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The Mechanism of Propylene Disproportionation*

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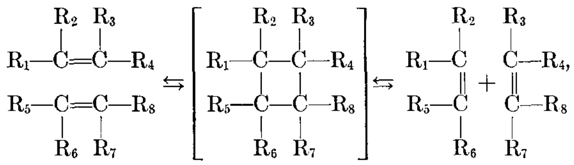
Disproportionation of [1-^{14}C] propene and [2-^{14}C] propene has shown that the postulated four-center mechanism is correct over a cobalt–molybdate–alumina catalyst. At temperatures above 60°C, the isomerization activity of the catalyst becomes a factor, so that at 160°C, nearly one-half the [1-^{14}C] propene has isomerized to [3-^{14}C] propene prior to disproportionation. From experimental values of the rate constant for disproportionation and the degree of isomerization, rate constants for isomerization are calculated. The apparent energy of activation of the disproportionation reaction was found to be 7.7 kcal/mole and for the isomerization reaction 17.3 kcal/mole.

I. INTRODUCTION

Olefin disproportionation, a new catalytic reaction reported by Banks and Bailey (*1*) in 1964, may be depicted for acyclic monoolefins as follows:



$$\begin{array}{c} R_1{-}\overset{R_2}{\overset{|}{C}}{=}\overset{R_3}{\overset{|}{C}}{-}R_4 \\ R_5{-}\underset{R_6}{\underset{|}{C}}{=}\underset{R_7}{\underset{|}{C}}{-}R_8 \end{array} \leftrightarrows \left[\begin{array}{c} R_1{-}\overset{R_2}{\overset{|}{C}}{-}\overset{R_3}{\overset{|}{C}}{-}R_4 \\ \quad | \quad\ \ | \\ R_5{-}\underset{R_6}{\underset{|}{C}}{-}\underset{R_7}{\underset{|}{C}}{-}R_8 \end{array}\right] \leftrightarrows \begin{array}{c} R_1{-}\overset{R_2}{\overset{|}{C}} \\ \| \\ R_5{-}\underset{R_6}{\underset{|}{C}} \end{array} + \begin{array}{c} \overset{R_3}{\overset{|}{C}}{-}R_4, \\ \| \\ \underset{R_7}{\underset{|}{C}}{-}R_8 \end{array} \qquad (1)$$

where the R is hydrogen or hydrocarbon group. If both reactant molecules are identical and symmetrical about the double bond, no disproportionation will be observed. The intermediate in Eq. (1) signifies a four-center mechanism. Bradshaw *et al.* (*2*) were the first to publish a four-center type intermediate to explain the reaction. They studied the disproportionation of 1-butene as well as the reaction of ethylene with *cis*-2-butene and with 4-methyl-2-pentene, using a cobalt–molybdate catalyst. When isomerization of product olefins was taken into account, all results were consistent with a four-center mechanism. Calderon *et al.* (*3, 4*) proposed a similar mechanism for the disproportionation of internal olefins in the presence of a homogeneous catalyst derived from WCl_6, C_2H_5OH, and $C_2H_5AlCl_2$. They found that the distribution of deuterium in the products from the interaction of 2-butene with 2-butene-d_8 was consistent with the four-center mechanism. Using a rhenium oxide–alumina catalyst, Mol *et al.* (*5*) studied the disproportionation of propylene labeled with ^{14}C in each of the three positions. In experiments with [2-^{14}C] propene, the ethylene formed showed no radio activity, while the butene showed a specific radioactivity twice that of the starting material. The result supports a four-center mechanism and rules out a linear mechanism. When the reactant was [1-^{14}C] propene, the radioactivity was found in the ethylene. According to these authors (*5*), their results showed that the methyl groups retained

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their identity throughout the disproportionation and thus excluded the possibility of a π-allylic intermediate in which the end carbons of propene become indistinguishable. In the present paper, results of an investigation of the disproportionation of propylene over cobalt–molybdate catalyst are reported with emphasis on the significance of isomerization reactions.

II. Experimental Methods

The apparatus used for this work is shown in Fig. 1. Helium from a cylinder was dried with $Mg(ClO_4)_2$ and passed through the reference side of a Gow-Mac model 9285-D hot wire chromatographic detector. It was then mixed with propylene (containing a small quantity of ^{14}C-labeled propylene) by means of a Perkin-Elmer 154-0068 gas-sampling valve with the sampling loop replaced by a T-junction having one end connected to the propylene source. The mixture was then passed through the glass reactor and back through the sample side of the hot wire detector. This detector was used to monitor the flow of propylene and to indicate the emergence of products from the reactor at the beginning of an experiment. The effluent from the reactor was sampled with a second Perkin-Elmer sampling valve equipped with a 25-ml loop. The chromatograph was a Perkin-Elmer model 154-D with a thermister detector. A 20-foot hexamethylphosphoramide column was mounted externally in an insulated box. The separated olefin products were passed through a radio-counting cell whose volume was 30 ml. A spiral design insured that gases would flow through the cell rapidly to prevent overlapping of two closely spaced peaks in the chromatographic effluent. The cell is placed on a double layer of aluminized Mylar (1.02 mg/cm^2 in each layer) on top of a plastic scintillation crystal. A 2-in. photomultiplier tube is attached to the associated electronics and strip chart recorder. Both chromatographic and ^{14}C analyses were made using the measured area of the peaks involved.

A typical commercial cobalt–molybdate–alumina catalyst containing 3.4 wt % MoO_3, and 85.6 wt % Al_2O_3 was used. It was ground to 20–40 mesh and activated at 550°C for 4 hr under flowing dry air. In order to keep the quantities of radioactive propylene handled at a minimum, the catalyst volume used in tests was reduced to about 1 ml.

III. Results and Discussion

The disproportionation of [1-^{14}C] propene at low temperatures indicates that the postulated four-center mechanism is correct. At 60°C essentially all of the activity in

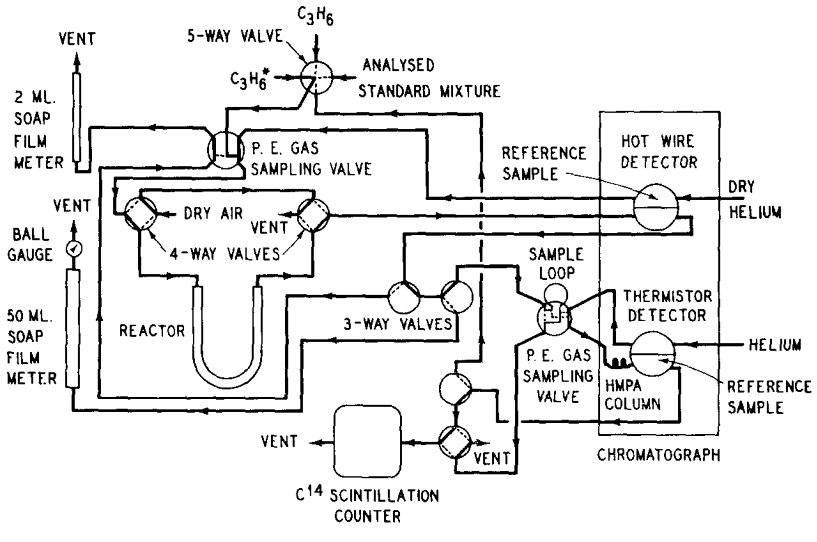


Fig. 1. Disproportionation apparatus.

the products is found in the ethylene and none in the butene. This is interpreted to mean that the carbon atoms originally in the 1-position end up in the ethylene while those in the 2- and 3-positions are transferred to the butene products. Since the catalyst is known to be an isomerization catalyst, it is not surprising that evidences of isomerization are observed. For example, small amounts of 1-butene are present in the product even though 2-butene is predicted by the mechanism. The amount of 1-butene increases with temperature, but remains below the thermodynamic equilibrium.

Similarly, as the temperature is increased above 60°C, isomerization of [1-^{14}C] propene to [3-^{14}C] propene yields disproportionation products with an increasing amount of activity in the butene, until at 160°C, nearly as much ^{14}C is present in the butene as in the ethylene. Thus measurements made at temperatures between 60 and 160°C yield data on the isomerization of propylene in competition with disproportionation, i.e., isomerization of [1-^{14}C] propene must occur prior to disproportionation to be recorded. Table 1 shows the average degree of isomerization of [1-^{14}C] propene as a function of temperature. The degree of isomerization, D, is referred to a state of one-half the product activity in the ethylene and one-half in the butene as 100% isomerization (equilibrium), and is defined as

TABLE 1
DEGREE OF ISOMERIZATION OF PROPYLENE AT VARIOUS TEMPERATURES

Temp. (°C)	Contact time[a] t (sec)	Degree of isomerization, $D \times 10^2$
60	2.68	0
80	1.27	10.7
100	1.20	24.7
120	0.57	43.2
140	0.30	60.0
160	0.30	83.2

[a] Based on 0.5 void space in catalyst bed.

$$D = \frac{2C_4^*}{C_2^* + C_4^*}, \tag{2}$$

where C_2^* and C_4^* represent the concentrations of radioactive ethylene and butene, respectively; D is a slowly varying function of contact time t [see Eq. (4)]. A very small amount of the ethylene was frequently used up in side reactions so that there was slightly more butenes in the reactor effluent. This was corrected by multiplying C_4^* by the ratio C_2/C_4 where C_2 and C_4 represent total quantities, radioactive and nonradioactive ethylene and butene. The value of D is independent of the proportion of radioactive isotope used. Radioactivity levels employed were extremely low.

Knowing the degree of isomerization, D, and the forward disproportionation rate constant, k_d, the rate constant for propylene isomerization, k, can be estimated. The following model is set up, assuming that there are no isotope effects, and that the disproportionation reaction takes place under conditions where the back-reaction can be neglected.

$$\begin{tikzcd} \mathrm{C_3\text{-}1\text{-}^{14}C} \arrow[r, "k_d"] \arrow[d, shift left, "k"] & \mathrm{C_2^*H_4 + C_4H_8} \\ \mathrm{C_3\text{-}3\text{-}^{14}C} \arrow[r, "k_d"] \arrow[u, shift left, "k"] & \mathrm{C_2H_4 + C_4^*H_8} \end{tikzcd} \qquad (3)$$

The disproportionation reaction is pseudo-first order in the region investigated. Conversion, $C = (1 - e^{-k_d t})$, was shown to be independent of propylene concentration in the temperature range 60–120°C. At higher temperatures, the kinetics become more complex, and the back-reaction could not be neglected at convenient contact times. In the conversion range $<15\%$, forward rate constants calculated with and without the back-reaction included did not differ by more than 5% from one another. An Arrhenius plot is shown in Fig. 2. The apparent activation energy is 7.7 kcal/mole.

The equation for determining k, the rate constant for propylene isomerization may be written

$$(1 - D)(1 - e^{-k_d t}) = \frac{k_d}{2k + k_d}(1 - e^{-(2k+k_d)t}), \tag{4}$$

and is derived as follows

Let the concentrations of C_3H_6-1-^{14}C, C_3H_6-3-^{14}C, and untagged propylene at time t be represented by N_1, N_3, and N_0, respectively. It can be shown for the case $N_1 + N_3 \ll N_0$ that

$$\frac{dN_1}{dt} = -kN_1 + kN_3 - k_dN_1,$$

$$\frac{dN_3}{dt} = -kN_3 + kN_1 - k_dN_3,$$

$$\frac{dN_0}{dt} = -k_dN_0, N_0 = (N_0)_Ie^{-k_dt},$$

$$\frac{d(N_1 + N_3 + N_0)}{dt} = \frac{dN}{dt} = -k_dN, N = N_Ie^{-k_dt}, \quad (5)$$

where $(N_0)_I$ and N_I are the initial concentrations of untagged and total propylene, respectively. Substituting

$$N_3 = N - N_1 - N_0 = N_Ie^{-k_dt} - N_1 - (N_0)_Ie^{-k_dt}, \quad (6)$$

in the above expresion for dN_1/dt, the equation

$$\frac{dN_1}{dt} = -(2k + k_d)N_1 + k[N_I - (N_0)_I]e^{-k_dt} \quad (7)$$

is obtained. Using the boundary condition, $t = 0$, $N_1 = N_I - (N_0)_I$, the solution is

$$N_1 = \frac{N_I - (N_0)_I}{2} e^{-k_dt}(1 + e^{-2kt}). \quad (8)$$

Now the fraction of propylene disproportionating as C_3H_6-1-^{14}C is $(1 - D/2)$, and the amount of *total* radioactive propylene reacting in time t is $[N_I - (N_0)_I](1 - e^{-k_dt})$. Therefore, the amount of C_3H_6-1-^{14}C disproportionating in time t is

$$\int_0^t k_dN_1dt = \left(1 - \frac{D}{2}\right) \times [N_I - (N_0)_I](1 - e^{-k_dt}) \quad (9)$$

which leads directly to Eq. (4), after substituting for N_1 from Eq. (8). Table 2 gives the experimental values of k_d, D, and t and the values of k calculated from them using Eq. (4). From values of k at 80, 100, and 120°C, an apparent activation energy of 17.3 kcal/mole is calculated.

To determine the effect on D, and thus on k, as a result of neglecting the disproportionation back-reaction, consider the reaction scheme in Eq. (3). Since the products shown are symmetrical, reactions with themselves result in no change. This is also true for $C_2{}^*H_4 + C_2H_4$ and $C_4{}^*H_8 + C_4H_8$. Other reactions between the products give C_3H_6, C_3H_6-1-^{14}C, and C_3H_6-3-^{14}C. These species will not affect D unless they undergo further disproportionation. Another complication could result from the isomerization of 2-butene to 1-butene which then could react with propylene, 1-butene, and 2-butene to give C_5 and C_6 olefins. These were present in the product in concentrations below 1%, so they are not expected to affect D. Equation (4) is believed to be reasonably valid. If the reaction is strongly

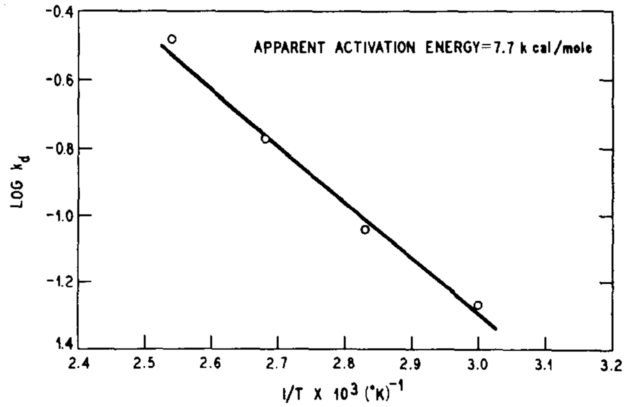


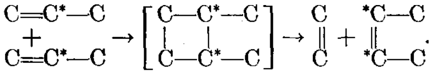
FIG. 2. Energy of activation determination for C_3H_6 disproportionation.

TABLE 2
CALCULATION OF ISOMERIZATION RATE CONSTANT, k

Temp. (°C)	Degree of isomerization $D \times 10^2$	Contact time t (sec)	Rate constants (secs^{-1})	
			Disproportionation, k_d	Isomerization, k
60	~0	2.68	0.057	0
80	10.7	1.27	0.090	0.093
100	24.7	1.20	0.17	0.260
120	43.2	0.57	0.33	1.16

diffusion-limited, difficulties in the interpretation of D would be encountered. In the kinetic studies, there were no indications that diffusion was limiting.

In further support of the four-center mechanism, experiments were repeated using C_3H_6-2-^{14}C. In this case, the reaction is


(10)

As expected, essentially all of the activity in the products was concentrated in the butene over the temperature range 60–160°C.

It is interesting to speculate briefly on a more detailed picture of isomerization and disproportionation. At temperatures below 60°C, where isomerization does not occur, the methyl groups of propylene retain their identity throughout the disproportionation reaction. Thus, the possibility of a π-allyl intermediate in which the two end carbons of a propylene molecule become structurally identical appears to be excluded. At higher temperatures, the π-allyl mechanism cannot be so easily dismissed. One could visualize two adjacently adsorbed, radioactive, π-allyl complexes having an equal chance of disproportionating to give radioactivity in the ethylene or in the butylene. As the reaction temperature is increased above 60°C, an increasing fraction of the reacting olefin may isomerize and disproportionate by such a combined mechanism. The slow step in this mechanism may be the dissociative adsorption of hydrogen atoms from methyl groups which results in the formation of π-allyl complexes. In this way, the higher activation energy of isomerization may be explained. Further experiments are planned to test these ideas.

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