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Dehydrogenation of Propane over Chromia–Alumina–Potassium Oxide Catalyst

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The dehydrogenation of propane and the hydrogenation of propylene were kinetically investigated over chromia–alumina–potassium oxide catalysts. The reactions were carried out in conventional closed static reactor at temperatures ranging from 443 to 505°C. The runs were performed on propane, propane + propylene, propane + hydrogen and propylene + hydrogen. The rates were obtained from the initial slope of the pressure–time curves. The reaction rate data were described satisfactorily with the rate equation such as

$$r = (\vec{k}_{\mathrm{II}}K_{\mathrm{I}}P_{\mathrm{C_3H_8}} - \overleftarrow{k}_{\mathrm{II}}K_{\mathrm{III}}K_{\mathrm{IV}}P_{\mathrm{H_2}}P_{\mathrm{C_3H_6}})/(1 + K_{\mathrm{IV}}P_{\mathrm{H_2}})(1 + K_{\mathrm{I}}P_{\mathrm{C_3H_8}} + K_{\mathrm{III}}P_{\mathrm{C_3H_6}}).$$

It was concluded that the rate determining step of the reaction was

$$(C_3H_8)_a \rightarrow (C_3H_6)_a + (H_2)_a.$$

INTRODUCTION

Catalytic reactions involving dehydrogenation, hydrogenation, cracking and isomerization are important processes in the petrochemical industry. Among these the dehydrogenation of butane over chromia-alumina catalysts is one of the most important processes for obtaining butenes and butadine. Besides being of commercial interest, both dehydrogenation and hydrogenation of C_4 hydrocarbons occur in a temperature range convenient for kinetic investigation. Both reactions have been extensively investigated from industrial and scientific points of view.

Dodd and Watson (*1*) made a pioneer study of butane and butene dehydrogenation over chromia–alumina catalyst. They set the pattern for much of the later work of the catalytic dehydrogenation of hydrocarbons. The kinetic data were treated by the rate equations developed by Hougen and Watson (*2*), and indicated the dual-site mechanism. In contrast with the results of Dodd and Watson (*1*), Balandin (*3*) described the rates of a large body of catalytic dehydrogenation using a single-site mechanism. Carra *et al.* (*4*) described butane dehydrogenation over chromia–alumina catalysts with allowance of the reversibility of the reaction and proposed a dual-site mechanism. Happel *et al.* (*5*) indicated that neither the dual-site mechanism nor the single-site mechanism was able to afford satisfactory description for butane dehydrogenation over chromia–alumina catalyst. Thereafter, they (*6*) determined both the forward and the reverse reaction rates in butane dehydrogenation with a mixture of *n*-butane, 1-butene and hydrogen in which one of the hydrocarbons was radioactively tagged.

The study of the reaction rate occurring in the dehydrogenation of butane involves many difficulties associated with the complexity of the system such as the formation of the butene isomers and the isomerization of the isomers. In this investigation,

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TABLE 1

Properties of Cr_2O_3–Al_2O_3–K_2O Catalyst

Catalyst No.	Composition (wt%)		Surface area (m^2/g)	Initial rate[a]
	Cr_2O_3	K_2O		
1	7.2	0	189	2.12
2	7.9	0.9	223	1.85
3	7.1	1.6	187	3.09
4	7.15	2.57	184	3.23
5	7.5	3.5	176	2.88
6	7.1	4.3	218	1.60
7	7.2	8.2	167	2.03

[a] Initial rate of dehydrogenation of propane at 443°C in units of 10^{10} molecules/sec cm^2. Initial pressure of propane: 10 Torr.

we performed a study of the kinetics of C_3 hydrocarbons because both the dehydrogenation and the hydrogenation of C_3 hydrocarbons occur in conventional temperature ranges and no isomers were formed in the reaction.

In this paper, we describe the mechanism of the dehydrogenation of propane over chromia–alumina–potassium oxide in some detail. The approach adopted was to set down logically many of the possible elementary steps and to derive rate equations to show that the experimental results conform to such a reaction mechanism.

EXPERIMENTAL METHODS

Catalyst

Alumina was used as a carrier and was prepared from alumina sol (Alumina Sol 200: Nissan Chemical Co. Ltd.) as follows. The alumina sol was dried to alumina gel over a water bath, then dried in a drying furnace overnight at 110°C. Then, the gel was crushed, sieved and sizes between 16–32 mesh were separated. The alumina gel was immersed in calculated amounts of mixed aqueous solutions of chromic nitrate at 70°C for 3 hr. The water was evaporated and calcined at 600°C. The weight percent of Cr_2O_3 and K_2O and the BET surface areas determined by adsorption of nitrogen are summarized in Table 1. The catalyst thus obtained was calcined under vacuum at 500°C for 2 hr and heated under 200 Torr of hydrogen for a certain number of hours at the same temperature. Then, the catalyst was calcined under vacuum at 500°C for 2 hr and used for the first run. The subsequent runs were performed after 2-hr evacuation at reaction temperature after the former runs.

Reactants

Hydrogen was supplied from Takachiho Chem. Ind. Co. Ltd. and purified by passage through copper powder heated at 400°C and through a liquid nitrogen trap. Propane and propylene were supplied from Takachiho Chem. Ind. Co. Ltd. and purified by repeated distillations.

No impurities were detected by gas–solid chromatography (GSC) analyses.

Gas Analyses

Analyses of hydrocarbons were performed by GSC with a 60-cm column of silica gel at 60°C. Helium was used as a carrier gas and its flow rate was about 40 ml/min.

Apparatus

The apparatus consists of 3000 ml Pyrex bulb equipped with a cavity for catalyst

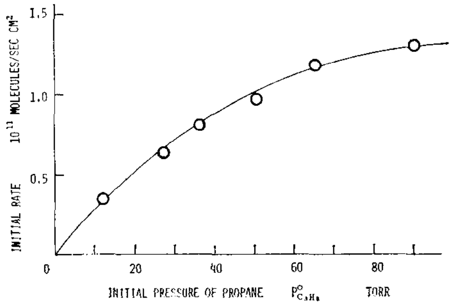

FIG. 1. Initial rate of dehydrogenation of propane as a function of initial pressure of propane over Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C.

bed, a preheater, an oil manometer and a gas handling device for GSC. The bulb, except for the cavity, was surrounded with a metal jacket filled with water maintained at a constant temperature as described previously (7).

RESULTS AND DISCUSSION

Preliminary Run

No products other than propylene and hydrogen were detected by gas chromatographic analyses in the initial stage at 443°C. Formation of methane and ethane (cracking), however, was observed with gas chromatographic analyses as the reaction proceeded and the propylene formed. Initial rate, therefore, was estimated from the initial slope of the pressure–time curve as described previously (7). The initial pressure of propane was obtained from a graphical extrapolation to zero time on the pressure–time curve. The initial dehydrogenation rates changed with increasing potassium content of the Cr_2O_3–Al_2O_3–K_2O catalysts and are tabulated in Table 1. Table 1 shows that No. 4 Cr_2O_3–Al_2O_3–K_2O catalyst is the most active of our catalysts and No. 4 catalyst was used in the following runs. The rate of dehydrogenation of propane changed also with the time of the hydrogen treatment. The maximum activity in the dehydrogenation was obtained with 1-hr hydrogen treatment when the catalyst was heated under 200 Torr of hydrogen at 500°C. The color of the catalyst changed to deep green from deep brown with the hydrogen treatment. The BET surface area determined with nitrogen adsorption at liquid nitrogen temperature did not change. The change in the activity of the dehydrogenation may, therefore, be attributed to the change in the oxidation state of the chromium. In the following experiments, we used as catalyst No. 4 Cr_2O_3–Al_2O_3–K_2O catalyst which was treated with 200 Torr of hydrogen for 1 hr at 500°C.

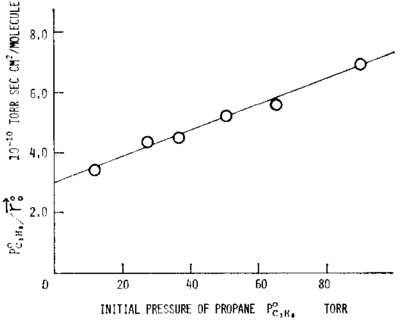

FIG. 2. Langmuir plot of dehydrogenation of propane over Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C. $P_{C_3H_8}{}^0$: initial pressure of propane; $\vec{r}_0{}^0$: initial rate of dehydrogenation of propane.

TABLE 2

Adsorption Equilibrium Constants at 443°C

$K_I \equiv \vec{k}_I/\overleftarrow{k}_I$	0.0145 ± 0.0012[a]	0.0160 ± 0.0012[d]
$K_{III} \equiv \overleftarrow{k}_{III}/\vec{k}_{III}$	0.035 ± 0.004[b]	0.038 ± 0.004[d]
$K_{IV} \equiv \overleftarrow{k}_{IV}/\vec{k}_{IV}$	0.038 ± 0.004[c]	0.034 ± 0.003[e]

[a] Obtained from Fig. 2.
[b] Obtained from Fig. 9.
[c] Obtained from Fig. 8.
[d] Obtained from Fig. 3.
[e] Obtained from Fig. 4 in units of $Torr^{-1}$.

Dehydrogenation of Propane

The catalytic activity decreased gradually with every run and reached a settled one. The settled initial rates of dehydrogenation of propane thus obtained were plotted against the initial pressures of propane as shown in Fig. 1. This behavior can be expressed with the Langmuir-type kinetic equation such as

$$\vec{r}_0{}^0 = \frac{k_1 K_1 P_{C_3H_8}{}^0}{1 + K_1 P_{C_3H_8}{}^0}, \qquad (1)$$

where k_1 and K_1 are constants, $\vec{r}_0{}^0$ and $P_{C_3H_8}{}^0$ are initial rate of the dehydrogenation and the initial pressure of propane, respectively. Equation (1) can be written as follows:

$$(P_{C_3H_8}{}^0/\vec{r}_0{}^0) = (1/k_1K_1) + (1/k_1)P_{C_3H_8}{}^0. \qquad (2)$$

This is a linear relation between $(P_{\mathrm{C_3H_8}}{}^0/\overrightarrow{r}_0{}^0)$ and $P_{\mathrm{C_3H_8}}{}^0$. Such a plot is given in Fig. 2. Constant K_1 obtained is tabulated in Table 2. From the plots of $\ln k_1$ and $\ln K_1$ vs $1/T$, the apparent activation energy 33.9 kcal/mole and the adsorption enthalpy 10.0 kcal/mole were obtained.

Reaction Mechanism and Rate Equation

Twenty-two possible reaction paths were considered which were constituted from several elementary reaction steps. In these reaction paths, we have considered an associative mechanism, dissociative mechanism, Langmuir–Hinshelwood mechanism, Eley–Rideal mechanism, single-site mechanism and dual-site mechanism (*8*). Rate equations can be derived on condition that one of the elementary steps is the rate determining one in each reaction path. One hundred and three of the possible rate equations were derived from 103 corresponding mechanisms. Ninty-three of these rate equations could not interpret the dependency of the initial rate of the dehydrogenation on the initial propane pressure described in Eq. (1), and these 93 rate equations were eliminated. The dependency of the initial rate on the initial pressure [Eq. (1)] seemingly could be interpreted with the other 10 rate equations described below.

$$r=\frac{\overrightarrow{k}_{\mathrm{II}}\frac{\overleftarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}-\overleftarrow{k}_{\mathrm{II}}\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}}P_{\mathrm{C_3H_6}}P_{\mathrm{H_2}}}{\left(1+\frac{\overleftarrow{k}_{\mathrm{I}}}{\overrightarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}\right)\left(1+\frac{\overleftarrow{k}_{\mathrm{III}}}{\overrightarrow{k}_{\mathrm{III}}}P_{\mathrm{C_3H_6}}\right)\left(1+\frac{\overleftarrow{k}_{\mathrm{IV}}}{\overrightarrow{k}_{\mathrm{IV}}}P_{\mathrm{H_2}}\right)}, \qquad \text{(D-II)}$$

$$r=\frac{\overrightarrow{k}_{\mathrm{II}}\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}-\overleftarrow{k}_{\mathrm{II}}\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}}P_{\mathrm{C_3H_6}}P_{\mathrm{H_2}}}{\left(1+\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}+\frac{\overleftarrow{k}_{\mathrm{III}}}{\overrightarrow{k}_{\mathrm{III}}}P_{\mathrm{C_3H_6}}\right)\left(1+\frac{\overleftarrow{k}_{\mathrm{IV}}}{\overrightarrow{k}_{\mathrm{IV}}}P_{\mathrm{H_2}}\right)}, \qquad \text{(E-II)}$$

$$r=\frac{\overrightarrow{k}_{\mathrm{II}}\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}-\overleftarrow{k}_{\mathrm{II}}\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}}P_{\mathrm{C_3H_6}}P_{\mathrm{H_2}}}{\left(1+\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}\right)\left(1+\frac{\overleftarrow{k}_{\mathrm{III}}}{\overrightarrow{k}_{\mathrm{III}}}P_{\mathrm{C_3H_6}}\right)\left\{1+\left(\frac{\overleftarrow{k}_{\mathrm{IV}}}{\overrightarrow{k}_{\mathrm{IV}}}\cdot P_{\mathrm{H_2}}\right)^{\frac{1}{2}}\right\}^2}, \qquad \text{(I-II)}$$

$$r=\frac{\overrightarrow{k}_{\mathrm{II}}\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}-\overleftarrow{k}_{\mathrm{II}}\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}}P_{\mathrm{C_3H_6}}P_{\mathrm{H_2}}}{\left(1+\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}+\frac{\overleftarrow{k}_{\mathrm{III}}}{\overrightarrow{k}_{\mathrm{III}}}P_{\mathrm{C_3H_6}}\right)\left\{1+\left(\frac{\overleftarrow{k}_{\mathrm{IV}}}{\overrightarrow{k}_{\mathrm{IV}}}\cdot P_{\mathrm{H_2}}\right)^{\frac{1}{2}}\right\}^2}, \qquad \text{(J-II)}$$

$$r=\frac{\overrightarrow{k}_{\mathrm{II}}\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}-\overleftarrow{k}_{\mathrm{II}}\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}}P_{\mathrm{C_3H_6}}P_{\mathrm{H_2}}}{\left(1+\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}\right)\left\{1+\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}}\left(\frac{\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{V}}}\cdot P_{\mathrm{H_2}}\right)^{\frac{1}{2}}P_{\mathrm{C_3H_6}}\right\}\left\{1+\left(\frac{\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{V}}}\cdot P_{\mathrm{H_2}}\right)^{\frac{1}{2}}\right\}}, \qquad \text{(O-II)}$$

$$r=\frac{\overrightarrow{k}_{\mathrm{II}}\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}-\overleftarrow{k}_{\mathrm{II}}\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}}P_{\mathrm{C_3H_6}}P_{\mathrm{H_2}}}{\left\{1+\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}+\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}}\left(\frac{\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{V}}}\cdot P_{\mathrm{H_2}}\right)^{\frac{1}{2}}\cdot P_{\mathrm{C_3H_6}}+\frac{\overleftarrow{k}_{\mathrm{IV}}}{\overrightarrow{k}_{\mathrm{IV}}}P_{\mathrm{C_3H_6}}\right\}\left\{1+\left(\frac{\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{V}}}\cdot P_{\mathrm{H_2}}\right)^{\frac{1}{2}}\right\}},\qquad\text{(P-II)}$$

$$r=\frac{\overrightarrow{k}_{\mathrm{II}}\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}-\overleftarrow{k}_{\mathrm{II}}\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}\overleftarrow{k}_{\mathrm{VI}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}\overrightarrow{k}_{\mathrm{VI}}}P_{\mathrm{C_3H_6}}P_{\mathrm{H_2}}}{\left(1+\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}\right)\left\{1+\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}}\left(\frac{\overleftarrow{k}_{\mathrm{VI}}}{\overrightarrow{k}_{\mathrm{VI}}}P_{\mathrm{H_2}}\right)^{\frac{1}{2}}P_{\mathrm{C_3H_6}}\right\}\left\{1+\left(\frac{\overleftarrow{k}_{\mathrm{VI}}}{\overrightarrow{k}_{\mathrm{VI}}}\cdot P_{\mathrm{H_2}}\right)\right\}^{\frac{1}{2}}},\qquad\text{(R-II)}$$

$$r=\frac{1}{\left\{1+\left(\frac{\overleftarrow{k}_{\mathrm{VI}}}{\overrightarrow{k}_{\mathrm{VI}}}\cdot P_{\mathrm{H_2}}\right)^{\frac{1}{2}}\right\}}$$

$$\times\frac{\overrightarrow{k}_{\mathrm{II}}\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}-\overleftarrow{k}_{\mathrm{II}}\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}\overleftarrow{k}_{\mathrm{VI}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}\overrightarrow{k}_{\mathrm{VI}}}P_{\mathrm{C_3H_6}}P_{\mathrm{H_2}}}{\left\{1+\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}+\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}}\left(\frac{\overleftarrow{k}_{\mathrm{VI}}}{\overrightarrow{k}_{\mathrm{VI}}}P_{\mathrm{H_2}}\right)^{\frac{1}{2}}P_{\mathrm{C_3H_6}}+\frac{\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}}\left(\frac{\overrightarrow{k}_{\mathrm{VI}}}{\overleftarrow{k}_{\mathrm{VI}}}\right)^{\frac{1}{2}}\frac{P_{\mathrm{C_3H_6}}}{(P_{\mathrm{H_2}})^{\frac{1}{2}}}+\frac{\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{V}}}P_{\mathrm{C_3H_6}}\right\}},\qquad\text{(S-II)}$$

$$r=\frac{\overrightarrow{k}_{\mathrm{II}}\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_6}}-\overleftarrow{k}_{\mathrm{II}}\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}\overleftarrow{k}_{\mathrm{VI}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}\overrightarrow{k}_{\mathrm{VI}}}P_{\mathrm{C_3H_6}}P_{\mathrm{H_2}}}{\left(1+\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}k_{\mathrm{C_3H_8}}\right)\left\{1+\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}}\left(\frac{\overleftarrow{k}_{\mathrm{VI}}\overleftarrow{k}_{\mathrm{VII}}}{\overrightarrow{k}_{\mathrm{VI}}\overrightarrow{k}_{\mathrm{VII}}}\cdot P_{\mathrm{H_2}}\right)^{\frac{1}{2}}P_{\mathrm{C_3H_6}}\right\}\left\{1+\left(\frac{\overleftarrow{k}_{\mathrm{VI}}\overleftarrow{k}_{\mathrm{VII}}}{\overrightarrow{k}_{\mathrm{VI}}\overrightarrow{k}_{\mathrm{VII}}}\cdot P_{\mathrm{H_2}}\right)^{\frac{1}{2}}\right\}},\qquad\text{(U-II)}$$

$$r=\frac{1}{\left\{1+\frac{\overleftarrow{k}_{\mathrm{VI}}}{\overrightarrow{k}_{\mathrm{VI}}}P_{\mathrm{H_2}}+\left(\frac{\overleftarrow{k}_{\mathrm{VI}}\overleftarrow{k}_{\mathrm{VII}}}{\overrightarrow{k}_{\mathrm{VI}}\overrightarrow{k}_{\mathrm{VII}}}P_{\mathrm{H_2}}\right)^{\frac{1}{2}}\right\}}$$

$$\times\frac{\overrightarrow{k}_{\mathrm{II}}\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}-\overleftarrow{k}_{\mathrm{II}}\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}\overleftarrow{k}_{\mathrm{VI}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}\overrightarrow{k}_{\mathrm{VI}}}P_{\mathrm{C_3H_6}}P_{\mathrm{H_2}}}{\left\{1+\frac{\overrightarrow{k}_{\mathrm{I}}}{\overleftarrow{k}_{\mathrm{I}}}P_{\mathrm{C_3H_8}}+\frac{\overleftarrow{k}_{\mathrm{III}}\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{III}}\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}}\left(\frac{\overleftarrow{k}_{\mathrm{VI}}\overleftarrow{k}_{\mathrm{VII}}}{\overrightarrow{k}_{\mathrm{VI}}\overrightarrow{k}_{\mathrm{VII}}}P_{\mathrm{H_2}}\right)^{\frac{1}{2}}P_{\mathrm{C_3H_6}}+\frac{\overleftarrow{k}_{\mathrm{IV}}\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{IV}}\overrightarrow{k}_{\mathrm{V}}}\left(\frac{\overrightarrow{k}_{\mathrm{VI}}\overrightarrow{k}_{\mathrm{VII}}}{\overleftarrow{k}_{\mathrm{VI}}\overleftarrow{k}_{\mathrm{VII}}}\right)^{\frac{1}{2}}\frac{P_{\mathrm{C_3H_6}}}{(P_{\mathrm{H_2}})^{\frac{1}{2}}}+\frac{\overleftarrow{k}_{\mathrm{V}}}{\overrightarrow{k}_{\mathrm{V}}}P_{\mathrm{C_3H_6}}\right\}},\qquad\text{(V-II)}$$

where $\overrightarrow{k}_{\mathrm{I}}$ and $\overleftarrow{k}_{\mathrm{I}}$ are the forward and the reverse rate constants in elementary reaction (I), respectively. $P_{\mathrm{H_2}}$, $P_{\mathrm{C_3H_8}}$ and $P_{\mathrm{C_3H_6}}$ are the pressures of hydrogen, propane and propylene, respectively. These rate equations were derived from the reaction paths described below on condition that the second step (II) was the rate determining one in the corresponding paths.

$$\mathrm{D}\left\{\begin{array}{lll}
\mathrm{C_3H_8 + S(1)} & \rightleftarrows \mathrm{C_3H_8S(1)}, & \mathrm{(I)} \\
\mathrm{C_3H_8S(1) + S(2) + S(3)} & \rightleftarrows \mathrm{C_3H_6S(2) + H_2S(3) + S(1)}, & \mathrm{(II)} \\
\mathrm{C_3H_6S(2)} & \rightleftarrows \mathrm{C_3H_6 + S(2)}, & \mathrm{(III)} \\
\mathrm{H_2S(3)} & \rightleftarrows \mathrm{H_2 + S(3)}, & \mathrm{(IV)}
\end{array}\right.$$

$$\mathrm{E}\left\{\begin{array}{lll}
\mathrm{C_3H_8 + S(1)} & \rightleftarrows \mathrm{C_3H_8S(1)}, & \mathrm{(I)} \\
\mathrm{C_3H_8S(1) + S(2)} & \rightleftarrows \mathrm{C_3H_6S(1) + H_2S(2)}, & \mathrm{(II)} \\
\mathrm{C_3H_6S(1)} & \rightleftarrows \mathrm{C_3H_6 + S(1)}, & \mathrm{(III)} \\
\mathrm{H_2S(2)} & \rightleftarrows \mathrm{H_2 + S(2)}, & \mathrm{(IV)}
\end{array}\right.$$

$$\mathrm{I}\left\{\begin{array}{lll}
\mathrm{C_3H_8 + S(1)} & \rightleftarrows \mathrm{C_3H_8S(1)}, & \mathrm{(I)} \\
\mathrm{C_3H_8S(1) + S(2) + 2S(3)} & \rightleftarrows \mathrm{C_3H_6S(2) + 2HS(3) + S(1)}, & \mathrm{(II)} \\
\mathrm{C_3H_6S(2)} & \rightleftarrows \mathrm{C_3H_6 + S(2)}, & \mathrm{(III)} \\
\mathrm{2HS(3)} & \rightleftarrows \mathrm{H_2 + 2S(3)}, & \mathrm{(IV)}
\end{array}\right.$$

$$\mathrm{J}\left\{\begin{array}{lll}
\mathrm{C_3H_8 + S(1)} & \rightleftarrows \mathrm{C_3H_8S(1)}, & \mathrm{(I)} \\
\mathrm{C_3H_8S(1) + 2S(2)} & \rightleftarrows \mathrm{C_3H_6S(1) + 2HS(2)}, & \mathrm{(II)} \\
\mathrm{C_3H_6S(1)} & \rightleftarrows \mathrm{C_3H_6 + S(1)}, & \mathrm{(III)} \\
\mathrm{2HS(2)} & \rightleftarrows \mathrm{H_2 + 2S(2)}, & \mathrm{(IV)}
\end{array}\right.$$

$$\mathrm{O}\left\{\begin{array}{lll}
\mathrm{C_3H_8 + S(1)} & \rightleftarrows \mathrm{C_3H_8S(1)}, & \mathrm{(I)} \\
\mathrm{C_3H_8S(1) + S(2) + S(3)} & \rightleftarrows \mathrm{C_3H_7S(2) + HS(3) + S(1)} & \mathrm{(II)} \\
\mathrm{C_3H_7S(2) + S(3) + S(4)} & \rightleftarrows \mathrm{C_3H_6S(4) + HS(3) + S(2)}, & \mathrm{(III)} \\
\mathrm{C_3H_6S(4)} & \rightleftarrows \mathrm{C_3H_6 + S(4)}, & \mathrm{(IV)} \\
\mathrm{2HS(3)} & \rightleftarrows \mathrm{H_2 + 2S(3)}, & \mathrm{(V)}
\end{array}\right.$$

$$\mathrm{P}\left\{\begin{array}{lll}
\mathrm{C_3H_8 + S(1)} & \rightleftarrows \mathrm{C_3H_8S(1)}, & \mathrm{(I)} \\
\mathrm{C_3H_8S(1) + S(2)} & \rightleftarrows \mathrm{C_3H_7S(1) + HS(2)}, & \mathrm{(II)} \\
\mathrm{C_3H_7S(1) + S(2)} & \rightleftarrows \mathrm{C_3H_6S(1) + HS(2)}, & \mathrm{(III)} \\
\mathrm{C_3H_6S(1)} & \rightleftarrows \mathrm{C_3H_6 + S(1)}, & \mathrm{(IV)} \\
\mathrm{2HS(2)} & \rightleftarrows \mathrm{H_2 + 2S(2)}, & \mathrm{(V)}
\end{array}\right.$$

$$\mathrm{R}\left\{\begin{array}{lll}
\mathrm{C_3H_8 + S(1)} & \rightleftarrows \mathrm{C_3H_8S(1)}, & \mathrm{(I)} \\
\mathrm{C_3H_8S(1) + S(2) + S(3)} & \rightleftarrows \mathrm{C_3H_7S(2) + HS(3) + S(1)}, & \mathrm{(II)} \\
\mathrm{C_3H_7S(2) + S(4) + 2S(3)} & \rightleftarrows \mathrm{C_3H_5S(4) + 2HS(3) + S(2)}, & \mathrm{(III)} \\
\mathrm{C_3H_5S(4) + HS(3) + S(5)} & \rightleftarrows \mathrm{C_3H_6S(5) + S(3) + S(4)}, & \mathrm{(IV)} \\
\mathrm{C_3H_6S(5)} & \rightleftarrows \mathrm{C_3H_6 + S(5)}, & \mathrm{(V)} \\
\mathrm{2HS(3)} & \rightleftarrows \mathrm{H_2 + 2S(3)}, & \mathrm{(VI)}
\end{array}\right.$$

$$\mathrm{S}\left\{\begin{array}{lll}
\mathrm{C_3H_8 + S(1)} & \rightleftarrows \mathrm{C_3H_8S(1)}, & \mathrm{(I)} \\
\mathrm{C_3H_8S(1) + S(2)} & \rightleftarrows \mathrm{C_3H_7S(1) + HS(2)}, & \mathrm{(II)} \\
\mathrm{C_3H_7S(1) + 2S(2)} & \rightleftarrows \mathrm{C_3H_5S(1) + 2HS(2)}, & \mathrm{(III)} \\
\mathrm{C_3H_5S(1) + HS(2)} & \rightleftarrows \mathrm{C_3H_6S(1) + S(2)}, & \mathrm{(IV)} \\
\mathrm{C_3H_6S(1)} & \rightleftarrows \mathrm{C_3H_6 + S(1)}, & \mathrm{(V)} \\
\mathrm{2HS(2)} & \rightleftarrows \mathrm{H_2 + 2S(2)}, & \mathrm{(VI)}
\end{array}\right.$$

$$
\mathrm{U}\left\{\begin{array}{lll}
\mathrm{C_3H_8 + S(1)} & \rightleftarrows \mathrm{C_3H_8S(1)}, & \mathrm{(I)}\\
\mathrm{C_3H_8S(1) + S(2) + S(3)} & \rightleftarrows \mathrm{C_3H_7S(2) + HS(3) + S(1)}, & \mathrm{(II)}\\
\mathrm{C_3H_7S(2) + S(4) + S(5)} & \rightleftarrows \mathrm{C_3H_5S(4) + H_2S(5) + S(2)}, & \mathrm{(III)}\\
\mathrm{C_3H_5S(4) + HS(3) + S(6)} & \rightleftarrows \mathrm{C_3H_6S(6) + S(4) + S(3)}, & \mathrm{(IV)}\\
\mathrm{C_3H_6S(6)} & \rightleftarrows \mathrm{C_3H_6 + S(6)}, & \mathrm{(V)}\\
\mathrm{H_2S(5)} & \rightleftarrows \mathrm{H_2 + S(5)}, & \mathrm{(VI)}\\
\mathrm{2HS(3) + S(5)} & \rightleftarrows \mathrm{H_2S(5) + 2S(3)}, & \mathrm{(VII)}
\end{array}\right.
$$

$$
\mathrm{V}\left\{\begin{array}{lll}
\mathrm{C_3H_8 + S(1)} & \rightleftarrows \mathrm{C_3H_8S(1)}, & \mathrm{(I)}\\
\mathrm{C_3H_8S(1) + S(2)} & \rightleftarrows \mathrm{C_3H_7S(1) + HS(2)}, & \mathrm{(II)}\\
\mathrm{C_3H_7S(1) + S(2)} & \rightleftarrows \mathrm{C_3H_5S(1) + H_2S(2)}, & \mathrm{(III)}\\
\mathrm{C_3H_5S(1) + HS(2)} & \rightleftarrows \mathrm{C_3H_6S(1) + S(2)}, & \mathrm{(IV)}\\
\mathrm{C_5H_6S(1)} & \rightleftarrows \mathrm{C_3H_6 + S(1)}, & \mathrm{(V)}\\
\mathrm{H_2S(2)} & \rightleftarrows \mathrm{H_2 + S(2)}, & \mathrm{(VI)}\\
\mathrm{2HS(2)} & \rightleftarrows \mathrm{H_2S(2) + S(2)}, & \mathrm{(VII)}
\end{array}\right.
$$

where S(1) and S(2) are the different vacant sites, and $C_3H_8S(1)$ and $C_3H_6S(2)$ represent the propane adsorbed on site 1 and the propylene adsorbed on site 2, respectively.

Dehydrogenation of Propane in the Presence of Propylene

These 10 rate equations described above were classified into four groups as shown in Table 3 on the basis of the relation between the initial pressure of propane and the ratio of the initial rate $\vec{r}^0$ of the dehydrogenation in the presence of propylene to that $\vec{r}_0{}^0$ in the absence of propylene. Some of these 10 rate equations must, therefore, be eliminated by the examination of the rates of the dehydrogenation in the presence of propylene. The dehydrogenations of propane in the presence of 24.3 Torr of

TABLE 3

Classification of Rate Equation

Dehydrogenation of propane in the presence of hydrogen ($P^0{}_{C_3H_6} = 0$, $P^0{}_{C_3H_8}$ = constant)	Dehydrogenation of propane in the presence of propylene ($P^0{}_{C_3H_6}$ = constant, $P^0{}_{H_2} = 0$)			
	$\dfrac{\vec{r}_0}{\vec{r}_0{}^0 - \vec{r}^0} = 0$ ($r^0 = 0$)	$\dfrac{\vec{r}^0}{\vec{r}_0{}^0 - \vec{r}^0} = \infty$ ($r^0 = r_0{}^0$)	$\dfrac{\vec{r}^0}{\vec{r}_0{}^0 - \vec{r}^0} = \dfrac{1}{K_{\mathrm{III}}P_{C_3H_6}}$ = constant	$\dfrac{\vec{r}^0}{\vec{r}_0{}^0 - \vec{r}^0} = \dfrac{1 + K_{\mathrm{I}}P_{C_3H_8}}{K_5{}^aP_{C_3H_6}}$
$\vec{r}_0{}^0/\vec{r}^0 = 1 + K_{\mathrm{IV}}P_{H_2}$			(D-II)	(E-II)
$(\vec{r}_0{}^0/\vec{r}^0)^{\frac{1}{2}} = 1 + (K_{\mathrm{IV}})^{\frac{1}{2}}(P_{H_2})^{\frac{1}{2}}$			(I-II)	(J-II)
$\vec{r}_0{}^0/\vec{r}^0 = 1 + (K_6)^{\frac{1}{2}b}(P_{H_2})^{\frac{1}{2}}$	(S-II)	(O-II) (R-II) (U-II)		(P-II)
$\vec{r}_0{}^0/\vec{r}_0 = 1 + K_{\mathrm{VI}}P_{H_2} + (K_4)^{\frac{1}{2}c}(P_{H_2})^{\frac{1}{2}}$		(V-II)		

[a] $K_5 = \overleftarrow{k}_{\mathrm{III}}/\overrightarrow{k}_{\mathrm{III}}$ (E-II, J-II), $\overleftarrow{k}_{\mathrm{IV}}/\overrightarrow{k}_{\mathrm{IV}}$ (P-II).

[b] $K_6 = \overleftarrow{k}_{\mathrm{V}}/\overrightarrow{k}_{\mathrm{V}}$ (O-II, P-II), $\overleftarrow{k}_{\mathrm{VI}}/\overrightarrow{k}_{\mathrm{VI}}$ (S-II), $\overleftarrow{k}_{\mathrm{VI}}\overleftarrow{k}_{\mathrm{VII}}/\overrightarrow{k}_{\mathrm{VI}}\overrightarrow{k}_{\mathrm{VII}}$ (U-II).

[c] $K_4 = \overleftarrow{k}_{\mathrm{VI}}\overleftarrow{k}_{\mathrm{VII}}/\overrightarrow{k}_{\mathrm{VI}}\overrightarrow{k}_{\mathrm{VII}}$.

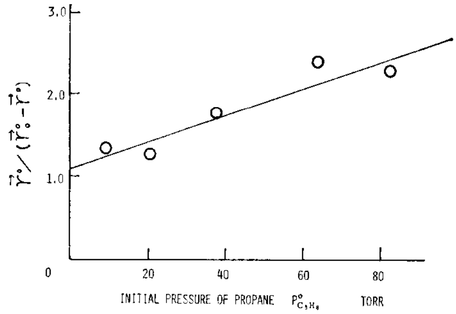

FIG. 3. Initial rate of dehydrogenation of propane in the presence of propylene over Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C. $\vec{r}^0$: initial rate of dehydrogenation of propane in the presence of 24.3 Torr of propylene; $\vec{r}_0^0$: initial rate of dehydrogenation of propane in the absence of propylene.

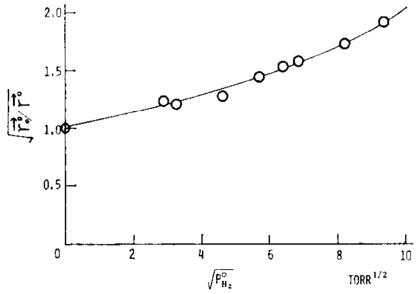

FIG. 5. Initial rate of dehydrogenation of propane in the presence of hydrogen over Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C. $\vec{r}^0$: initial rate of dehydrogenation of propane in the presence of 21.0 Torr of hydrogen; $\vec{r}_0^0$: initial rate of dehydrogenation of propane in the absence of hydrogen.

propylene were performed over the Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C. The ratios $(\vec{r}^0/\vec{r}_0^0)/(1-\vec{r}^0/\vec{r}_0^0) = \vec{r}^0/(\vec{r}_0^0-\vec{r}^0)$ obtained were plotted against the initial pressure of propane as shown in Fig. 3. The straight line with positive slope was obtained. Seven rate equations in the first, second and third columns of Table 3, (D-II), (I-II), (O-II), (R-II), (S-II), (U-II), and (V-II) can, therefore, be eliminated by Fig. 3.

Moreover, some of the other three rate equations in the fourth column of Table 3, (E-II), (J-II) and (P-II) will be eliminated by the examination of the dehydrogenation of propane in the presence of hydrogen according to the classification of Table 3.

Dehydrogenation of Propane in the Presence of Hydrogen

The dehydrogenations of propane in the presence of hydrogen were performed over the Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C. In these runs, the initial pressures of hydrogen were varied and the initial pressures of propane were kept constant (21.0 Torr). The plotting of the experimental data according to the first, second and the third rows of Table 3 are shown in Figs. 4, 5 and 6, respectively. The linearity of the experimental data shown in Fig. 4 was better than that in Figs. 5 and 6. The rate equation (E-II) is most applicable to the

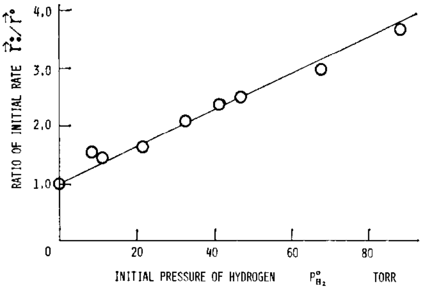

FIG. 4. Initial rate of dehydrogenation of propane in the presence of hydrogen over Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C. $\vec{r}^0$: initial rate of dehydrogenation of propane in the presence of 21.0 Torr of hydrogen; $\vec{r}_0^0$: initial rate of dehydrogenation of propane in the absence of hydrogen.

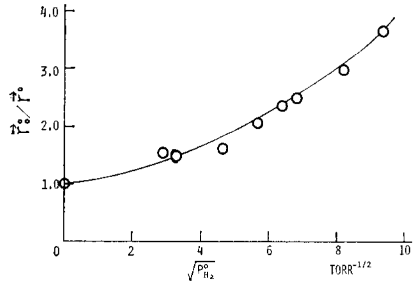

FIG. 6. Initial rate of dehydrogenation of propane in the presence of hydrogen over Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C. $\vec{r}^0$: initial rate of dehydrogenation of propane in the presence of 21.0 Torr of hydrogen, $\vec{r}_0^0$: initial rate of dehydrogenation of propane in the absence of hydrogen.

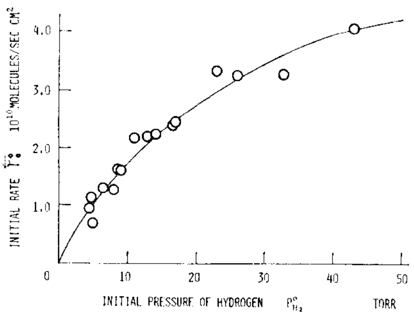

FIG. 7. Initial rate of hydrogenation of propylene as a function of initial pressure of hydrogen over Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C. Initial pressure of propylene: 15.5 Torr.

dehydrogenation of propane which is derived on condition that the second step is the rate determining one in the reaction path (E). Accordingly, the constants k_1 and K_1 in Eq. (1) are described as follows.

$$k_1 = \overrightarrow{k}_{II}, \tag{3}$$

$$K_1 = \overrightarrow{k}_{I}/\overleftarrow{k}_{I} \equiv K_{I}. \tag{4}$$

The adsorption equilibrium constants $K_{I} = (\overrightarrow{k}_{I}/\overleftarrow{k}_{I})$, $K_{III} = (\overleftarrow{k}_{III}/\overrightarrow{k}_{III})$ and $K_{IV} = (\overleftarrow{k}_{IV}/\overrightarrow{k}_{IV})$ obtained from Fig. 3 and Fig. 4 are tabulated in Table 2.

Hydrogenation of Propylene

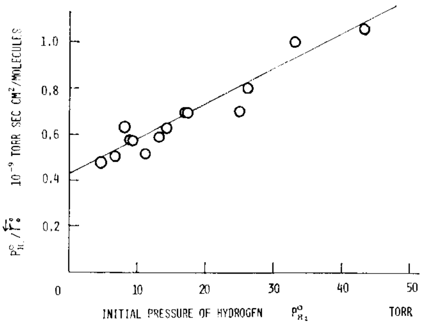

FIG. 8. Langmuir plot of hydrogenation of propylene over Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C. Initial pressure of propylene: 15.5 Torr; $P_{H_2}{}^0$: initial pressure of hydrogen; $\overrightarrow{r}_0{}^0$: initial rate of hydrogenation of propylene.

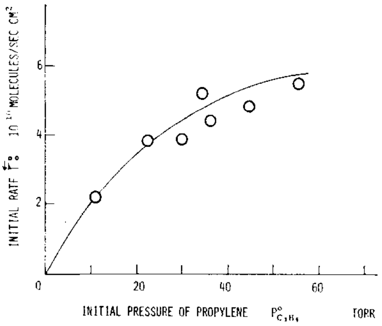

FIG. 9. Initial rate of hydrogenation of propylene as a function of initial pressure of propylene over Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C. Initial pressure of hydrogen: 8.8 Torr.

The hydrogenation of propylene was performed over the Cr_2O_3–Al_2O_3–K_2O catalyst at 443°C. The formation of methane and ethane (cracking) was observed with GSC analysis and the rate of cracking was obtained. The initial rate of hydrogenation of propylene was, therefore, obtained by calculation from the difference between the initial slope of the pressure–time curve and the initial rate of cracking. The initial rates thus obtained at constant pressures of propylene (15.5 Torr) were plotted against the initial pressures of hydrogen as shown in Fig. 7. The Langmuir plot of the experimental data is shown in Fig. 8 and the rate was, therefore, expressed as

$$\overrightarrow{r}_0{}^0 = \frac{k_2 K_2 P_{H_2}{}^0}{1 + K_2 P_{H_2}{}^0}, \tag{5}$$

where k_2 and K_2 are constants and $P_{H_2}{}^0$ is the initial pressure of hydrogen.

The initial rates obtained at constant initial pressures of hydrogen (8.8 Torr) were plotted against the initial pressures of propylene (Fig. 9). The initial rate was, therefore, expressed as

$$\overrightarrow{r}_0{}^0 = \frac{k_3 K_3 P_{C_3H_6}{}^0}{1 + K_3 P_{C_3H_6}{}^0}, \tag{6}$$

where k_3 and K_3 are constants and $P_{C_3H_6}{}^0$ is the initial pressure of propylene.

These initial rate Eqs. (5) and (6) can be derived from the rate equation (E-II) on condition that the initial pressure of propane is zero and the initial pressure of propylene or that of hydrogen is constant, respectively. The constants k_2, K_2, k_3, and K_3 are described as follows

$$k_2 = \overleftarrow{k}_{\mathrm{II}} \frac{(\overleftarrow{k}_{\mathrm{III}}/\overrightarrow{k}_{\mathrm{III}})P_{\mathrm{C_3H_6}}{}^0}{1 + (\overleftarrow{k}_{\mathrm{III}}/\overrightarrow{k}_{\mathrm{III}})P_{\mathrm{C_3H_6}}{}^0}$$

$$= \overleftarrow{k}_{\mathrm{II}} \frac{15.5(\overleftarrow{k}_{\mathrm{III}}/\overrightarrow{k}_{\mathrm{III}})}{1 + 15.5(\overleftarrow{k}_{\mathrm{III}}/\overrightarrow{k}_{\mathrm{III}})}, \qquad (7)$$

$$K_2 = \overleftarrow{k}_{\mathrm{IV}}/\overrightarrow{k}_{\mathrm{IV}} \equiv K_{\mathrm{IV}}, \qquad (8)$$

$$k_3 = \overleftarrow{k}_{\mathrm{II}} \frac{(\overleftarrow{k}_{\mathrm{IV}}/\overrightarrow{k}_{\mathrm{IV}})P_{\mathrm{H_2}}{}^0}{1 + (\overleftarrow{k}_{\mathrm{IV}}/\overrightarrow{k}_{\mathrm{IV}})P_{\mathrm{H_2}}{}^0}$$

$$= \overleftarrow{k}_{\mathrm{II}} \frac{8.8(\overleftarrow{k}_{\mathrm{IV}}/\overrightarrow{k}_{\mathrm{IV}})}{1 + 8.8(\overleftarrow{k}_{\mathrm{IV}}/\overrightarrow{k}_{\mathrm{IV}})}, \qquad (9)$$

$$K_3 = \overleftarrow{k}_{\mathrm{III}}/\overrightarrow{k}_{\mathrm{III}} = K_{\mathrm{III}}. \qquad (10)$$

The adsorption equilibrium constants obtained from Figs. 8 and 9 are tabulated in Table 2. The adsorption equilibrium constants $K_1 = K_{\mathrm{I}}$, $K_2 = K_{\mathrm{IV}}$ and $K_3 = K_{\mathrm{III}}$ obtained independently from the dehydrogenation of propane or the hydrogenation of propylene agree within experimental error as shown in Table 2. This agreement shows that the dehydrogenation of propane over the Cr_2O_3–Al_2O_3–K_2O catalyst proceeds in reaction path E and the second step (II) of the path is the rate determining one.

The reaction mechanism proposed involves the adsorption of hydrogen molecule but not hydrogen atom. This mechanism may agree with the experimental results obtained by Burwell *et al.* (*9*) that the deuteration of *cis*- and *trans*-2-butene over chromium oxide gel produced *meso*- and *dl*-butane-2,3-d_2, respectively.

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