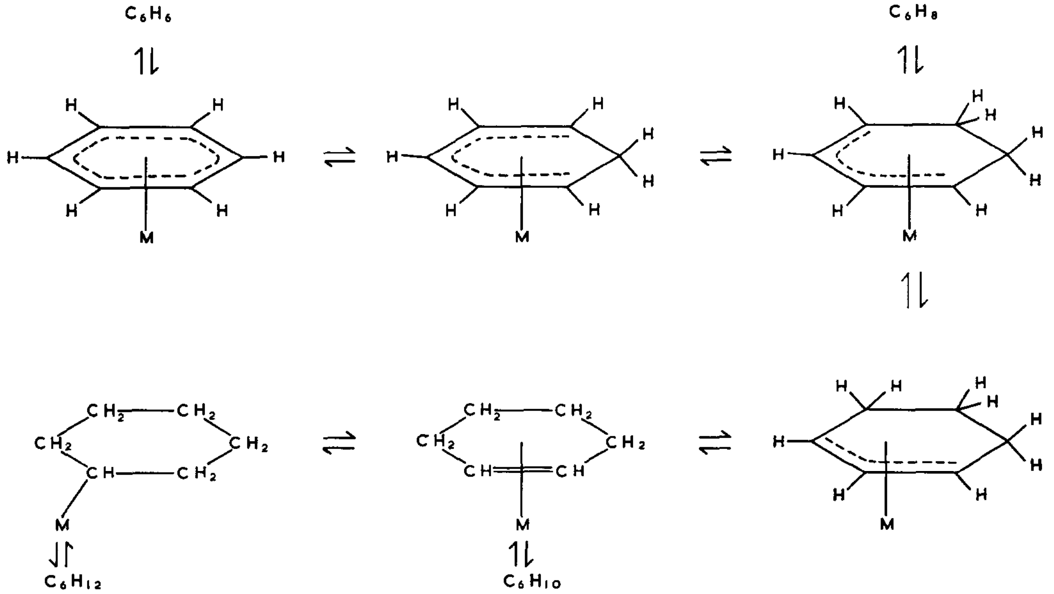

FIG. 2. Schematic representation of mechanisms involving π-bonded intermediates for various reactions of six-membered cyclic hydrocarbons on metal catalysts.

bons on metal catalysts. A comprehensive explanation of hydrogenation, dehydrogenation, disproportionation, and exchange reactions is provided by the scheme shown in Fig. 2, and at the same time the manner in which these reactions are related is clearly apparent. The exchange and hydrogenation of benzene with deuterium involve the same mechanism, in agreement with the conclusions of Hartog, Tebben, and Zwietering (*9*) from studies of these reactions on Raney nickel catalyst. Crawford and Kemball (*10*) have recently found evidence for the participation of π-bonded complexes in the exchange of alkylbenzenes with deuterium on nickel films and Garnett and co-workers (*11*) have arrived at similar conclusions from studies of the exchange of various aromatic compounds with deuterium oxide on supported platinum catalysts. The two possible reaction paths for cyclohexene and cyclohexadiene also explain disproportionation. The scheme can also account for double bond shift in substituted cycloalkenes and the hydrogenation of 1,2-disubstituted cycloalkenes to *cis* and *trans* isomers of the corresponding cycloalkanes. It is significant that Smith and Siegel (*12*) have observed that not only does isomerization of 1,2-dimethylcyclohexene take place in the presence of hydrogen on supported palladium catalysts in addition to the formation of *cis*- and *trans*-1,2-dimethylcyclohexane but a small amount of dehydrogenation to *ortho*-xylene occurs simultaneously.

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