Evidence of a π-Allyl Intermediate in the Deuterium Propylene Exchange Reaction over $C_{24}K$

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(Received December 24, 1971)

The deuterium propylene exchange reaction was studied over the potassium graphite intercalation compound $C_{24}K$. The deep blue $C_{24}K$[1] was prepared by heating 2.0 g of spectroscopic powder graphite (Union Carbide Co.) with *ca.* 0.5 g of distilled potassium metal in *vacuo* at 380°C for 24 hr. A conventional closed circulating system was used to study the exchange reaction. Mass and microwave spectroscopic techniques[2] were used to determine the deuterium content and its distribution in the propylene.

Deuterium (*ca.* 200 mmHg) was circulated over $C_{24}K$ at 120°C for about 15 hr and the system was then evacuated for about 10 min. When a mixture of propylene and D_2 was introduced onto the catalyst at 120°C, simultaneous deuteration and exchange of the propylene took place. The amounts of the various propylenes d_1, d_2,$\cdots d_6$, were determined by mass spectrometry, using an ionization voltage of 10 V to avoid fragmentation. No propylene-d_6 was detected throughout the reaction. The hydrogen exchange reaction did not proceed through a multiple exchange process, but through successive single exchange steps.

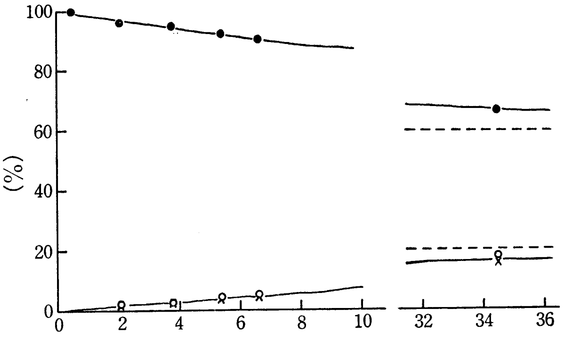

Fig. 1. Hyperfine deuterium distribution of propylene-d_1 at 120°C over $C_{24}K$.
Mean deuterium content Ψ is represented by the equation $\Psi=100(\sum_{i=1}^{6} id_i/6\sum_{i=0}^{6} d_i)$. ●: 3-$d_1$, ×: *cis*-1-$d_1$, ○: *trans*-1-$d_1$

The results of microwave spectroscopic measurements of propylene-d_1, C_3H_5D, as shown in Fig. 1, demonstrated that propylene-3-d_1, $CH_2DCH{=}CH_2$, was the only reaction product in the initial stage of the reaction. As the reaction proceeded, *cis*-1-d_1 and *trans*-1-d_1[3] propylene were formed. However, no propylene-2-d_1, $CH_3CD{=}CH_2$, was observed during the reaction. This indicates that the normal propyl species ($CH_3CH_2\underset{*}{C}H_2$) is not the intermediate of this exchange reaction. Also, the isopropyl species ($CH_3\underset{*}{C}HCH_3$) cannot be the intermediate since it should give a deuterium distribution of 60% 3-d_1, 20% *trans*-1-d_1, and 20% *cis*-1-d_1 which should not vary with reaction time. Accordingly, the intermediate of this exchange reaction cannot be of the half-hydrogenated state of propylene.

If the exchange reaction proceeded by the concerted mechanism (push-pull mechanism),[4] propylene-3-d_1 should predominate in the initial stage of the reaction and be followed by *cis*-1-d_1 and *trans*-1-d_1 propylene. The deuterium distribution of propylene-d_1 in the concerted mechanism shows good agreement with the results in Fig. 1.

Table 1. Hyperfine deuterium distribution of propylene-d_2 in the initial stage of the reaction (Ψ=6.6%) at 120°C over $C_{24}K$

1,1-d_2	3 (%)
cis-1,3-d_2	22
trans-1,3-d_2	25
3,3-d_2	50

However, the deuterium distribution of propylene-d_2, $C_3H_4D_2$, as shown in Table 1, cannot be explained by a concerted mechanism, because this mechanism would require an initial $C_3H_4D_2$ propylene distribution of 50% *cis*-1,3-d_2 and 50% *trans*-1,3-d_2. In contrast, the results in Table 1 show that the main product in the initial stage is propylene-3,3-d_2, $CHD_2{-}CH{=}CH_2$, (50%) and that the *cis*-1,3-d_2 and *trans*-1,3-d_2 propylene account for only 22% and 25%, respectively, of the total propylene-d_2. This initial distribution of propylene-d_2 indicates that in the reaction intermediate 1 and 3-carbons are equivalent.

The propylene-d_1 distribution shown in Fig. 1 can also be explained by a π-allyl intermediate ($CH_2{\overset{\dots}{=}}CH{\overset{\dots}{=}}CH_2$) mechanism.[5] The mechanism would predict an initial propylene-d_2 distribution of 50% 3,3-d_2, 25% *cis*-1,3-d_2, and 25% *trans*-1,3-d_2. The distribution is in good agreement with that given in Table 1. Other dissociative intermediates (*e.g.*, $\underset{*}{C}H_2{-}CH{=}CH_2$, $CH_3{-}\underset{*}{C}{=}CH_2$, $CH_3{-}CH{=}\underset{*}{C}H$) are also excluded by our results. It is thus concluded that the intermediate of the exchange reaction of propylene with deuterium over $C_{24}K$ is most probably the π-allyl species, and definitely neither an associative nor dissociative species and no concerted mechanism is involved.

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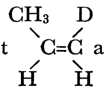
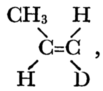
[1] D. E. Nixon and G. S. Parry, *Brit. J. Appl. Phys.*, **1968**, Ser. 2, Vol. 1, 291.

[2] K. Hirota, Y. Hironaka, and E. Hirota, *Tetrahedron Lett.*, **1964**, 1645; K. Hirota, N. Yoshida, S. Teratani, S. Saito, *J. Catal.*, **15**, 425 (1969).

[3] *Cis*-1-d_1 and *trans*-1-d_1 represent  $(CH_3)(D)C{=}C(H)(H)$ and  $(CH_3)(H)C{=}C(H)(D)$, respectively.

[4] D. M. Brouwer, *J. Catal.*, **1**, 22 (1962).

[5] S. Naito, Y. Sakurai, H. Shimizu, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **67**, 1529 (1971).