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MICROWAVE SPECTROSCOPIC STUDY ON THE MECHANISM OF BASE-CATALYZED PROPYLENE H-D EXCHANGE REACTION OVER POTASSIUM tert-BUTOXIDE AND DMSO-d_6 SYSTEM

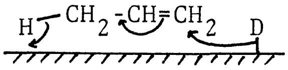
Kiyoshi UCHIDA, Shuichi NAITO, Takaharu ONISHI, and Kenzi TAMARU
Department of Chemistry, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

The mechanism of hydrogen exchange reaction between propylene and deuterated dimethyl sulfoxide (DMSO-d_6) in the presence of potassium t-butoxide (t-BuOK) was studied by means of microwave spectroscopy, which leads to a conclusion that the reaction proceeds via the π-allyl intermediate.

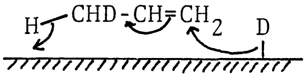
Olefin isomerization takes place by base as well as acid catalyst. The isomerization of 1-butene over solid-base-catalyst predominantly takes place to form cis-2-butene, markedly deviating from the thermodynamic equilibrium composition. In a similar manner, when the olefin isomerization takes place in a liquid phase, cis-2-olefin predominates over trans-2-olefin. From the results of 1-olefin isomerization by alkali metal t-butoxide and DMSO systems, Bank et al. reported that these reactions occur through a common intermediate, cis-allylic anion, although no real evidences for this intermediate were confirmed.[1)]

In the hydrogen exchange reaction between propylene and deuterium, a new method was developed to determine the mechanism of exchange reaction by means of microwave spectroscopy, quantitatively analyzing the distribution of propylene-d_1 and -d_2 species formed during the course of the reaction.[2)]

In the hydrogen exchange reaction between propylene and deuterium, we can imagine three types of the reaction mechanism, that is, associattive type, dissociative type and concerted type. In the associative type there are two possible reaction intermediates, n-propyl and isopropyl species. In the former mechanism, the exchange reaction proceeds via an intermediate, $\underline{CH_3CHDCH_2}$, which produces 2-d_1 species $CH_3CD{=}CH_2$. In the latter case, the exchange reaction proceeds via an intermediate, CH_3CHCH_2D , which produces 1-d_1 species $CH_3CH{=}CHD$ and 3-d_1 species $CH_2{=}CHCH_2D$ in the ratio of 2 to 3 (this ratio is the same as that of the equilibrated d_1 species). In the dissociative mechanism, four reaction intermediates are possible, n-propenyl, isopropenyl, σ-allyl and π-allyl species. In the case of n-propenyl, the exchange reaction proceeds via an intermediate $CH_3CH{=}CH$, which produces 1-d_1 species; in the isopropenyl case, via an intermediate $CH_3C{=}CH_2$, which produces 2-d_1 species; in the σ-allyl, via an intermediate $CH_2CH{=}CH_2$, which produces 3-d_1; and in the π-allyl via an intermediate $CH_2{\cdots}CH{\cdots}CH_2$, which produces only 3-$d_1$ initially, but in the equilibrium 1-d_1 species also appears and the ratio of 1-d_1 to 3-d_1 is 2 : 3. In the concerted mechanism, the bond between allylic hydrogen and 3-C is broken at the moment when 1-C is attacked by deuterium to form new C-D bond as follows:



According to this mechanism, the d_1 species initially produced is only 3-d_1 species, but in the equilibrium 1-d_1 species also appears and the ratio of 1-d_1 to 3-d_1 is the same as that of the π-allyl or the isopropyl type. Thus the distribution of propylene-d_1 isomers during the H-D exchange reaction by the concerted mechanism is the same as that of the exchange reaction via the π-allyl intermediate. However when we consider the propylene-d_2 distribution of the exchange reaction, we can distinguish the one from another. Initially produced 3-d_1 propylene reacts with D as follows; when the reaction proceeds through the π-allyl intermediate, the intermediate $CHD{\cdots}CH{\cdots}CH_2$ appears, which produces 3,3-d_2 $CHD_2CH{=}CH_2$ and 1,3-d_2 $CHD{=}CHCH_2D$ in the ratio of 1 : 1 in the initial stage. When the reaction proceeds through concerted mechanism, d_2-species appears as the following scheme shows.



Thus initially produced d_2-species is the only 1,3-d_2 species. That is, we can distinguish the both mechanism, analyzing the initially produced d_2-species.

In this communication, we studied the mechanism of propylene H-D exchange reaction over t-BuOK + DMSO-d_6 (+ t-BuOH) system by means of microwave spectroscopy. These experiments were carried out in a closed circulating system (ca. 360 ml) for propylene (ca. 40 cmHg) and the liquid catalyst system was stirred magnetically at 50 ∿ 60°C. The results are given in Tables I and II.

The results shown in the tables exclude the n-propyl and isopropenyl intermediates because of the absence of 2-d_1 species. The n-propenyl and σ-allyl intermediates are also excluded by the presence of 3-d_1 and 1-d_1 species, respectively. In the case of isopropyl intermediate, the composition of the reaction products should be 3-d_1 species (60 %) and 1-d_1 species (40 %), the composition staying unchanged during the course of the reaction, which is not the case in the tables.

From the distribution of d_1-species, both the π-allyl and concerted mechanisms are probable. But from the distribution of d_2-species, 1,3-d_2 and 3,3-d_2 produced equally, the concerted one is excluded. And the results given also agree well with the π-allyl mechanism. Accordingly we concluded that the propylene H-D exchange reaction in t-BuOK + DMSO-d_6 takes place via the π-allyl intermediate. When t-BuOH was added to the system as a proton donor, the mechanism still stayed unchanged, although the rate of exchange reaction was markedly decreased.

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Table I. Distribution of Propylene-d_1 and -d_2 Species during the H-D Exchange Reaction between Propylene and t-BuOK* + DMSO-d_6 at 55°C

Time (min)	95	225	360	600	5760 (4 days)
$\psi^{a)}$ (%)	1.5	2.5	4.2	5.8	33.1
3-d_1 (%)	84.5		77.1		63.3
1-d_1	15.5		22.9		36.7
cis-1-d_1	7.9		12.2		16.9
trans-1-d_1	7.6		10.7		19.8
3,3-d_2 (%)	--	53.8	52.3	46.7	41.3
1,3-d_2 (%)	--	46.2	47.7	47.2	51.4
cis-1,3-d_2	--	23.4	25.5	24.1	25.3
trans-1,3-d_2	--	22.8	22.2	23.1	26.1
1,1-d_2	--	--	--	6.1	7.3

a) Mean deuterium content of propylene is given by the equation

$$\psi = 100 \left(\sum_{i=1}^{6} i d_i / 6 \sum_{i=0}^{6} d_i \right)$$

* 0.65 M

Table II. Distribution of Propylene-d_1 and -d_2 Species during the H-D Exchange Reaction between Propylene and t-BuOK + t-BuOH + DMSO-d_6

Experiment	A		B		
Time	540 (min)	6 (days)	1.5 (days)	3 (days)	22 (days)
ψ (%)	4.7	36.7	1.3	2.1	16.7
3-d_1 (%)	77.1	64.3	90.3	84.6	65.7
1-d_1	22.9	35.7	9.7	15.4	34.3
cis-1-d_1	12.0	19.1	4.4	8.0	19.5
trans-1-d_1	10.9	16.6	5.3	7.4	14.8
3,3-d_2	--	41.6	--	--	38.9
1,3-d_2	--	51.1	--	--	54.5
cis-1,3-d_2	--	24.7	--	--	26.0
trans-1,3-d_2	--	26.4	--	--	28.5
1,1-d_2	--	7.3	--	--	6.6

A ; t-BuOH 3 %, t-BuOK 0.63 M, at 52°C

B ; t-BuOH 9 %, t-BuOK 0.59 M, at 55°C

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