On the Relationship between *cis–trans* Epimerization and Extensive Exchange in the Reaction between Deuterium and Dimethylcyclohexanes on a Palladium Catalyst

In catalyzed exchange reactions between deuterium and cycloalkanes, a "set" of hydrogen atoms is defined as those hydrogens which can be initially exchanged by interconversion of *cis*-1,2-diadsorbed intermediates on the catalyst surface (the alpha–beta process) (*1*). Multi-set or extensive exchange is also known to occur, especially on Pd catalysts, and a more complex mechanism has to be invoked in order to explain it. In appropriate molecules extensive exchange is associated with racemization of an optically active carbon atom (*2*) or with *cis-trans* epimerization (*1, 3*). An alpha–alpha intermediate cannot lead to epimerisation (*1*) and its production on Pd surfaces is, in any case, unlikely (*7*). Two mechanisms have been discussed as being capable of explaining reported data on multi-set exchange, racemization, and *cis–trans* epimerization, namely, the π-allyl mechanism of Rooney (*3, 4*) and the "roll-over" mechanism of Burwell (*1*). Until recently it has not been possible to distinguish adequately between them (*5*).

The relationship between *cis–trans* epimerization and extensive exchange was first noticed by Gault, Rooney, and Kemball (*3*) with polymethyl cyclopentanes, and later appeared more clearly from studies of Burwell and Schrage, who separated the epimers after reaction and measured their deuterium content individually (*1*). They concluded that for 1,2-dimethylcyclopentane, a common intermediate gave extensively exchanged *cis* and extensively exchanged *trans* products in the ratio 1:3. Starting with the *cis* epimer, the degree to which epimerization accompanies extensive exchange may be expressed as a ratio

$$\frac{\text{percent } trans \text{ product}}{\text{percent multi-set exchange}}.$$

For 1,2-dimethylcyclopentane this ratio is accordingly 0.75.

We measured this ratio separately for the *cis*-1,2- and *cis*-1,4-isomers of dimethylcyclohexane and found a large difference in the value for the two molecules. This may have mechanistic significance.

The reactions were performed by introducing 1 mm of hydrocarbon (Aldrich: 99.5% pure) and a 12/1 ratio of deuterium (purified by passage through a Pd thimble) into a reaction vessel on which an evaporated Pd film had been deposited at 0°C according to the method of Kemball (*6*). The vessel was connected to an MS-10 mass spectrometer operating at an ionizing voltage of 16 eV via a continuous capillary leak. The usual corrections to the observed peak heights were made for natural isotope abundance and for fragmentation due to the loss of 1 X (X = H or D: 3% of parent). Fragmentation of the type CX_3, CX_4, CX_5 was severe but did not interfere with the parent peak.

Exchange occurred very slowly at room temperature, and by warming the vessel to between 60 and 100°C an appreciable amount of conversion could be obtained. The reaction was then stopped by surrounding the vessel with liquid nitrogen and the hydrocarbon products were later analyzed by glc to determine the degree of epimerization.

The fact that no significant change in the distribution pattern was observed during the progress of the reaction was taken as evidence that the distribution pattern obtained when the reaction was quenched still corresponded to initial exchange.

The alpha–beta process can only exchange 12 hydrogens in either isomer so that $\Sigma d_{13} - d_{16}$ represents the degree of multi-set exchange. As the results in Table 1 indicate, epimerization during multi-set exchange is much more pronounced in *cis*-1,4-dimethylcyclohexane than in the 1,2-isomer.

The strong tendency towards total exchange in both isomers indicates that, whatever the intermediate process, there is a high probability for it to occur. Thus rather than a single, allylic species forming, being saturated, and desorbing, one would envisage the allylic species being propagated many times around the ring before the molecule finishes its sojourn on the surface and desorbs. The final saturation of the allylic species is thought to occur in two stages (*3*): first, D addition (from above or below) to one of the terminal carbons which reverts to the sp^3 hybridized state, leaving an adsorbed olefinic species which is then saturated by the usual *cis* addition of D_2 from the catalyst side. It is the first of these stages which dictates the stereochemistry of the product. If the terminal carbon happens to be methyl-substituted and if the D addition is top-side then epimerization occurs (provided that the other methyl-substituted ring carbon is not already inverted). Thus not every allylic species which is capable of forming, has the potentiality to cause epimerization upon saturation.

TABLE 1
PRODUCT DISTRIBUTIONS FOR *cis*-1,2,- AND *cis*-1,4-DIMETHYLCYCLOHEXANES

Compound		*cis*-1,2	*cis*-1,4
Reaction temp. (°C)		100	60
% of exchanged products	d_0	56.1	86.0
	d_1	15.3	3.75
	d_2	3.7	0.5
	d_3	1.45	0.5
	d_4	1.65	0.5
	d_5–d_{11}	each <0.5	each <0.5
	d_{12}	1.0	0.5
	d_{13}	1.0	0.75
	d_{14}	2.0	1.8
	d_{15}	6.0	4.2
	d_{16}	9.4	5.0
$\Sigma d_{13} - d_{16}$		18.4	11.7_5
% *trans*		3.0	8.6
% *trans*/$\Sigma d_{13} - d_{16}$		0.16	0.73

On comparison of the 1,2- and 1,4-isomers, there is no reason to suspect that the 1,4-molecule is capable of producing more allylic intermediates with epimerizing potential than the 1,2-isomer; nor is there any reason to suspect that the 1,4-isomer has any preferred tendency (relative to the 1,2-molecule) to have the final saturation prior to desorption occur at one of its allylic species with epimerizing potential. Thus, if we assume that the relative amount of top-side to bottom-side addition of deuterium will be the same for both isomers and that all the carbon atoms are equally likely as starting points for adsorption, then the large increase in concomitant epimerization during extensive exchange as we go from 1,2- to 1,4-dimethylcyclohexane is not readily explained in terms of π-allylic intermediates.

If in the intermediate process the molecule "rolls over" about one of its C–C bonds, then both carbon atoms forming the bond become inverted. If one of them is substituted, then epimerization occurs. If both are substituted, then the original epimer is regenerated. In the 1,2-isomer, it is clear that there are four C–C bonds in the ring which have no epimerizing potential, i.e., about which roll-over of the molecule would not produce epimerization. In the 1,4-molecule, on the other hand, there are only two such bonds ineffective for epimerization. This mechanism then offers a direct explanation for the relatively greater epimerization with the 1,4-molecule. The results may also be interpreted by assuming that an epimerizing roll-over will be discouraged in the *cis*-1,2-isomer by the presence of the vicinal methyl group. This is certainly possible for a roll-over mechanism, but it may be argued that it should be much less important for a π-allylic route. The objection does not, therefore, support the latter but rather argues for an alternative mechanism.

Recently, Rooney and co-workers have found strong evidence for roll-over rather than π-allylic intermediates from deuterium exchange and epimerization studies on bicyclic hydrocarbons of specially designed structure (*8*).

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Adsorption of Carbon Monoxide, Nitrogen, and Krypton on Ultrastable Y Zeolite

When amorphous silica–alumina cracking catalyst (13% alumina) was evacuated at 800°C overnight, it was found to adsorb nitrogen and carbon monoxide specifically (*1*). The CO adsorption at room temperature had an initial uptake of about 0.8 cc(STP)/g below 20 Torr pressure. The heats of adsorption at 0.1% surface coverage were determined to be 9 and 15 kcal/mole, respectively, for nitrogen and carbon monoxide. They decreased to about 3 kcal/mole above 2% coverage. On the other hand, adsorption isotherms of argon and krypton were all linear at room temperature and the heat values were only 2.5 and 3.3 kcal/mole, respectively. They were independent of surface coverage. These results indicate that, after extensive heat treatment of the amorphous material, a very small fraction of highly energetic sites were formed, which were selective in adsorbing gas molecules with large quadrupole moment.

It is of interest to examine the crystalline material to see if similar type of energetic sites are present. Ultrastable Y zeolite was thus selected for the comparison.

EXPERIMENTAL METHODS

Research grade krypton and C. P. grade carbon monoxide, both supplied from Matheson Gas Products, were further purified by condensing, respectively, in a liquid nitrogen cold trap, pumping off the top portion, and distilling the middle portion into storage bulbs. H. P. grade nitrogen, also from Matheson Gas Products, was slowly passed through a liquid nitrogen cold trap before storage.

The ultrastable Y zeolite sample was provided by W. R. Grace Company. It had originally been ion exchanged from Linde NaY zeolite by ammonium sulfate solution. After the first exchange process, the sample, which yielded 3% Na_2O from chemical analysis, was calcined at 760°C and then exchanged again with ammonium sulfate