Mechanisms of Hydrogenation and Hydrogen Exchange of Propylene over the Electron Donor-Acceptor Complexes of Polynaphthoquinones with Potassium

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The mechanisms of the deuterium addition to propylene and the propylene-deuterium exchange reaction over the electron donor-acceptor (EDA) complex of polynaphthoquinone with potassium were investigated by means of mass and microwave spectrometry and gas chromatography in the range from room temperature to 200 °C. The hydrogenation as well as the exchange reaction proceeded *via* the half-hydrogenated state of propylene formed from the adsorbed propylene and the dissociatively-adsorbed deuterium atom on the EDA complex. However, the rate of the exchange reaction decreased upon the Fe addition to the complex, while the hydrogenation was markedly accelerated. The intermediate of the propylene-deuterium exchange reaction was determined to be the half-hydrogenated isopropyl species, whereas the deuterium addition to propylene was suggested to occur *via* another half-hydrogenated state, the *n*-propyl species.

The electron donor-acceptor (EDA) complex of the polynaphthoquinone with potassium exhibits high activities for various catalytic reactions, such as the H_2–D_2 exchange reaction, the isomerization of butene, and the synthesis of ammonia from a mixture of nitrogen and hydrogen, as was reported in a previous paper.[1] The EDA complex also readily catalyzes the hydrogen exchange of propylene with deuterium. It was concluded[1,2] by means of the microwave technique[3] that the half-hydrogenated state of propylene, the isopropyl species, is the reaction intermediate in the propylene-deuterium exchange reaction. The rate of the hydrogenation of propylene with hydrogen was expressed by the following equation: $v=k(\text{propylene})(H_2)^{1/2}$, indicating that the half-hydrogenated state may also be the reaction intermediate in the hydrogenation reaction.

However, it does not follow that the hydrogenation or deuterogenation of propylene also proceeds through the half-hydrogenated state of isopropyl species. In other words, the reaction intermediates of the hydrogenation and the exhange reaction are not necessarily the same half-hydrogenated state, even if both reactions will follow the same rate equation.

In the present experiment, the mechanisms of the deuterium addition to propylene and the exchange reaction of propylene with deuterium over the EDA complex of potassium with the polynaphthoquinone were investigated in detail, and the intermediates of the deuterium addition to propylene were examined by means of mass and microwave spectrometries and gas chromatography.

Experimental

The polynaphthoquinone employed was obtained by oxidizing 1,7-naphthalenediol with nitric acid in air, followed by treating at 350 °C for 12 hr, as was reported in a previous paper.[4] The polynaphthoquinone containing $FeCl_3$ was prepared by mixing metal-free polynaphthoquinone and $FeCl_3$ (15 wt% against polynaphthoquinone) in ethyl alcohol and then evaporating the solvent. The polynaphthoquinones thus obtained were treated at 350 °C for 6 hr *in vacuo* before use. The EDA catalysts were prepared by adding potassium vapour to the polynaphthoquinones in the absence of air. The composition of the EDA complex was found to be one potassium monomer to three naphthoquinone monomers.

The reactions were carried out over the EDA complex including 0.1 g of the polynaphthoquinone in a closed circulating system (175 cm^3). The rate of the propane formation by the hydrogenation of propylene was determined by gas chromatography, while the deuterated propylene formed by the exchange reaction of propylene with deuterium was quantatively analyzed by mass and microwave spectroscopy. The mass spectroscopy was also used for analyzing the deuterated propane.

Results and Discussion

The Mechanism of the Propylene-deuterium Exchange Reaction. The exchange reaction of propylene with deuterium over the EDA complex of potassium with the polynaphthoquinone was studied by means of the microwave technique in the range from room temperature to 200 °C. The rate of the formation of deuteriopropylene was determined by mass spectrometry. The formation of deuteriopropylene is plotted against the reaction time in Fig. 1; the figure shows that hydrogen in propylene successively exchanges with deuterium over the EDA catalyst.

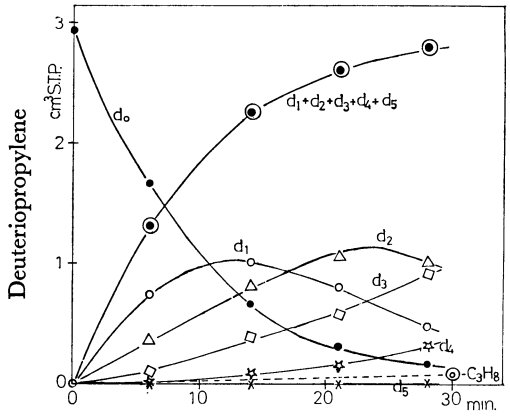


Fig. 1. Amounts of deuteriopropylenes, produced by the hydrogen exchange of propylene (1.4 cmHg) with deuterium (3.4 cmHg), against reaction time at 95 °C.

According to microwave spectrometry, three kinds of monodeuteriopropylenes, CHD=CH–CH_3(*cis*-1-d_1 and *trans*-1-d_1) and CH_2=CH–CH_2D(propylene-3-d_1), were produced in an approximate ratio of 1 : 1 : 3, and the propylene-d_2 species formed were 1,1-d_2, 3,3-d_2, and 1,3-d_2, in the approximate ratio of 1 : 3 : 6. It is concluded from these results[2] that the half-hydrogenated isopropyl species is the main reaction intermediate of the hydrogen exchange reaction over the EDA complex in the range from room temperature to 200 °C.

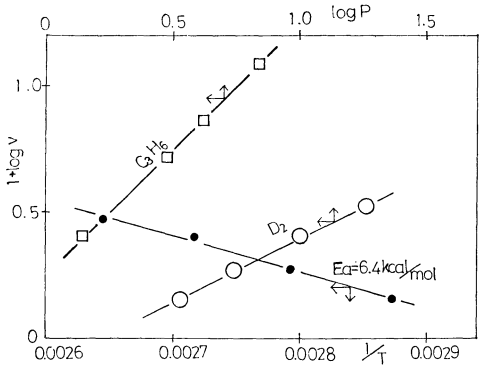


Fig. 2. Dependence of the rate of the exchange reaction upon the pressures of propylene and deuterium at 75 °C and the activation energy of the reaction.

The rate of the propylene-d_1 formation was found to be of the first-order with respect to the partial pressure of propylene and half-order with respect to the deuterium pressure as is shown in Fig. 2, where the activation energy is also given as 6.4 kcal/mol. A very small amount of propylene was reversibly adsorbed on the 1.0 g EDA complex, while the adsorption of deuterium was not appreciable under similar conditions. It was indicated in a previous paper[2] that HD in the H_2–D_2 exchange reaction was produced from hydrogen and deuterium atoms dissociated from each of the gases on the catalyst surface. The half-hydrogenated state of the isopropyl species, as the reaction intermediate, may be formed from the surface reaction of the adsorbed propylene with the deuterium atom dissociatively adsorbed on the EDA catalyst.

Consequently, the scheme of the propylene-deuterium exchange reaction may be expressed as follows;

$$C_3H_6(g) \overset{K_1}{\rightleftharpoons} C_3H_6(ad) \quad (1)$$

$$D_2(g) \overset{K_2}{\rightleftharpoons} 2D(ad) \quad (2)$$

$$C_3H_6(ad) + D(ad) \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} CH_2D\text{–}\underset{*}{CH}\text{–}CH_3 \quad (3)$$

$$CH_2D\text{–}\underset{*}{CH}\text{–}CH_3 \overset{k_4}{\longrightarrow} \underline{C_3H_5D}(ad) + H(ad) \quad (4)$$

where $CH_2D\text{–}\underset{*}{CH}\text{–}CH_3$ and C_3H_5D represent the half-hydrogenated state of the isopropyl species and monodeuteriopropylene(*cis*-1-d_1, *trans*-1-d_1 or 3-d_1) respectively.

The rate in the initial stage of the hydrogen exchange reaction is given as follows in the steady state according to the ordinary procedures:

provided $(C_3H_6)_{ad}=K_1(C_3H_6)_g$ and $(D)_{ad}=K_2^{1/2}(D_2)_g^{1/2}$, where $(C_3H_6)_{ad}$ and $(D)_{ad}$ were very small in amount,

$$d(CH_2D\text{–}\underset{*}{CH}\text{–}CH_3)/dt = k_3(C_3H_6)_{ad}(D)_{ad} - k_3'(CH_2D\text{–}\underset{*}{CH}\text{–}CH_3) - k_4(CH_2D\text{–}\underset{*}{CH}\text{–}CH_3) = 0,$$

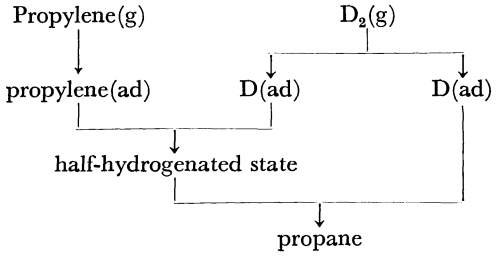
$$\therefore (CH_2D\text{–}\underset{*}{CH}\text{–}CH_3) = (k_3/(k_3'+k_4))(C_3H_6)_{ad}(D)_{ad},$$

$$v_{ex} = d(C_3H_5D)/dt = k_4(CH_2D\text{–}\underset{*}{CH}\text{–}CH_3) = (k_3k_4/(k_3'+k_4))(C_3H_6)_{ad}(D)_{ad} = \frac{k_3k_4}{k_3'+k_4}K_1K_2^{1/2}(C_3H_6)_g(D_2)_g^{1/2} = k_{ex}(C_3H_6)_g(D_2)_g^{1/2}.$$

The rate constant for the exchange reaction, k_{ex}, is, consequently, equal to $k_3k_4K_1K_2^{1/2}/(k_3'+k_4)$.

Therefore, the exchange reaction between propylene and deuterium may be interpreted as proceeding between the adsorbed propylene and the dissociatively-adsorbed deuterium *via* the half-hydrogenated state, the isopropyl species, as the reaction intermediate, as is shown in Steps (3) and (4).

The Mechanism and the Reaction Intermediate of the Hydrogenation of Propylene. The hydrogenation of propylene to form propane proceeded over the EDA complex of potassium with the polynaphthoquinone in the temperature range from 70 to 200 °C. As is shown in Fig. 3, the rate of the deuterogenation was found to be proportional to the partial pressure of propylene and to be half-order with respect to the deuterium pressure: $d(propane)/dt=k_d(propylene)_g(D_2)_g^{1/2}$. Accordingly, the overall reaction may be expressed as follows:



The hydrogenation of propylene to propane proceeded with hydrogen more easily by a factor of about 1.4 than with deuterium at 140 °C. The activation energy

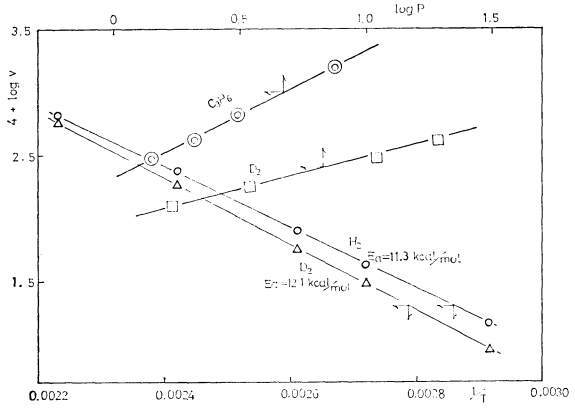


Fig. 3. Dependence of the deuterogenation upon pressures of propylene and deuterium at 140 °C and the activation energies of the reactions.

Table 1. The rates and the activation energies of reactions over the EDA catalysts

EDA catalysts[a)]	Initial rate of the monodeuterio-propylene formation (1-d_1 and 3-d_1) at 95 °C (cm³/min)	Activation energy (kcal/mol)	Initial rate of the propane formation[c)] at 140 °C (cm³/min)	Activation energy (kcal/mol)	Initial rate of the propylene-2-d_1 formation[c)] at 140 °C (cm³/min)
Q–K complex	0.40	6.4	0.027	12.1	0.010
Q–$FeCl_3$–K complex	0.20	6.6	0.123	4.7	0.010

a) Q: polynaphthoquinone. b) propylene=1.4 cmHg, D_2=10 cmHg. c) propylene=1.4 cmHg, D_2=5.6 cmHg.

for the hydrogenation reaction was found to be 11.3 kcal/mol, as is given in Fig. 3.

It was confirmed in Section (1) that the half-hydrogenated state (isopropyl species) is the reaction intermediate in the hydrogen-exchange reaction of propylene with deuterium. When the deuterium addition to propylene also proceeds through the same reaction intermediate, propane will be produced by the following process (5):

$$CH_2D\text{-}\underset{*}{CH}\text{-}CH_3 + D(ad) \xrightarrow{k_5} C_3H_6D_2 \qquad (5)$$

When propane is formed by the deuterium-atom addition to the half-hydrogenated isopropyl species in Eq. (5), the rate equation in the initial stage of the reaction may be expressed as follows:

In the steady state;

$$d(CH_2D\text{-}\underset{*}{CH}\text{-}CH_3)/dt = k_3(C_3H_6)_{ad}(D)_{ad} - (k_3'+k_4)(CH_2D\text{-}\underset{*}{CH}\text{-}CH_3) - k_5(CH_2D\text{-}\underset{*}{CH}\text{-}CH_3)(D)_{ad} = 0,$$

$$(CH_2D\text{-}\underset{*}{CH}\text{-}CH_3) = \frac{k_3(C_3H_6)_{ad}(D)_{ad}}{k_3'+k_4+k_5(D)_{ad}},$$

Accordingly,

$$d(C_3H_6D_2)/dt = k_5(CH_2D\text{-}\underset{*}{CH}\text{-}CH_3)(D)_{ad} = \frac{k_3k_5(C_3H_6)_{ad}(D)_{ad}^2}{k_3'+k_4+k_5(D)_{ad}}.$$

The propylene-deuterium exchange reaction proceeded much more rapidly than the deuterogenation, as is shown in Fig. 1; that is, $k_4 \gg k_5(D)_{ad}$, or $k_3'+k_4 \gg k_5(D)_{ad}$. Accordingly, the rate of the formation of propane, $d(C_3H_6D_2)/dt$, is reduced to $(k_3k_5/(k_3'+k_4))(C_3H_6)_{ad}(D)_{ad}^2$. For $(C_3H_6)_{ad}=K_1(C_3H_6)_g$ and $(D)_{ad}=K_2^{1/2}(D_2)_g^{1/2}$, the rate is given by $(k_3k_5/(k_3'+k_4))K_1K_2(C_3H_6)_g(D_2)_g$ or, accordingly, $k'(C_3H_6)_g(D_2)_g$, where k' is equal to $(k_3k_5/(k_3'+k_4))K_1K_2$. However, the rate equation thus obtained is in disagreement with the experimental results given in Fig. 3, where the initial rate of the propane formation is first-order with respect to propylene and half-order with respect to the deuterium pressure, which excludes the mechanism of the deuterium addition through the half-hydrogenated isopropyl species in Reaction Step (5).

Though the hydrogen-exchange reaction of propylene with deuterium took place through the half-hydrogenated state, the isopropyl species, propylene-2-d_1 (CH_2=CD–CH_2) could also be observed in the temperature range higher than 70 °C. Table 1 shows the results on the EDA complexes of potassium with the polynaphthoquinone both with and without $FeCl_3$, exhibiting that another half-hydrogenated state, the normal propyl species, is present on the surface of the EDA catalyst throughout the reaction.

If the half-hydrogenated state of the normal propyl species is the reaction intermediate in the deuterogenation of propylene, the scheme of the reaction may be expressed as follows:

$$C_3H_6(ad) + D(ad) \underset{k_6'}{\overset{k_6}{\rightleftharpoons}} \underset{*}{CH_2}\text{-}CHD\text{-}CH_3 \qquad (6)$$

$$\underset{*}{CH_2}\text{-}CHD\text{-}CH_3 \xrightarrow{k_7} CH_2\text{=}CD\text{-}CH_3(ad) + H(ad) \qquad (7)$$

$$\underset{*}{CH_2}\text{-}CHD\text{-}CH_3 + D(ad) \xrightarrow{k_8} \underline{C_3H_6D_2} \qquad (8)$$

$$2\underset{*}{CH_2}\text{-}CHD\text{-}CH_3 \xrightarrow{k_9} \underline{C_3H_6D_2} + CH_2\text{=}CH\text{-}CH_3 \quad \underline{C_3H_7D} + CH_2\text{=}CD\text{-}CH_3 \qquad (9)$$

where $\underset{*}{CH_2}$–CHD–CH_3 represents the half-hydrogenated state of the normal propyl species adsorbed on the EDA catalyst. Step (8) shows that propane is produced successively from the half-hydrogenated normal propyl species and the adsorbed deuterium atom, while the propane formation by the disproportionation of the normal propyl species adsorbed on the EDA catalyst is given in Step (9).

When propane is produced successively *via* Reaction Steps (6) and (8) through the half-hydrogenated normal propyl species under the condition of a negligible hydrogen exchange, propane-d_2 ($C_3H_6D_2$) should be the only product in the deuterogenation of propylene (C_3H_6) and the formation of propane-d_1 (C_3H_7D) will not be appreciable. Propylene-d_5 (CD_2=CH–CD_3) was employed to examine clearly the deuterium content in the deuterated propane, where CD_2=CH–CD_3 remained unchanged by the rapid exchange reaction with deuterium through the isopropyl species and where the amount of the CD_2=CD–CD_3 formation through the normal propyl species was small under the present reaction conditions. The main product in the deu-

Table 2. The formation of deuterated propane in the deuterogenation of C_3HD_5 at 140 °C

EDA catalysts	The relative ratio in deuterated propane		
	$C_3H_2D_6$ (propane-d_1)	C_3HD_7 (propane-d_2)	C_3D_8 (propane-d_3)
Q–K complex	2%	81%	17%
Q–$FeCl_3$–K complex	2%	92%	6%

terium addition to CD_2=CH–CD_3(C_3HD_5) was found to be C_3HD_7, as is shown in Table 2; a small amount of C_3D_8 was also produced from the deuterium addition to CD_2=CD–CD_3, CD_2=CD–CD_3 being formed by the propylene-d_5—deuterium exchange reaction *via* the normal propyl species. Reaction Process (9) may, consequently, be excluded.

Accordingly, the initial rate of the formation of propane may be given by the following equation:

In the steady state, the *n*-propyl species on the surface stays constant,

$$\mathrm{d}(\overset{*}{\mathrm{CH_2}}\text{–CHD–}\mathrm{CH_3})/\mathrm{d}t = k_6(\mathrm{C_3H_6})_{\mathrm{ad}}(\mathrm{D})_{\mathrm{ad}} - (k_6'+k_7)(\overset{*}{\mathrm{CH_2}}\text{–CHD–}\mathrm{CH_3}) - k_8(\overset{*}{\mathrm{CH_2}}\text{–CHD–}\mathrm{CH_3})(\mathrm{D})_{\mathrm{ad}} = 0,$$

$$\therefore\ (\overset{*}{\mathrm{CH_2}}\text{–CHD–}\mathrm{CH_3}) = \frac{k_6(\mathrm{C_3H_6})_{\mathrm{ad}}(\mathrm{D})_{\mathrm{ad}}}{k_6'+k_7+k_8(\mathrm{D})_{\mathrm{ad}}},$$

$$v_{\mathrm{d}} = \mathrm{d}(\mathrm{C_3H_6D_2})/\mathrm{d}t = k_8(\overset{*}{\mathrm{CH_2}}\text{–CHD–}\mathrm{CH_3})(\mathrm{D})_{\mathrm{ad}} = \frac{k_6k_8(\mathrm{C_3H_6})_{\mathrm{ad}}(\mathrm{D})_{\mathrm{ad}}^2}{k_6'+k_7+k_8(\mathrm{D})_{\mathrm{ad}}}.$$

The rates of the deuterogenation were found to be larger than those of the propylene-2-d_1 formation by a factor of 2.7 on the Fe-free complex (Q–K complex) and by one of 12.3 over the Fe-containing complex (Q–$FeCl_3$–K complex), as is shown in Table 1. The difference in the values of k'_6 and k_7 corresponds to the isotope effect, and k_6' seems to be smaller than k_7. These observations lead to the $(k_6'+k_7)<k_8(\mathrm{D})_{\mathrm{ad}}$ relation. Accordingly, the rate equation is reduced as follows:

$$v_{\mathrm{d}} = k_6(\mathrm{C_3H_6})_{\mathrm{ad}}(\mathrm{D})_{\mathrm{ad}} = k_6K_1K_2^{1/2}(\mathrm{C_3H_6})_{\mathrm{g}}(\mathrm{D_2})_{\mathrm{g}}^{1/2},$$

$$\text{provided}\ (\mathrm{C_3H_6})_{\mathrm{ad}} = K_1(\mathrm{C_3H_6})_{\mathrm{g}}\ \text{and}\ (\mathrm{D})_{\mathrm{ad}} = K_2^{1/2}(\mathrm{D_2})_{\mathrm{g}}^{1/2}.$$

The rate equation is in agreement with the results, suggesting that the formation of propane occurs *via* the half-hydrogenated normal propyl species in Reaction Steps (6) and (8).

On the Fe-containing complex as well as over the Fe-free complex the half-hydrogenated state of propylene, the isopropyl species, was found to be the reaction intermediate of the propylene-deuterium exchange. As is given in Table 1, the activation energy of the exchange reaction was much less affected by the Fe addition to the complex. However, the activation energy of the deuterogenation markedly decreased upon the Fe addition. The value, 4.7 kcal/mol, for the deuterogenation of propylene was also smaller than that for the propylene-deuterium exchange reaction. The rate of the deuterium addition to propylene, $v_{\mathrm{d}}'=k_{\mathrm{d}}'(\mathrm{propylene})_{\mathrm{g}}(\mathrm{D_2})_{\mathrm{g}}^{1/2}$, was markedly accelerated by the Fe addition to the complex. Consequently, the difference in the effect of the Fe addition on the propylene-deuterium exchange and the deuterium addition to propylene was observed, also suggesting that the hydrogenation and the hydrogen exchange of propylene over the EDA complexes of the polynaphthoquinones proceed through different half-hydrogenated states of propylene.

Consequently, the hydrogen-exchange reaction of propylene with deuterium proceeded through the half-hydrogenated state of isopropyl species, while the half-hydrogenated state of normal propyl species was indicated to be the reaction intermediate in the hydrogenation of propylene. It is of interest to note that the half-hydrogenated state is the reaction intermediate in both the propylene-deuterium exchange and the deuterogenation of propylene over the EDA complexes of potassium with the polynaphthoquinones, but that the former reaction proceeds through the half-hydrogenated state, the isopropyl species, and the latter, through another half-hydrogenated state, the normal propyl species.

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