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Oxidative Dehydroaromatization

III. The Mechanism of Oxidative Dehydrodimerization Process of C_3–C_4 Olefins Over Bi_2O_3–SnO_2 Catalyst

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The mechanism of the oxidative dehydrodimerization from lower olefins was studied from the dependence of the reaction rate on the partial pressure of olefin and from the competitive reaction between two kinds of olefin. The formation rates of dimers such as 1,5-hexadiene from propylene and 2,5-dimethyl-1,5-hexadiene from isobutene, were well expressed by an equation of Langmuir–Hinshelwood type, $V = k[K \cdot P/(1 + K \cdot P)]^2$ and those of co-dimers such as 2-methyl-1,5-hexadiene from propylene and isobutene, were written by $V = k \cdot K_1K_2P_1P_2/(1 + K_1P_1 + K_2P_2)^2$. Based on these kinetic equations, adsorption constants and rate constants in this reaction were evaluated. From the kinetic equations, the trend of adsorption constants, and the relation between rate constants and dissociation energies of allyl hydrogens, the following reaction steps were proposed: (1) adsorption of olefin, (2) conversion of adsorbed olefins into two π-allyl intermediates coordinated to a single active site, (3) dimerization into hexadiene, and several consecutive steps into aromatics, where step (2) is rate-determining.

INTRODUCTION

The catalytic oxidation of lower olefins to form unsaturated aldehydes or conjugated dienes is well known (*1, 2*), and the catalytic reaction of this type is classified as an allylic oxidation which proceeds via allyl intermediate. As reported before, we found another type of allylic oxidation to form 1,5-hexadienes and aromatics (oxidative dehydroaromatization) over bismuth phosphate catalyst (*3*). Afterwards, a wide variety of single and binary oxides such as ZnO, SnO_2, CdO, In_2O_3, Tl_2O_3, Bi_2O_3–As_2O_5, Bi_2O_3–TiO_2, Bi_2O_3–SnO_2 and SnO_2–Na_2O were reported also to catalyze this selective oxidation by Seiyama *et al.* (*4–6*), Trimm and Doerr (*7*) and Ohdan *et al.* (*8*). Swift, Bozik and Ondrey (*9*) also have reported the same reaction by using Bi_2O_3 as the oxidant. It has been discussed in previous papers (*4, 5*) that selectivity between benzene and acrolein formation depends on the electronic picture of adsorbed allyl intermediate influenced by the acid–base properties of catalysts. For the reaction scheme of the oxidative dehydroaromatization, the following consecutive steps have been already established (*10, 11*); olefins → allyl intermediates → 1,5-hexadienes → hexatrienes → 1,3-cyclohexadienes → aromatics. Benzene formation was also observed in the reaction of allyl halides over Bi_2O_3–SnO_2 catalyst, supporting the above scheme (*12*).

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Thus, the oxidative dehydroaromatization has been extensively developed with respect to both catalytic properties and reaction scheme. However, details of the reaction mechanism particularly the rate-determining step and definite structure of the intermediate, are still in question. In the present work, we have studied these problems from kinetic studies which include LFER and competitive reaction methods.

EXPERIMENTAL METHODS

The catalyst used was Bi_2O_3–SnO_2 with the atomic ratio Bi/Sn = 1, which was prepared by calcining a mixture of the commercial bismuth oxide and stannic oxide for 12 hr at 720°C (*10*).

The oxidation reaction was carried out in a flow system at atmospheric pressure, using a Pyrex glass tube reactor with a fixed bed of 48–80 mesh catalyst granules. The formation rate of product was obtained at conversions lower than 10%, and at contact times of 0.15–0.20 g·sec/ml. Under such conditions dehydrodimerization was predominant and aromatization was little. The influence of internal or external diffusion on the oxidation rate was negligible. In kinetic studies the partial pressure of olefin was varied from 0.01 to 0.10 atm with a fixed oxygen pressure of 0.12 atm. The dependence of the rate on the partial pressure of oxygen was also examined in the range of 0.03–0.13 atm ($P_{\mathrm{olefin}} = 0.07$ atm). The total pressure was always balanced by nitrogen. In competitive reaction of two olefins the partial pressure of one olefin was varied from 0.01 to 0.06 atm with a fixed partial pressure of the other olefin (0.06 atm). The activation energies were determined from the temperature dependence of reaction rate in the range of 475–541°C.

Analyses were carried out with gas chromatography and mass spectroscopy. The following columns were used for gc: molecular sieve 13X for N_2, O_2, CO and CH_4; Porapak Q for CO_2, ethylene and propylene; 20% liquid paraffin on alumina for butene isomers and butadiene; 10% PEG 1000 on Celite 545 or 5% Bentone 34 + 5% DIDP on Uniport K for dienes and aromatics.

RESULTS AND DISCUSSION

Kinetic Studies

In the oxidation of propylene at 500°C, main products from propylene were carbon dioxide by complete oxidation and 1,5-hexadiene by oxidative dehydrodimerization. These products were formed by parallel reactions and the consecutive oxidation of 1,5-hexadiene to carbon dioxide was negligible at low conversion levels (*9*). Figure 1 shows the dependence of their formation rates on the partial pressure of propylene. From the slopes of correlation lines in Fig. 1, the rates of 1,5-hexadiene and carbon dioxide formation were calculated to be 1.6 and 0.8 order in propylene, respectively. The rate of dimerization was independent of the partial pressure of oxygen, while that of carbon dioxide was 0.5 order in oxygen.

The rate of 2,5-dimethyl-1,5-hexadiene formation from isobutene, which is the oxidative dehydrodimerization product, was 1.5 order in isobutene. Although the dimerization products were identical to each other in the case of *n*-butenes, butadiene formation occurred more preferentially than dimer formation as shown in Fig. 2. Dimers observed were 3-methyl-1,5-hexa-

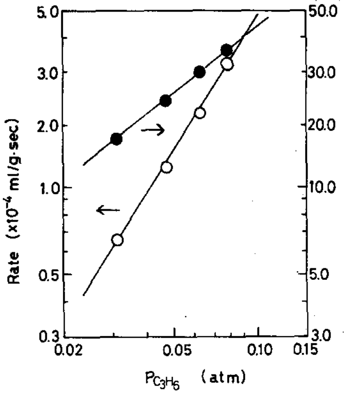

FIG. 1. Dependence of the rates of propylene oxidations on the partial pressure of propylene at 500°C. (○) 1,5-hexadiene formation, (●) carbon dioxide formation.

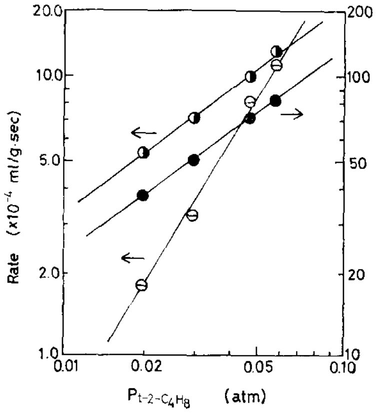

FIG. 2. Dependence of the rates of *trans*-2-butene oxidations on the partial pressure of *trans*-2-butene at 500°C. (⊖) dimers formation, (◑) butadiene formation, (●) carbon dioxide formation.

diene and 1,5-heptadiene as C_7 diene and 3-methyl-1,5-heptadiene, 3,4-dimethyl-1,5-hexadiene and 2,6-octadiene as C_8 diene. We assume at present that C_7 dienes are formed by the consecutive elimination of methyl group from the C_8 dimers. The reaction orders with respect to olefins in these oxidations are summarized in Table 1. In every case, the formation of carbon dioxide was approximately first order in olefin. Butadiene formation is also first order in *n*-butene, being consistent with the previous observations over bismuth molybdate, where the rate-determining step is concluded to be the step of allyl intermediate formation by the allyl hydrogen abstraction (*13*).

TABLE 1
REACTION ORDER WITH RESPECT TO OLEFIN

Product: Reactant	Dehydro-dimers	Carbon dioxide	Butadiene
Propylene	1.6	0.8	—
Isobutene	1.5	1.1	—
1-Butene	2.0	1.1	1.2
cis-2-Butene	1.9	1.1	1.1
trans-2-Butene	1.9	0.8	0.8

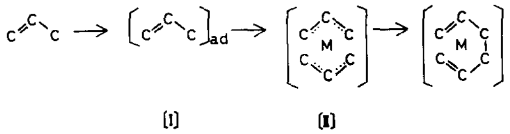

FIG. 3. Reaction scheme of oxidative dehydrodimerization. (M means single active site for dimerization of two adsorbed olefins.)

On the other hand, the second order kinetics are most reliable for oxidative dehydrodimerization. It should be noted that dimers were the only product in the allylic oxidation of one group of olefins (propylene and isobutene), whereas for another group (*n*-butenes), butadiene as well as the dimers were formed via the allyl intermediate which has another hydrogen to be eliminated towards conjugated double bond formation. The second order equation suggests the mechanism in which the bimolecular surface-reaction step to form intermediate (II) is rate-determining in a series of consecutive steps described in Fig. 3. Trimm and Doerr (*7*) proposed a similar mechanism for dimerization reaction of olefin on indium oxide catalyst. A simple Langmuir adsorption isotherm of one component** is applicable to the calculation of surface concentration of the adsorbed species (I). Thus, the rate V of oxidative dehydrodimerization may be written as

$$V = k[K \cdot P/(1 + K \cdot P)]^2, \qquad (1)$$

where P is the partial pressure of olefin in feed gas, k the rate constant, and K the adsorption constant. Equation (1) can be written as

$$1/(V)^{1/2} = 1/(k)^{1/2} + 1/(k)^{1/2} \cdot K \cdot P. \quad (2)$$

Plots of $1/(V)^{1/2}$ against $1/P$ in the propylene and isobutene oxidation give straight lines as shown in Fig. 4. Such linear correlations were also observed in the cases of three kinds of *n*-butene isomers. Another reaction scheme might be assumed in which the allyl formation is in equilibrium with olefin in vapor phase and its dimerization

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** In this treatment, only the absorption concerning the allylic oxidation was taken into account, and that of carbon dioxide formation was disregarded based on the assumption that the adsorbed species leading to complete oxidation would differ from those leading to allylic oxidation.

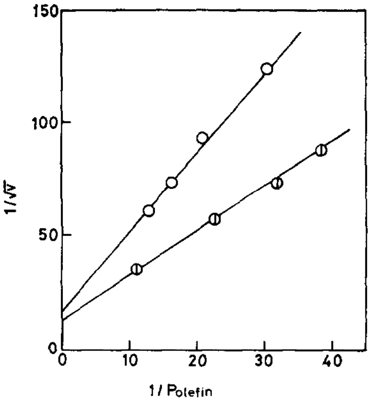

FIG. 4. Plot of $1/(V)^{1/2}$ versus $1/P$ in the dimerization of propylene (○) and isobutene (◐).

step is rate-determining.†† However, such a scheme should be abandoned for the reasons discussed below.

Apparent activation energies, E_a, of five olefins in the oxidative dehydrodimerization are listed in Table 2.

Competitive Reaction

Oxidative dehydro-co-dimerization between propylene and isobutene was carried out by introduction of the mixture of two olefins into the reaction system. The formation of C_6 diene from propylene and C_8 diene from isobutene occurred competitively in addition to the co-dimerization to C_7 diene. The results are shown in Fig. 5a and b, where the partial pressure of isobutene or propylene was varied individually at a fixed pressure of the other component. As shown in Fig. 5a, when the partial pressure of isobutene was increased, the rate of formation of 2-methyl-1,5-hexadiene, the co-dimerization product from both olefins, increased with the slope of 1.0. The formation of 1,5-hexadiene from propylene decreased linearly with the slope of 0.7 and that of 2,5-dimethyl-1,5-hexadiene from isobutene increased with the reaction order of 1.5. Similar changes in reactivity of isobutene by the presence of propylene were observed as shown in Fig. 5b, except for the smaller slope (0.21) of decrease of 2,5-dimethyl-1,5-hexadiene formation rate in comparison with that of 1,5-hexadiene formation rate.

These results should also be explained by the Langmuir–Hinshelwood mechanism, and the rate equation for the co-dimerization can be written as

$$V = k \cdot K_1K_2P_1P_2/(1 + K_1P_1 + K_2P_2)^2, \quad (3)$$

where k is the rate constant of rate-deter-

TABLE 2
RATE CONSTANT k OF DIMERIZATION, ADSORPTION CONSTANT K OF OLEFIN AND APPARENT ACTIVATION ENERGY E_a

Reactant	k (ml/g · sec)	K (atm^{-1})	E_a (kcal/mol)	K on NiO (*14*)	K with Ag^+ ion (*15*)
Ethylene	—	Small	—	Small	1.99
Propylene	0.0036	4.7	44.2	0.20	0.85
Isobutene	0.0043	7.5	49.3	1.41	—
1-Butene	1.0	0.3	43.4	1.00	1.00
cis-2-Butene	0.16	1.8	48.4	1.45	0.56
trans-2-Butene	0.16	1.4	51	1.46	0.18

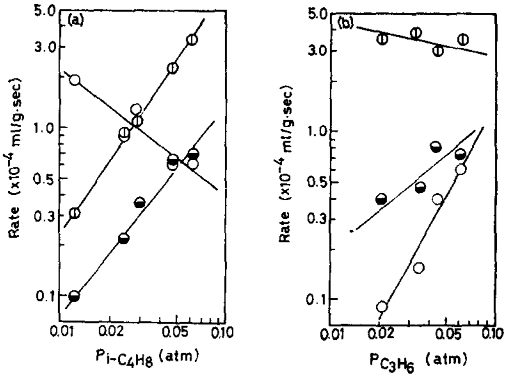

FIG. 5. Co-dimerization between propylene and isobutene at 500°C. Dependence of dimerization rates on the partial pressure of isobutene [(a) $P_{C_3H_6} = 0.062$ atm] and on that of propylene [(b) $P_{i\text{-}C_4H_8} = 0.067$ atm] (○) 1,5-hexadiene from propylene, (◐) 2,5-dimethyl-1,5-hexadiene from isobutene, (◒) 2-methyl-1,5-hexadiene from both olefins.

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†† The second order kinetics deny the step of the single allyl formation as the rate-determining one.

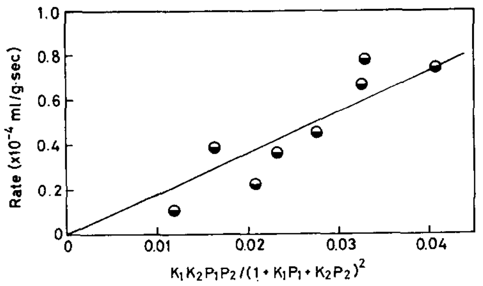

FIG. 6. Plot of the rate of co-dimerization between propylene and isobutene by using Eq. (3).

mining step; K_1, K_2 and P_1, P_2 are the adsorption constants and the partial pressures of propylene and isobutene, respectively. The values of V were plotted against $K_1K_2P_1P_2/(1 + K_1P_1 + K_2P_2)^2$, by using K_1 and K_2 values (Tables 2) from the individual oxidation results, to examine the validity of the assumed mechanism. The plots gave an excellent linear relation as shown in Fig. 6.

The suppression of self-dimerization by the presence of the second component may also be explained by Langmuir–Hinshelwood equation.

$$V = k[K_1P_1/(1 + K_1P_1 + K_2P_2)]^2. \quad (4)$$

The difference of retardation effects between propylene and isobutene may be ascribed to that of their adsorption constants. The calculated values of the retardation by using the adsorption constants in Table 2 were reasonably consistent with the experimental results in Fig. 5a and b.

Neither co-dimerization nor the decrease of the rate of 1,5-hexadiene formation was observed as a result of ethylene addition to the reaction system of propylene, implying that the adsorption of ethylene is much weaker than that of propylene probably due to the lack of any allyl hydrogen.

DISCUSSION

To discuss the adsorption species, the values of adsorption constants K and rate constants k were obtained from the Langmuir plots of Eq. (1) and summarized in Table 2. The trend of adsorption constants of five olefins in this reaction clearly differs from that of adsorption in the complete oxidation over NiO catalyst (*14*), and from that of equilibrium constants of silver-ion–olefin complex formation (*15*). This trend is also different from that of allylic adsorption which should be in accordance with the order of dissociation energies of allyl hydrogens of olefins. As one of possible models for the species (I), an adsorption state may be conceivable in which the double bond of olefin may interact with the metal ion of the catalyst and its allylic hydrogen may interact weakly with the adjacent surface oxygen.‡‡ The interaction of this adsorbed species with the catalyst surface may not be affected significantly by the structure of olefin. However, the steric hindrance around the allyl hydrogen and the double bond may have a considerable effect on the stability of adsorbed species, where the number of allyl hydrogens also should be taken into account. The adsorption constants of assumed models may be consistent with the observed order of isobutene > propylene > *cis*-2-butene ~ *trans*-2-butene ≫ 1-butene.

On the other hand, the rate constant of the rate-determining step increased with the decrease of the dissociation energy of allyl hydrogen as shown in Fig. 7. This

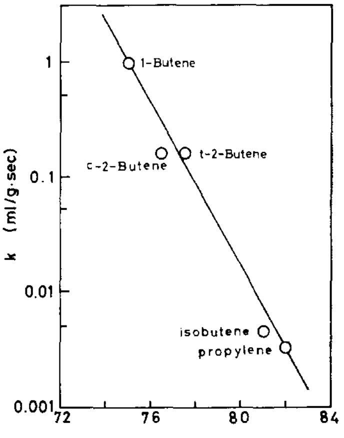

FIG. 7. Correlation between the rate constant k of dimerization and the dissociation energy $D_{C\text{-}H}$ of an allylic C–H bond.

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‡‡ Matsuura and Schuit (*16*) proposed a similar model for the dissociative adsorption of olefin over Bi–Mo catalyst.

TABLE 3
CORRELATION BETWEEN THE APPARENT ACTIVATION ENERGY E_a, THE TRUE ACTIVATION ENERGY E_t AND THE ADSORPTION HEAT q (kcal/mole)

Reactant	E_t	q	$E_t - 2q$	E_a
Propylene	69.0	13.3	42.4	44.2
Isobutene	71.8	12.5	46.8	49.3

correlation supports the reaction scheme described above, because the rate-determining step includes the rupture of the allylic C–H bond.

Based on the assumed rate-equation, the apparent activation energy should be related to the heat of adsorption and the activation energy of the rate-determining step as below, neglecting the retardation term of Eq. (1).

$$E_a = E_t - (q_1 + q_2), \qquad (5)$$

where E_t is true activation energy of the rate-determining step, q_1 and q_2 are adsorption heats of olefin-1 and olefin-2, respectively. E_t and q were obtained from the temperature dependence of the rate constant k and adsorption constant K, respectively, as listed in Table 3. Table 3 shows a fair coincidence of observed E_a with those estimated by Eq. (5) using the values of E_t, q_1 and q_2.

Thus, the fairly large values of apparent activation energies are primarily due to the large value of E_t, which may be reasonably accepted because the large energy should be required in the activation of the adsorption species [I] to the allyl intermediate [II] arranged so as to dimerize. The values of heats of adsorption, q, are comparable to that of 2-methyl-1-butene over Bi–Mo catalyst reported by Watanabe, Kuwajima and Echigoya (*17*). Such small values may not be in conflict with the rather weak adsorption of the proposed model.

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