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REACTION STRUCTURE OF ETHYLENE HYDROGENATION ON METALLIC CATALYSTS: Part 4. Analysis with Reaction of Equimolar d0- and d4-ethylene with Equimolar Hydrogen and Deuterium

Author(s)
SATO, Shinri; MIYAHARA, Koshiro

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REACTION STRUCTURE
OF ETHYLENE HYDROGENATION ON
METALLIC CATALYSTS

Part 4. Analysis with Reaction of Equimolar
d_{0} and d_{4}-ethylene with Equimolar
Hydrogen and Deuterium

By

Shinri Sato and Koshiro Miyahara*

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Abstract

A new method is proposed for evaluation of the rates of elementary steps in ethylene hydrogenation over metallic catalysts. This method is based on analysis of the evolution rates of d_{1-}, d_{2}-ethylene and d_{1}-hydrogen in course of the reaction of equimolar d_{0} and d_{4}-ethylene with equimolar hydrogen and deuterium. The results of analysis with the reaction over evaporated Cu, Rh, Ni and Pt films show that the method is advantageous in a case of ethylene hydrogenation accompanying a fast isotopic mixing of hydrogen in ethylene.

Introduction

Rates of the following elementary steps I\textsubscript{a}, etc. in deuteration of light ethylene over various metal catalysts have been evaluated in previous works.\textsuperscript{1-6)}

\[ \begin{align*}
\text{C}_2\text{H}_4 & \xrightarrow{\text{I}_{\text{s}}} \text{C}_2\text{H}_4\text{(a)} & \text{II} & \xrightarrow{\text{I}_{\text{b}}} \text{C}_2\text{H}_5\text{(a)} & \text{III} & \xrightarrow{\text{H}_2} \text{C}_2\text{H}_6.
\end{align*} \]

In these works the rates of steps are given as functions of two parameters, \textit{i.e.}, the deuterium fractions of adsorbed ethylene and adsorbed hydrogen atoms, which are evaluated from the evolution rates of deuterio-substituted ethylene, hydrogen and ethane measured at the initial stage of ethylene deuteration. This method, however, has a disadvantage that usual mass-

*) Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan.
spectrometric measurement of the amounts of deutero-ethanes is inevitably so inaccurate as to give a considerable error in evaluation of the rates of steps. Method of the mass-spectrometric measurement has been improved\cite{5,7,8} but not sufficiently reliable. It is consequently advisable to develop a new method for evaluation of the rates of steps without measuring the evolution rates of deutero-ethanes.

When an equimolar mixture of d\textsubscript{0} and d\textsubscript{r}-ethylene reacts with an equimolar mixture of hydrogen and deuterium, the parameters mentioned above are constantly 0.5 with neglect of isotopic effect, and the rates of steps I\textsubscript{a} and II of scheme (1) can be evaluated from the rate of hydrogen mixing in ethylene as developed in the present paper, while the rate of step I\textsubscript{b} has been shown\cite{2,3} to be evaluated from the rate of isotopic equilibration of hydrogen and deuterium during the reaction. As a matter of course, this method is not applicable to a case where hydrogen mixing in ethylene or hydrogen proceeds on sites inactive for ethylene hydrogenation as concluded with Co oxide catalyst\cite{9} or \emph{via} any steps other than the steps of scheme (1), \emph{e.g.}, dissociative adsorption of ethylene as observed with freshly evaporated Ni film\cite{2,10}.

The present method is applied to the reaction over evaporated Cu, Rh, Ni and Pt films and the results are discussed in comparison with the previous results\cite{1,3}.

\textbf{Calculation of Rates of Elementary Steps}

Symbols used are summarized below.

\begin{itemize}
  \item $V_s$: steady rate of ethylene hydrogenation,
  \item $v_+(s)$, $v_-(s)$: forward or backward unidirectional rate of step $s$,
  \item P, D, H: protium, deuterium or hydrogen atom (irrespective of P or D),
  \item $V^{E_l}$, $V^{H_m}$, $V^{A_n}$: evolution rate of d\textsubscript{r}-ethylene (E\textsubscript{r}), d\textsubscript{m}-hydrogen (H\textsubscript{m}) or d\textsubscript{n}-ethane (A\textsubscript{n}),
  \item $X_t$, $x_t$: fraction of d\textsubscript{r}-ethylene in gas or adsorbed phase,
  \item $Y_m$, $Z_n$: fraction of d\textsubscript{m}-hydrogen in H\textsubscript{2} or d\textsubscript{n}-ethane in C\textsubscript{2}H\textsubscript{6},
  \item $y_i$, $y_0$: fraction of D(a) or P(a) in H(a),
  \item $P_E$, $P_H$: partial pressure of ethylene or hydrogen.
\end{itemize}

Evolution rates of deutero-substituted ethylene, hydrogen and ethane are given according to scheme (1) as

\begin{equation}
V^{E_l} = x_l v_-(I_a) - X_l v_+(I_a), \quad (l=0, \ldots, 4),
\end{equation}

\begin{equation}
V^{H_m} = \frac{2!}{(2-m)!m!} y_0^{2-m} y_1^n v_-(I_b) - Y_m v_+(I_b), \quad (m=0, 1, 2),
\end{equation}
Reaction Structure of Ethylene Hydrogenation, Part 4

and

\[ V_{\text{H}} = \left( y_0^0 x_n + 2 y_0 y_1 x_{n-1} + y_0^2 x_{n-2} \right) v_+ (\text{II}), \quad (n = 0, \ldots, 6), \quad (4) \]

respectively, where isotopic effect is ignored and the term including \( v_- (\text{III}) \) is neglected in Eq. (4) as step III is perfectly irreversible under usual experimental conditions.\(^\text{10}\) Steady rate of ethylene hydrogenation is given as

\[ V_s = -dP_e/\text{d}t = v_+(s) - v_-(s), \quad (s = I_1, I_2, I_3 \text{ or } I_4). \quad (5) \]

Steady state condition for adsorbed \( d_1 \)-ethylene is given as\(^*\)

\[
\begin{bmatrix}
  b_0 & c_0 & 0 & 0 & 0 \\
  a_1 & b_1 & c_1 & 0 & 0 \\
  0 & a_2 & b_2 & c_2 & 0 \\
  0 & 0 & a_3 & b_3 & c_3 \\
  0 & 0 & 0 & a_4 & b_4
\end{bmatrix}
\begin{bmatrix}
  x_0 \\
  x_1 \\
  x_2 \\
  x_3 \\
  x_4
\end{bmatrix}
= \begin{bmatrix}
  X_0 \\
  X_1 \\
  X_2 \\
  X_3 \\
  X_4
\end{bmatrix}
\]

(6)

where

\[
\begin{align*}
  \alpha &= (l-5) y_1 v_- (\text{II})/6v_+(I_1), \\
  b_1 &= 1 + (4y_1 - y_1 + y_0) v_- (\text{II})/6v_+(I_1), \\
  c_1 &= -(l + 1) y_0 v_- (\text{II})/6v_+(I_1).
\end{align*}
\]

(7)

On the other hand, \( V_{\text{st}} \) is expressed in terms of \( X_t \) and \( P_e \) as

\[ V_{\text{st}} \equiv \frac{d(X_t P_e)}{dt} = \frac{dX_t}{dt} P_e + \frac{dP_e}{dt} X_t. \quad (8) \]

Eliminating \( V_{\text{st}} \) and \( v_+(I_k) \) from Eqs. (2), (5) and (8), we have

\[ dX_t/dt = -(X_t - x_t) v_- (I_1)/P_e \quad (9) \]

and, further,

\[ dX_t/dt = -\left( X_t - \sum_{i=1}^{5} \frac{M_{t+1}}{M} X_{t-1} \right) \frac{v_- (I_1)}{P_e} \quad (10) \]

by substitution of \( x_t \) from Eq. (6). In Eq. (10), \( M \) is the coefficient matrix of \( x_t \) in the left side of Eq. (6) and \( M_{t+1} \) is the cofactor of \((i, l+1)\) element of \( M \).

The following relations hold throughout the reaction of equimolar \( d_0 \)- and \( d_1 \)-ethylene with equimolar \( P_2 \) and \( D_2 \), with neglect of isotopic effect:

\[ y_1 = y_0 = 0.5, \quad (11) \]

\(^*\) Cf. ref. 4, p. 178 or ref. 10, p. 44.
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\[ X_0 = X_b, \quad X_1 = X_b, \quad X_2 = 1 - 2(X_0 + X_1), \quad (12) \]
\[ x_0 = x_b, \quad x_1 = x_b, \quad x_2 = 1 - 2(x_0 + x_1). \quad (13) \]

Equation (10) is accordingly simplified as

\[ \frac{dX_0}{dt} = \left( -X_0 + \frac{3v_+(I_a)}{4(3v_+(I_a) + 2v_-(II))} X_1 + \frac{v_-(II)}{8(3v_+(I_a) + 2v_-(II))} \right) \]
\[ \frac{v_-(I_a) v_-(II)}{(3v_+(I_a) + v_-(II)) P_E}, \quad (14) \]
\[ \frac{dX_1}{dt} = \left( \frac{1}{2} - 2X_1 \right) \frac{v_-(I_a) v_-(II)}{(3v_+(I_a) + 2v_-(II)) P_E}, \quad (15) \]
\[ \frac{dX_2}{dt} = -2 \left( \frac{dX_0}{dt} + \frac{dX_1}{dt} \right). \quad (16) \]

By using the initial condition of reaction, \( X_0 = 0.5 \) and \( X_1 = 0 \), the following equation is derived from Eqs. (14) and (15):

\[ \left( \frac{dX_2}{dX_1} \right)_0 = \left( -1 + \frac{v_-(II)}{4(3v_+(I_a) + 2v_-(II))} \right) \frac{3v_+(I_a) + 2v_-(II)}{3v_+(I_a) + v_-(II)} \cdot (17) \]

Second term in the parentheses of Eq. (17) attains a maximum value of 1/8 when \( v_+(I_a)/v_-(II) = 0 \), and hence it is neglected as compared with unity. Accordingly, we have

\[ v_+(I_a)/v_-(II) = \left\{ 2(dX_1/dX_2)_0 - 1 \right\}/3 \quad (18) \]

from Eqs. (16) and (17). Initial evolution rate of \( d_1 \)-ethylene, on the other hand, is given by Eq. (8) as

\[ V_b = P_E(dX_1/dt)_0. \quad (19) \]

Substituting \( dX_1/dt \) of Eq. (15) into Eq. (19) we have

\[ v_-(I_a) = 2V_b(3v_+(I_a)/v_-(II) + 2). \quad (20) \]

Thus, the unidirectional rates of steps I_\text{a} and II can be evaluated according to Eqs. (5), (18) and (20) by measurements of \( V_a, V^b_1 \) and \( V^b_2 \).

Backward rate of step I_\text{b} is given by Eqs. (3) and (11) by taking account of the initial condition of reaction, \( Y_1 = 0 \), as

\[ v_-(I_b) = 2V_b^{pd}, \quad (21) \]

and, accordingly, forward rate of step I_\text{a} is evaluated by Eq. (5).

Ratio of \( v_-(II) \) to \( v_+(I_a) \) is evaluated otherwise from the evolution rates of deutero-ethanes as follows. In the present reaction, the evolution rate of \( d_\text{a} \)-ethane is given in terms of \( x_0, x_1 \) and \( V_s (=v_+(III)) \) as
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\[ V^{A_0} = V^{A_1} = x_0 V_s / 4, \]
\[ V^{A_1} = V^{A_2} = (x_0 / 2 + x_1 / 4) V_s, \]
\[ V^{A_2} = V^{A_1} = (1 - x_1) V_s / 4 = (1/4 - V^{A_1}) V_s, \]
\[ V^{A_1} = (1/2 - x_0 - x_1 / 2) V_s = (1/2 - 2 V^{A_1}) V_s, \]

(22)

according to Eqs. (4), (11) and (13). In Eqs. (22) \( x_0 \) and \( x_1 \) at initial stage of the reaction are expressed as solutions of Eq. (6) as

\[ x_0 = \frac{3}{6 + 2R} + \frac{R}{8(3 + R)(3 + 2R)}, \]
\[ x_1 = \frac{R}{2(3 + 2R)}, \]

(23)

(24)

where \( R = \frac{v_- (II)/v_+ (I_s)}{v_+ (I_s)}. \) According to these equations, the relative evolution rates \( V^{A_0} / V_s \)'s at the initial stage are calculated as functions of \( R \) as shown in Figs. 1 a) and b). With reference to these figures, the values of \( R \) can be estimated by measuring \( V^{A_0} / V_s \)'s.

Fig. 1. Calculated evolution rates of deutero-ethanes at the initial stage of reaction of an equimolar mixture of \( C_2P_4 \) and \( C_2D_4 \) with an equimolar mixture of \( P_2 \) and \( D_2 \). \( (R = v_- (II)/v_+ (I_s)). \)

**Experimental**

Apparatus, materials and experimental procedures are the same as described in the previous papers.\(^1\)\(^-\)\(^3\) Reaction was carried out with equimolar \( C_2P_4, C_2D_4, P_2, \) and \( D_2 \) at 40 mmHg of the initial total pressure and reacting gas was sampled at times for mass-spectrometric analysis.\(^1\)
Results and Discussion

Reaction on Cu film. Reaction was carried out at 101 and 137°C and time courses of d_{1}-ethylene evolution are plotted in Figs. 2 a) and b). Relatively large amount of d_{1}-ethylene is due to reactant ethylene originally involving ca. 2% of d_{3}-ethylene. Relative rates of steps I, and II are evaluated as given in Table 1 from the evolution rates of d_{1}- and d_{3}-ethylene after the induction period. Table 1 shows that both of steps I, and II are far faster than hydrogenation of ethylene and step I, is ca. 2.4 times as fast as step II.

Table 1. Evolution rates of d_{1}- and d_{3}-ethylene and relative rates of steps I, and II at the initial stage of reaction with equimolar C_{2}P_{4}, C_{2}D_{4}, P_{2} and D_{2} on Cu film.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>(dX_1/dt) (%/min.)</th>
<th>(dX_3/dt) (%/min.)</th>
<th>(v_+ (I,)/V_s)</th>
<th>(v_+ (II)/V_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>0.43</td>
<td>0.10</td>
<td>610</td>
<td>250</td>
</tr>
<tr>
<td>137</td>
<td>1.6</td>
<td>0.39</td>
<td>740</td>
<td>310</td>
</tr>
</tbody>
</table>

Fig. 2. Hydrogen mixing between C_{2}P_{4} and C_{2}D_{4} during the reaction on Cu film with equimolar C_{2}P_{4}, C_{2}D_{4}, P_{2} and D_{2} at 101°C (a) and 137°C (b).
In order to make sure the result of Table 1, the time course of hydrogen mixing in ethylene was simulated according to Eqs. (5) and (10) by a computer. In this simulation, the origin of reaction time is adjusted to the end of induction period, \( y_t \) is set constantly at 0.5, the initial values of \( X_i \)'s and \( P_e \) are adjusted to the experimental condition, and the values of \( v_+ (I_s) \) etc. are given from Table 1 as constants throughout the time course. Results of the simulation according to Runge-Kutta-Gill method\(^{11}\) are shown in Figs. 2 a) and b) with full lines. Good agreement between the simulation and the experiment suggests adequacy of the presumptions for simulation, i.e., (i) hydrogen mixing in ethylene takes place \( \text{via} \) steps I\(_s\) and II of scheme (1), (ii) the rates of these steps are given according to Eqs. (5), (18) and (20), and (iii) isotopic effect on the rate of hydrogen mixing in ethylene is negligible.

The rates of these steps evaluated previously\(^1\) from the results of ethylene deuteriation are considerably smaller than the present ones owing to the inaccurate measurement of the evolution rates of deutero-ethanes in the previous work.\(^1\)

Rate of step I\(_b\) in this reaction was not determined since simultaneous \( P_2-D_2 \) equilibration was immeasurably slow.

**Reaction on Rh film.** Table 2 shows the results of reaction carried out at temperatures from \(-45\) to \(23^\circ\)C with evaporated Rh film. Relative rates of steps I\(_s\) and II given in Table 2 are in agreement with those evaluated previously\(^3\), indicating that the previous method mainly based on analysis of the evolution rates of deutero-ethanes is sufficiently reliable in a case of steps I\(_s\) and II being relatively slow. Figure 3 shows the distribution of deutero-ethanes formed by the reaction at \(-13^\circ\)C; the fraction \( Z_n \) of d\(_n\)-ethane is equal to \( V^{n=1}/V_s \) in this case since the distribution of deutero-ethanes is practically unchanged throughout the reaction. Even though the mass-spectrometric analysis of deutero-ethanes is not accurate, the distribution shown in Fig. 3 is obviously far from its equilibrium. With

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>( \frac{dX_1}{dt} ) (%/min.)</th>
<th>( \frac{dX_2}{dt} ) (%/min.)</th>
<th>( \frac{v_+ (I_s)}{V_s} )</th>
<th>( \frac{v_+ (II)}{V_s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>2.3</td>
<td>1.0</td>
<td>2.3</td>
<td>2.9</td>
</tr>
<tr>
<td>0</td>
<td>0.92</td>
<td>0.48</td>
<td>1.9</td>
<td>3.0</td>
</tr>
<tr>
<td>(-22)</td>
<td>0.15</td>
<td>0.07</td>
<td>1.5</td>
<td>2.4</td>
</tr>
<tr>
<td>(-45)</td>
<td>0.08</td>
<td>0.07</td>
<td>1.6</td>
<td>2.2</td>
</tr>
</tbody>
</table>
TABLE 3. Relative rates of steps I_a and II on Ni film estimated by the simulation method.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>(v_+(I_a)/V_s)</th>
<th>(v_+(II)/V_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>29</td>
<td>25</td>
</tr>
<tr>
<td>24</td>
<td>24</td>
<td>32</td>
</tr>
<tr>
<td>0</td>
<td>30</td>
<td>36</td>
</tr>
</tbody>
</table>

reference to Fig. 1, the value of \(R(=v_-(II)/v_+(I_a))\) is estimated as 3~5 in agreement with the above conclusion.

The present method is not applicable to evaluation of the rate of step I_a since the step is composed of two elementary steps as concluded previously,\(^3\) while the previous method\(^2,3\) is still useful.

**Reaction on Ni film.** Relative rates of steps I_a and II were estimated as given in Table 3 by simulating the time course of deutero-ethylene formation observed in the previous work\(^3\); these rates obtained are larger than those evaluated previously\(^2\) similarly to the case of Cu film.

**Reaction on Pt film.** Hydrogen mixing in ethylene was so slow that the evolution rate of \(d_2\)-ethylene was not determined accurately. From the distribution of deutero-ethanes produced by the reaction (Fig. 4), the value of \(R\) is estimated to be nearly equal to that on Rh film in agreement with the previous result.\(^3\)

**Summary**

It was shown that the rates of steps I_a and II of scheme (1) can be evaluated easily and accurately from the rate of hydrogen mixing between \(C_2P_4\) and \(C_2D_4\) during the reaction of an equimolar mixture of \(C_2P_4\) and
C\textsubscript{2}D\textsubscript{4}, with an equimolar mixture of P\textsubscript{2} and D\textsubscript{2}. The present method is especially useful in a case of ethylene hydrogenation accompanying fast hydrogen mixing in ethylene. Differences between the present and the previous results are mainly due to error in the mass-spectrometric analysis of deuteroethanes in the previous works\textsuperscript{1-3)} but the error is not so significant as to revise the previous conclusions on the reaction structure of ethylene hydrogenation.

References

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