The Mechanisms of Isomerization and Exchange of Olefins Over Metal Catalysts*

I. Reactions of Dimethylcyclopentenes in the Presence of Perdeuteropropene on Palladium Films*

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The isomerization and exchange of 1,2-dimethyl- and 2,3-dimethylcyclopentenes have been effected on palladium films at 150–200°C in presence of a large excess of perdeuteropropene. As far as isomerization is concerned, the results are substantially the same as the ones obtained when these molecules are reacting in presence of deuterium.

The comparison between the deuterium distributions of the exchanged and the isomerized hydrocarbons suggests that double bond migration takes place by a direct hydrogen intramolecular shift. Exchange by dissociative adsorption of the olefin at an allylic position is also suggested.

INTRODUCTION

Several mechanisms have been proposed to explain the double bond migration in olefins on metal catalysts. The most commonly known is the Horiuti–Polanyi mechanism (1), which supposes a common intermediate, the half-hydrogenated state, for both reactions of hydrogenation and isomerization. However, in 1948, Dibeler and Taylor (2) first presented evidence, mainly based on a comparison between the deuterium product distributions of exchanged olefins and saturated hydrocarbons, that hydrogenation and double bond migration proceed through two different mechanisms. A hydrogen switch mechanism involving an adsorbed hydrogen or deuterium atom was suggested to explain the isomerization (3).

In a recent study of deuteration, isomerization and exchange of cycloolefins over

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palladium catalyst (4), it was demonstrated that deuteration and isomerization do indeed occur by two independent processes. On the one hand, deuteration takes place via di- and monoadsorbed species, according to the Horiuti–Polanyi mechanism, and interconversions between diadsorbed species and π-allylic species were believed to determine the stereoselectivity in hydrogenation. Although recent studies (5, 6) in the field of exchange of saturated hydrocarbons have shown that the π-allylic species in the proposed mechanism have to be replaced by olefin-like species which roll-over on the surface, with (5) or without (6) residual bonding to the metal, this mechanism may still be considered as correct. On the other hand, the analysis of the exchanged and isomerized olefins provide the following information:

1. Very large amounts of light molecules (d_0) are present in the isomerization products; this observation strongly supports the idea that double migration involves a simple *intramolecular hydrogen shift*.

2. The deuterium distribution of the re-

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acting molecules suggests that *olefins dissociatively adsorbed at an allylic position* are responsible for the exchange reaction.

In order to confirm the above proposals, it was felt necessary to work in such conditions that only exchange and isomerization take place, and *not* deuteration; the absence of deuteration would allow a more accurate analysis of the exchanged and isomerized olefins. After several attempts, it appeared to us that the replacement of deuterium by a perdeuterated olefin such as perdeuteropropene could fulfill this requirement. Flanagan and Rabinovitch have indeed shown that the exchange between ethylene and perdeuteroethylene and also the isomerization and disproportionation of *trans*-dideuteroethylene (7–9) involve the same mechanisms and the same intermediate species as the exchange of ethylene with deuterium.

In a series of papers [present work (13, 14)] we shall report the study of the exchange and isomerization of several cyclic and acyclic molecules in the presence of an excess of C_3D_5 on various metal films. This first paper deals with the reactions of cycloolefins on palladium catalysts. In this paper it is verified that the exchange of cyclic molecules with C_3D_5 gives essentially the same type of distributions as their exchange with deuterium.

EXPERIMENTAL METHODS

Materials and Catalyst

A mixture (85/15) of 1,2-dimethylcyclopentene (I: 1,2-DMCP) and 2,3-dimethylcyclopentene (II: 2,3-DMCP) was prepared by adding 2-methylcyclopentanone to methylmagnesium iodide, hydrolyzing the adduct and dehydrating the tertiary alcohol which was obtained. Both olefins were then separated twice successively by preparative vpc, first on a 5 m silicone oil column at 50°C and then on a 5 m dimethylsulfolane column at 37°C. The purity was better than 99.5%.

The perdeuteropropene, from Merck Sharp Dohme, contained 6.4% of C_3D_5H.

Metal films were prepared in a conventional high vacuum system by evaporation of specpure palladium (Johnson & Matthey).

Apparatus, Procedure and Analysis

A mixture of 63 Torr of C_3D_6 and 3 Torr of cycloolefin (nominal D/H ratio of 9.4) was introduced on the freshly prepared film at the reaction temperature.

The reaction vessel (400 ml), part of a conventional high vacuum system, was connected to an AEI MS 2 mass spectrometer, so that the reaction could be followed with time. After a few minutes, when the conversion reached about 5%, the reaction was stopped by trapping the reaction products in a side tube at liquid nitrogen temperature. After a small portion of the sample was removed for gas–liquid chromatographic analysis, the various isomers were separated by gas chromatography on 5 m of dimethylsulfolane at 40°C and analyzed for their deuterium content.

The analysis of the various deuteromolecules was effected mass spectrometrically by using the parent ions obtained with 25 eV electrons. The usual corrections were made for natural isotopes and the first C–H fragmentation. For this latter correction the C–H and C–D fragmentation were assumed to be equal; the error introduced by this assumption is not very large on account of the low deuterium content of the reaction products.

RESULTS

Exchange and Isomerization of 1,2-Dimethylcyclopentene (I)

The reaction of (I) in the presence of C_3D_6 was studied at 200°C, a temperature at which the conversion reached only 2 to 5% after 15 min; only olefins were obtained as reaction products. Their deuterium distributions are given in Table 1 for four experiments effected under exactly the same conditions and with the same contact time.

These four experiments may be classified into two sets as for *the exchange pattern of the reacting molecules:*

1. In Expts 1 and 2, the deuterium distribution of the 1,2-dimethylcyclopentenes

TABLE 1

EXCHANGE AND ISOMERIZATION OF 1,2-DIMETHYLCYCLOPENTENE IN THE PRESENCE OF C_3D_6 ON PALLADIUM FILMS AT 200°C

Run:	Pd-Pumice at 25°C [Ref. (4)]			1			2			3			4		
Dimethylcyclopentene:	1,2		2,3	1,2		2,3	1,2		2,3	1,2		2,3	1,2		2,3
Isomerization (%):	99.94		0.06	95		5	97.7		2.3	95.7		4.3	97.1		2.9
d_0	98.7		41.7	94.2		23.6	97.4		29	95.7		41.3	96.4		40.8
d_1	0.41	31.5	41.0	3.12	53.8	39.7	1.4	53	34.5	1.3	30.2	30.5	1.2	32.9	28.2
d_2	0.56	43.1	4.1	0.55	9.4	7.8	0.20	7.7	6.6	0.53	12.2	5.9	0.42	11.7	6.3
d_3	0.15	11.5	1.3	0.30	5.25	3.4	0.15	5.9	3.1	0.20	4.6	3.4	0.16	4.6	3.6
d_4	0.07	5.4	1.0	0.24	4.2	2.7	0.09	3.6	2.3	0.17	4	2.15	0.15	4.1	2.3
d_5	0.06	4.6	0.6	0.16	2.6	2.2	0.05	2	1.2	0.17	3.9	2	0.12	3.4	2.1
d_6	0.05	3.8	0.7	0.15	2.55	1.65	0.08	3.1	1.4	0.22	5.2	1.55	0.26	7.3	1.7
d_7			0.6	0.15	2.55	1.4	0.07	2.6	1.4	0.43	10	1.45	0.34	9.6	1.7
d_8			0.8	0.17	3	1.45	0.08	3.3	1.8	0.66	15.4	1.50	0.58	15.9	1.8
d_9			0.8	0.19	3.35	2.1	0.09	3.4	2.5	0.13	3	1.35	0.07	1.9	2
d_{10}				0.30	5.2	3.8	0.10	3.9	2.8	0.15	3.6	2.5	0.09	2.7	2.5
d_{11}			1.3	0.31	5.3	5.9	0.15	5.9	6.6	0.20	4.6	2.8	0.11	3.2	3.5
d_{12}			1.0	0.16	2.8	4.3	0.14	5.6	6.8	0.14	3.3	3.6	0.10	2.7	3.5
	—a	—b	—a	—a	—b	—a	—a	—b	—a	—a	—b	—a	—a	—b	—a

$^a \sum\limits_{i=0}^{12} d_i = 100.$

$^b \sum\limits_{i=1}^{12} d_i = 100.$

(I) is decreasing from d_1 which is the predominant exchange product to d_6–d_7 and then slightly increasing up to d_{11}–d_{12}.

2. In Expts 3 and 4, a pronounced secondary maximum in d_8 appears in the product distribution.

In any experiment, the two main deuteromolecules obtained *by isomerization* are the d_0 and d_1-2,3-dimethylcyclopentenes formed in approximately equal amounts; they represent 60 to 75% of the total isomers. The rest of the distribution consists of a U-shape pattern with a slight maximum for the perdeuteroisomers.

It is interesting to notice that the distributions obtained by Hilaire and Gault (4) for the *isomerization* of (I) in presence of deuterium over Pd–pumice are substantially the same as the ones obtained in the presence of C_3D_6. The comparison between the distributions of the *exhanged* molecules in both experiments is not pos-

sible on account of the low accuracy for the determination of the highly exchanged molecules in the deuterium exchange experiment.

Exchange and Isomerization of 2,3-Dimethylcyclopentene (II)

The deuterium distributions of (I) and (II) are given in Table 2 for two experiments effected at 150 and 200°C, respectively.

The distribution of the 2,3-dimethylcyclopentenes is continuously decreasing except for a slight rise appearing at the heavy molecules d_8–d_{10}.

The two main deuteromolecules obtained by isomerization are the d_0 and d_1 1,2-dimethylcyclopentenes (representing 70–80% of the total isomerized molecules). The rest of the product distribution is first decreasing and then contains a very slight plateau at d_8–d_{10}.

TABLE 2

EXCHANGE AND ISOMERIZATION OF 2,3-DIMETHYLCYCLOPENTENE
IN THE PRESENCE OF C_3D_6 ON PALLADIUM FILMS

Run:	5			6		
Temperature (°C):	200			150		
Dimethyl-cyclopentene:	2,3		1,2	2,3		1,2
Isomerization (%):	90.6		9.4	93		7
d_0	84.9		51.7	89.1		31.3
d_1	5.5	36.4	29.2	5.6	51.3	37.6
d_2	1.8	12.2	5.8	1.85	16.9	7.8
d_3	1.5	10	3.1	1.1	10.3	5.2
d_4	1.3	8.6	1.85	0.93	8.5	4.3
d_5	0.7	4.5	1.26	0.4	3.7	3
d_6	0.4	2.75	1.18	0.22	2	2.1
d_7	0.4	2.75	1.10	0.15	1.4	1.7
d_8	0.6	3.90	1.32	0.19	1.7	1.8
d_9	0.8	5.2	1.33	0.17	1.6	1.7
d_{10}	0.9	5.9	1	0.13	1.2	1.4
d_{11}	0.8	5.2	0.84	0.11	1	1.4
d_{12}	0.4	2.6	0.32	0.05	0.4	0.7
	—a	—b	—a	—a	—b	—a

a $\sum\limits_{i=0}^{12} d_i = 100$.

b $\sum\limits_{i=1}^{12} d_i = 100$.

The amounts of highly deuterated molecules exchanged and isomerized are much higher at 200°C than at 150°C.

DISCUSSION

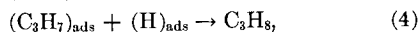### Comparison Between the Reactions of Cycloolefins in the Presence of Deuterium and in the Presence of Perdeuteropropene
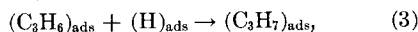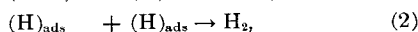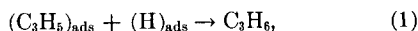
The close similarity of the deuterium distribution obtained in the two types of experiment for the isomerized molecules strongly suggests that for double bond shift at least the same mechanisms and the same intermediate species are intervening. It means that in the experiments effected in presence of C_3D_6, only the adsorbed deuterium formed by dissociative adsorption of C_3D_6 are involved in the reactions and that interchange reactions between heavy and light adsorbed olefins do not play a significant role.

The comparison between the distribution of the exchanged molecules† obtained by the 2 methods is not so convincing; however, since the deuterium distributions are much more complicated for the deuteromolecules obtained by exchange than for the ones obtained by isomerization and seem also to be much more sensitive to experimental conditions, a good comparison between both methods of tracing is difficult as far as exchange is concerned. However, Flanagan and Rabinovitch (7) in their study of exchange of deuteroethylenes have shown that the same mechanisms and intermediate species are involved in the exchange of ethylene and deuterium and in the exchange between d_0 and d_4 ethylene (7–9). We shall therefore consider that in the exchange of cycloolefins, as in the isomerization, only the adsorbed deuterium formed by dissociative adsorption of perdeuteroolefins and not adsorbed propene have to be considered.

Another interesting feature is that no hydrogen and only extremely small

† "Exchanged molecules" here and further in the text refer to those molecules which have been exchanged but not isomerized.

amounts of saturated products are detected in the gas phase. This could imply that reaction (1) in the following set of reactions:

$$(C_3H_5)_{ads} + (H)_{ads} \rightarrow C_3H_6, \qquad (1)$$
$$(H)_{ads} + (H)_{ads} \rightarrow H_2, \qquad (2)$$
$$(C_3H_6)_{ads} + (H)_{ads} \rightarrow (C_3H_7)_{ads}, \qquad (3)$$
$$(C_3H_7)_{ads} + (H)_{ads} \rightarrow C_3H_8, \qquad (4)$$

is much faster than reactions (2) to (4). Another explanation would be that the hydrogen species involved in isomerization or exchange and obtained by dissociative adsorption of olefins are not adsorbed on the same sites as the hydrogen species involved in hydrogenation. This explanation includes the preceding one and is strongly supported by the fact that isomerization, exchange and hydrogenation do not take place on the same catalytic sites (4).

Exchange of the Reacting Molecules

The pronounced maximum in d_8 obtained in some of the distributions of the 1,2-dimethylcyclopentenes is best interpreted by assuming that six primary and two secondary allylic hydrogens (the ones directed towards the surface) are easily exchanged during the process. Therefore, in order to interpret the exchange reaction, special emphasis should be placed on the dissociative adsorption of the olefins at an allylic position.

This view is supported by the work of Hirota and co-workers who showed by using microwave spectroscopy that over palladium propene-3-d is the major product in the exchange of propene with deuterium on palladium (10, 11).

If only allylic hydrogens are involved in the exchange of olefins over palladium, the intermediate species should be either a dissociatively σ-adsorbed olefin B or a σ–π diadsorbed olefin D (or a π-allylic species F).
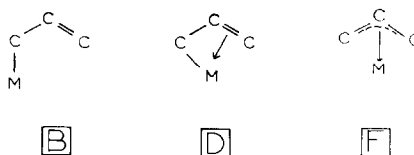
The existence of a multiple exchange leading to d_8-1,2-DMCP is in favor of species D or F and the exchange reactions could be pictured by Scheme 1 where p represents the ratio of the chances for an associatively adsorbed olefin A to give an allylic species or to desorb.
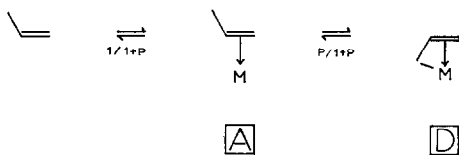
<center>SCHEME 1</center>

It is clear that two different types of exchange take place on palladium film:

1. A simple or quasi-simple exchange Ⓐ producing a decreasing distribution and mainly d_1 corresponds to a very small value of p.

2. A multiple exchange Ⓑ yielding d_8-1,2-DMCP is associated with a high value of p.

While mechanism Ⓑ seems to be very sensitive to experimental conditions, mechanism Ⓐ is always more important and takes place in any condition. It is interesting to note concerning mechanism Ⓑ that on supported catalyst a differentiation may

viously the two secondary allylic hydrogens, are exchanged on supported palladium catalyst at 25°C instead of eight on palladium films at 200°C.

Now the allylic exchange is not sufficient to explain the exchange pattern of the cycloolefins; 10 to 20% of the deuteromolecules contain more deuterium atoms than expected by an allylic exchange mechanism. A possible explanation for the formation of the perdeuteromolecules is suggested by the profile of the distribution which much resembles the one obtained for the saturated hydrocarbon when C_3D_6 is replaced by D_2. In the deuteration reaction interconversions between $\alpha\beta$-diadsorbed species and roll-over species are responsible for the formation of the most exchanged molecules. Obviously the same species and the same interconversion process could explain the presence of perdeuteroolefins in the product distributions.

Isomerization

In a preceding paper *(4)*, on account of the very large amounts of d_0 isomers formed, it was suggested that double bond shift takes place by *a simple intramolecular shift*. If this is the case, the reaction mechanism may be pictured by Scheme 2.
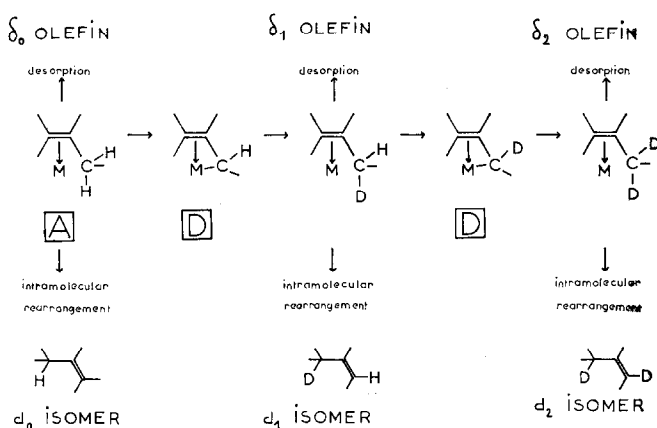
<center>SCHEME 2</center>

appear between the secondary and the primary allylic hydrogens in the molecules: two hydrogen atoms of 1,2-DMCP, ob-

According to this scheme, one should find a close parallelism between the distributions of isomerized and exchanged olefins.

TABLE 3

RATIOS $r_i = \delta_i/d_i$ BETWEEN THE CORRESPONDING EXCHANGED AND ISOMERIZED OLEFINS

Run:	1	2	3	4
r_1	1.36	1.53	1.0	1.16
r_2	1.20	1.2	2.1	1.85
r_3	1.54	1.9	1.35	1.27
r_4	1.55	1.56	1.86	1.78
r_5	1.2	1.65	1.9	1.62
r_6	1.55	2.2	3.35	4.3
r_7	1.8	1.8	6.9	5.6
r_8	2.1	1.8	10.2	8.8
r_9	1.6	1.4	2.2	0.95
r_{10}	1.37	1.4	1.44	1.1
r_{11}	0.9	0.8	1.65	0.9
r_{12}	0.6	0.8	0.9	0.8

When neglecting isotopic effects, the following relationships $r_i = \delta_i/d_i =$ constant are expected where δ_i and d_i represent the percentage of exchanged and isomerized olefins, respectively. In Table 3 the ratios r_i are reported for the various experiments: in runs 1 and 2, r_i remains roughly constant except for d_7 and d_8 where it outpaces the mean value; in runs 3 and 4 on the contrary r_i increases with the number of deuterium atoms in the molecules. This can easily be explained if one assumes that isomerization in Scheme 2 is related to the quasi-simple type of exchange α and not to the multiple exchange β.

exchange of cyclohexene with deuterium on platinum. The transition state E for this intramolecular rearrangement has already been thoroughly discussed (4, 12). A hydrogen atom is bridged between carbon atoms C_1 and C_3, whose orbitals, intermediate between p and sp^3 orbitals, are only loosely overlapping with the metal orbitals.
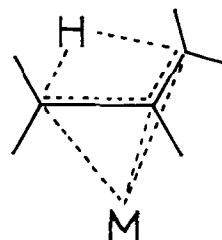
In our opinion the driving force for this isomerization process could be related to the electron-attracting character of the metal atoms in a metal surface, i.e., to the charge transfer from the adsorbed hydrocarbon to the metal, which has been demonstrated many times by work function measurements.

Several other isomerization mechanisms had been proposed in the paper by Hilaire and Gault (4). One of them involves as precursor a dissociatively adsorbed olefin
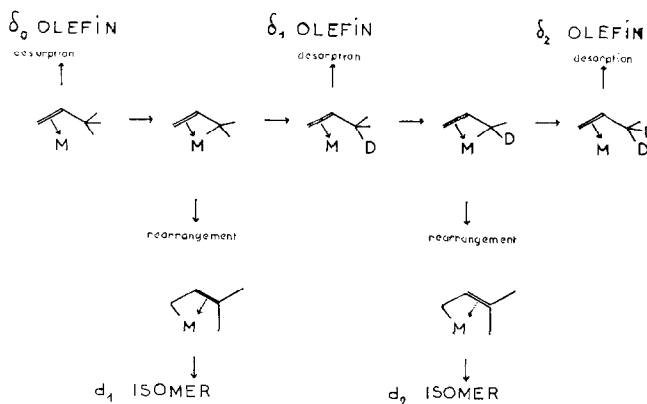
SCHEME 3

The concept of intramolecular rearrangement was first introduced by Smith and Swoap (12) to explain their results in the

at an allylic position (Scheme 3); another is very close to the one proposed by Dibeler and Taylor (2) (Scheme 4). How-
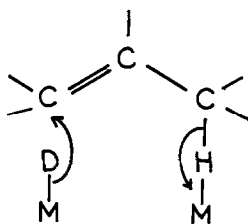
SCHEME 4

ever, it is obvious that only d_1–d_8 deuteromolecules could be obtained according to these mechanisms; the presence of large amounts of d_0 isomers allows us to reject all of them, except if d_0 is the result of a local isotopic dilution.

Let us examine further this latter possibility. The two exchange distribution patterns $\mathfrak{A}$ and $\mathfrak{B}$, as well as the presence of d_0 in the isomerized molecules, could formally be explained if one assumes that the *same* mechanism, for example the one described in Scheme 3, operates on two different types of sites, with a high and with a low concentration of deuterium on the surface respectively, i.e., if one assumes that perdeuteropropene does not populate similarly with deuterium the two types of sites $\mathfrak{A}$ and $\mathfrak{B}$. If that was the case, first of all the ratios d_i/δ_i should remain constant throughout the entire distribution pattern, which is not true in Exps. 3 and 4. Therefore, according to the isotopic dilution hypothesis, again two mechanisms should be considered, one involving *both* exchange and isomerization on a hydrogen-rich region, the other one involving *only* exchange on a deuterium-rich region. Secondly, the maximum in d_8 observed for the exchange distribution patterns $\mathfrak{B}$ shows that *eight*

hydrogen atoms are involved in the exchange of dimethylcyclopentenes. Suppose now that the exchange distribution $\mathfrak{A}$ and the deuterium pattern of the isomers are only the result of an isotopic dilution distorting a "true" deuterium distribution pattern with a predominant d_8: one should observe then a ratio $r_2 = d_2{}^2/d_1d_3$ not very far from $(C_8{}^2)^2/C_8{}^1C_8{}^0 = 1.75$ and a ratio $r_1 = d_1{}^2/d_0d_2$ equal to $(C_8{}^1)^2/(C_8{}^2)(C_8{}^0) = 2.3$. The experimental values obtained for r_2 and r_1 are reported in Table 4. One sees that the observed values for r_2 in the deuterium patterns of the exchanged and isomerized molecules are always different and much *smaller* than the calculated values, while the observed values for r_1 are much *higher*.

Any explanation of both types of exchange $\mathfrak{A}$ and $\mathfrak{B}$ by a simple mechanism and different isotopic dilutions should therefore be rejected. In our opinion, the only alternative explanation of our results, besides the one given above and represented in Schemes 1 and 2, would involve the combination of three processes:

i. An intramolecular hydrogen shift yields the d_0 isomer via the transition state E;

ii. A mechanism similar to the one described in Scheme 3 could explain the exchanged and isomerized molecules with a low deuterium content (and d_i/δ_i constant). In this mechanism the σ–π diadsorbed species could better be replaced by π-allylic species;

iii. The third mechanism would be associated with the d_8 maxima which appear in some of the exchange patterns, but *not* in the deuterium distributions of the isom-

TABLE 4

CALCULATED AND OBSERVED VALUES OR r_2 AND r_1 IN ISOMERIZATION AND EXCHANGE DISTRIBUTION PATTERNS[a]

Expt. no.:	1	2	3	4	Calculated values
r_2 in exchange	0.3	0.2	1.1	0.90	1.75
in isomerization	0.45	0.41	0.34	0.39	1.75
r_1 in isomerization	8.6	6.2	3.8	3.1	2.3

[a] $r_1 = d_1{}^2/d_0d_2$; $r_2 = d_2{}^2/d_1d_3$.

erized molecules. This mechanism is best represented in Scheme 1, but in this case allylic species D cannot be replaced by the symmetrical π-allylic species.

This composite mechanism involves then three types of sites (instead of two) and the deuterium populations of these sites, and therefore their reactivities would depend upon the form and the source of the deuterium adsorbed on the surface.

CONCLUSION

Three main conclusions may be drawn out of this study of isomerization and exchange of dimethylcyclopentenes in the presence of perdeuteropropene.

1. The mechanisms and the intermediate species involved are the same as the ones intervening in deuterium–olefin interaction.

2. Exchange affects mainly the hydrogen atom in an allylic position.

3. Isomerization consists of an intramolecular rearrangement assisted by the adsorption (π-bonding) of the olefins to the metal.

REFERENCES

1. HORIUTI, J., AND POLANYI, M., *Trans. Faraday Soc.* **30**, 1164 (1934); see also SIEGEL, S., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 16, p. 123. Academic Press, New York; BOND, G. C., AND WELLS, P. B., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 15, p. 91. Academic Press, New York.

2. DIBELER, V. H., AND TAYLOR, T. I., *J. Chem. Phys.* **16**, 1008 (1948).

3. WEISS, A. R., AND TAYLOR, T. I., unpublished dissertation quoted in Catalysis, Vol. 5, p. 373. Reinhold, New York, 1957.

4. HILAIRE, L., AND GAULT, F. G., *J. Catal.* **20**, 267 (1971).

5. BURWELL, R. L., AND SCHRAGE, K., *Discuss. Faraday Soc.* **41**, 215 (1966); SCHRAGE, K., AND BURWELL, R. L., *J. Amer. Chem. Soc.* **88**, 4555 (1966).

6. QUINN, H. A., GRAHAM, J. H., MC KERVEY, M. A., AND ROONEY, J. J., *J. Catal.* **22**, 35 (1971).

7. FLANAGAN, T. B., AND RABINOVITCH, B. S., *J. Phys. Chem.* **60**, 724 (1956).

8. FLANAGAN, T. B., AND RABINOVITCH, B. S., *J. Phys. Chem.* **60**, 720 (1956).

9. FLANAGAN, T. B., AND RABINOVITCH, B. S., *J. Phys. Chem.* **61**, 664 (1957).

10. HIROTA, K., AND HIRONAKA, Y., *J. Catal.* **4**, 602 (1965).

11. VEDA, T., HARA, J. HIROTA, K., TETRATANI, S., AND YOSHIDA, N., *Z. Phys. Chem. (Frankfurt am Main)* **64**, 64 (1969).

12. SMITH, G. V., AND SWOAP, J. R., *J. Org. Chem.* **31**, 3904 (1966).

13. TOUROUDE, R., AND GAULT, F. G., *J. Catal.* **32**, 288 (1974).

14. TOUROUDE, R., AND GAULT, F. G., *J. Catal.* **32**, 1294 (1974).