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Catalytic Oxidation of Olefins over Oxide Catalysts Containing Molybdenum

VI. Kinetics of Propylene Oxidation to Form Acetone over SnO_2–MoO_3

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The reaction mechanism of propylene oxidation to acetone over SnO_2–MoO_3 catalyst has been investigated in terms of the kinetics at 130°C. Isopropyl alcohol (IPA) showed the behavior of an intermediate product. The selectivity to IPA approached 100% in the very beginning of the oxidation. Thus it was confirmed that acetone formation proceeds first through hydration to IPA, followed by oxidative dehydrogenation. The kinetics of the propylene oxidation disclosed a significant retardation by ketone. Comparison of the rates for hydration of propylene, dehydration of IPA, and oxidative dehydrogenation of IPA suggested that there is no single rate-determining step in the formation of acetone from propylene.

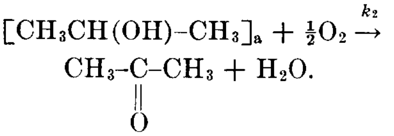
INTRODUCTION

It was reported previously that olefins are oxidized to corresponding saturated carbonyl compounds over various binary oxide catalysts containing molybdenum in the presence of water vapor (*1–7, 16–18*). The selective ketone formation from lower *n*-olefins proceeded particularly over SnO_2–MoO_3 and Co_3O_4–MoO_3 at low temperatures (120–200°C).

The authors proposed the following consecutive reaction mechanism for acetone formation, based on the results that (i) a significant amount of isopropyl alcohol (IPA) is obtained in the oxidation of propylene by any effective catalyst; (ii) IPA is easily oxidized to acetone over SnO_2–MoO_3 and Co_3O_4–MoO_3 at a much lower temperature compared with that of propylene oxidation; (iii) *n*-butenes are readily isomerized during the oxidation of butenes to methylethyl ketone (MEK).

$$H_2C{=}CH{-}CH_3 + [H^+] \rightleftharpoons [CH_3{-}\overset{+}{C}H{-}CH_3], \qquad (1)$$

$$[CH_3{-}\overset{+}{C}H{-}CH_3] + [H_2O]_a \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [CH_3{-}CH(OH){-}CH_3]_a + [H^+], \qquad (2)$$



$$[CH_3CH(OH){-}CH_3]_a + \tfrac{1}{2}O_2 \xrightarrow{k_2} CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + H_2O. \qquad (3)$$

The validity of this reaction mechanism has been demonstrated by the linear relationship between the activity to form acetone and the acidity of the catalysts (*7*), and also by ^{18}O incorporation from $H_2{}^{18}O$ into the formed acetone (*3, 6*).

The mechanism of acetone formation has

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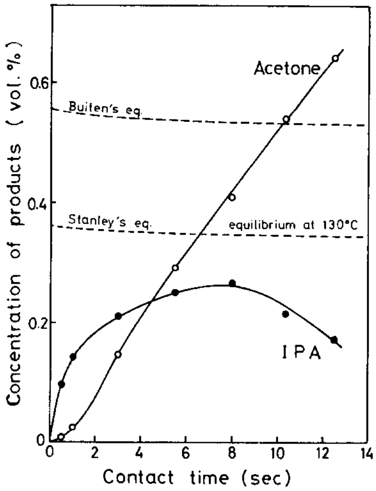


FIG. 1. Product concentration in the oxidation of propylene as a function of contact time. Catalyst: SnO_2–MoO_3 (Sn/Mo = 9/1); temperature: 130°C; feed gas rate: 116.5 cm^3/min; feed gas composition: 20 vol% propylene, 20% nitrogen, 30% oxygen, 30% water vapor. Broken line indicates the concentration of IPA at the equilibrium of propylene hydration at 130°C.

been further examined by a kinetic method and is reported in this paper.

EXPERIMENTAL

SnO_2–MoO_3 (Sn/Mo = 9/1) catalyst (40–60 mesh) was prepared from stannous chloride and ammonium molybdate by the same method as described in a previous paper (*2*).

Catalytic reactions were carried out using a conventional flow reactor with a fixed catalyst bed.

The contact time was defined by V/F (seconds), where V is the apparent catalyst volume (cm^3), F is the feed gas rate (cm^3 STP per second), the apparent density of the SnO_2–MoO_3 (Sn/Mo = 9/1) catalyst being 1.64 g/cm^3. Usually reactions were carried out at a contact time of 5.15 sec. The contact time was varied by changing the volume of catalyst used, and a small amount of silicon carbide grains of the same size was added in the case of very low contact time.

The kinetic data were obtained after a stationary activity was established in an oxidation run of 10 hr at 150°C.

RESULTS

(*i*) *Effect of Contact Time*

According to the mechanism represented in Eqs. (1)–(3), isopropyl alcohol is expected to behave as an intermediate. From this point of view, the product distribution of propylene oxidation was examined as a function of contact time (V/F) over SnO_2–MoO_3 at 130°C as shown in Fig. 1. The products were acetone, IPA, and a very small amount of carbon dioxide (selectivity to CO_2 normalized by carbon balance was at most about 4% of the propylene reacted). The concentration of acetone in the effluent gas increases monotonically with contact time. The IPA concentration also increases with contact time, but passes through a maximum at a V/F of 5–6 sec, in conformity with the intermediate formation of IPA, which is more clearly demonstrated in Fig. 2, where the selectivities are plotted against contact time. Selectivity to acetone decreases with decrease in contact time, while IPA increases complementarily giving an extrapolated selectivity of around 100%.

(*ii*) *Effect of Partial Pressures on the Rate of Propylene Oxidation to Acetone*

The effects of propylene, oxygen, and water vapor pressures on the rate of

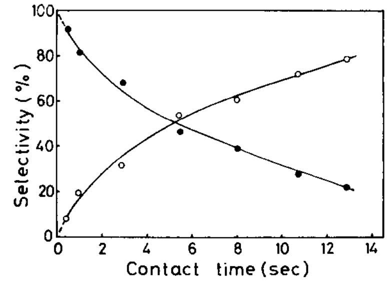


FIG. 2. The selectivity of propylene oxidation as a function of contact time. Reaction conditions are the same as in Fig. 1.

propylene consumption were examined. The rate of propylene consumption at a contact time of 5.2 sec was determined from concentrations of IPA and acetone in the effluent gas. The conversion of propylene was in the range of 2–3%. The rate is independent of oxygen and water pressures, but shows an order of 0.8 as regards dependence on propylene pressure (Fig. 3). The effect of the product, ketone, was studied separately. Methylethyl ketone (MEK), instead of acetone, was added in the reactant gas mixture to examine the effect of product acetone. The use of methylethyl ketone was expected to minimize the experimental difficulty. As shown in Fig. 4, the rate of propylene consumption decreases as MEK pressure increases, showing an approximate reaction order of −1. Therefore it can be said that the average rate of propylene consumption is retarded by the formed acetone.

(*iii*) *Kinetics of Propylene Hydration to IPA*

Since the selectivity to IPA extrapolated to a contact time of zero approaches 100%, the initial rate of propylene consumption may be regarded as the rate of propylene hydration. The initial rate of propylene consumption was found to be zero order with respect to water and oxygen and first order with respect to propylene, as shown in Fig. 5. From these results, the initial rate of propylene consumption ($-dP^0{}_{C_3H_6}/dt$) is expressed as follows.

$$-\frac{dP_{C_3H_6}{}^0}{dt} = k_1{}^0 \cdot P_{C_3H_6}{}^1 \cdot P_{H_2O}{}^0 \cdot P_{O_2}{}^0, \qquad (4)$$

where $k_1{}^0$ is an apparent rate constant. Retardation of acetone formation no longer occurred, at zero contact time.

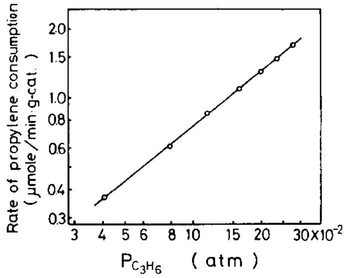


FIG. 3. The effect of propylene partial pressure on the rate of propylene consumption. Catalyst: SnO_2–MoO_3 (Sn/Mo = 9/1), 16.4 g; temperature: 130°C; feed gas rate: 116.5 cm^3/min; feed gas composition: 30% oxygen, 30% water vapor, 4–28% propylene, nitrogen balance.

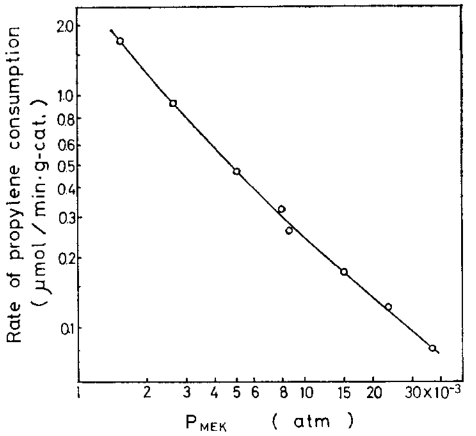


FIG. 4. The effect of partial pressure of methylethyl ketone on the rate of propylene consumption. Feed gas composition: 20% propylene, 0.051–3.5% methylethyl ketone, nitrogen balance. Other conditions are the same as in Fig. 3.

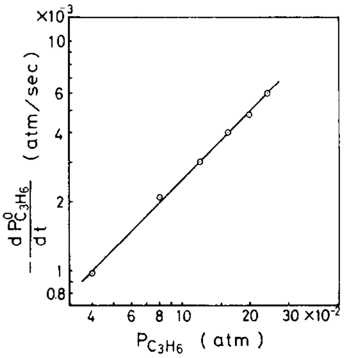


FIG. 5. The effect of the partial pressure of propylene on the initial rate of propylene consumption. Feed gas composition: 4–24% propylene, nitrogen balance. Other conditions are the same as in Fig. 3.

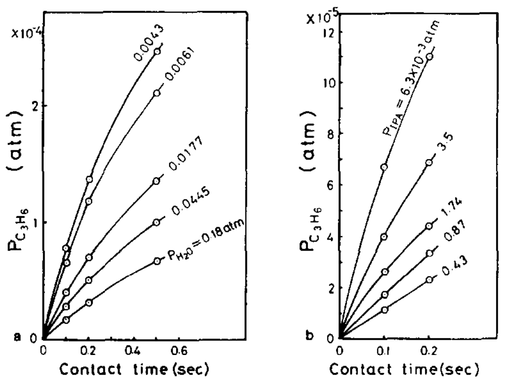


FIG. 6. The dehydration of IPA; the effect of contact time on propylene partial pressure in the effluent gas. Feed gas composition: (a) 0.9% IPA, 30% oxygen, 0.43–18% water vapor, nitrogen balance; (b) 30% oxygen, 30% water vapor, 0.043–0.63% IPA, nitrogen balance. Other conditions are the same as in Fig. 3.

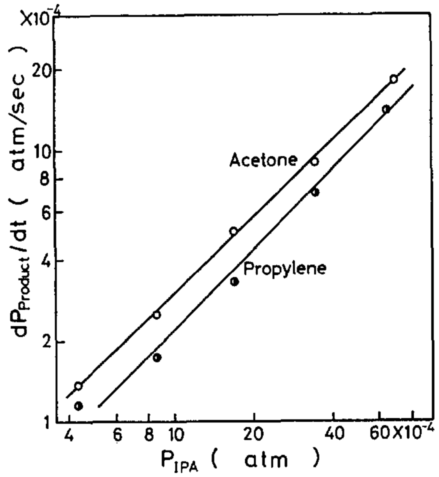


FIG. 8. The effect of the partial pressure of IPA on the initial reaction rate of IPA. Feed gas composition: 30% oxygen, 30% water vapor, 0.04–0.70% IPA, nitrogen balance. Other conditions are the same as in Fig. 3.

(iv) Kinetics of Reactions of IPA

The SnO_2–MoO_3 catalyst used in this study has been shown to be acidic. It is known that IPA is readily dehydrated over acid catalysts (*11*). In fact, when IPA premixed with O_2 and N_2 was passed over the SnO_2–MoO_3 catalyst at 80–150°C, considerable amounts of propylene were formed in addition to acetone. Since IPA has been regarded as an intermediate product to acetone, knowledge of the relative rates of dehydration to propylene and of oxidation to acetone would be important to understand the mechanism.

The kinetics of IPA reactions were thus studied over the SnO_2–MoO_3 catalyst at 130°C in the presence of water vapor. As shown in Figs. 6 and 7, the rates of propylene and acetone formation given by the slope of the curve depend on P_{IPA} and P_{H_2O}, while it was separately confirmed that these rates were independent of P_{O_2}. The initial rates given by the slope near the origin are plotted vs P_{IPA} and P_{H_2O} in Figs. 8 and 9, giving straight lines with the

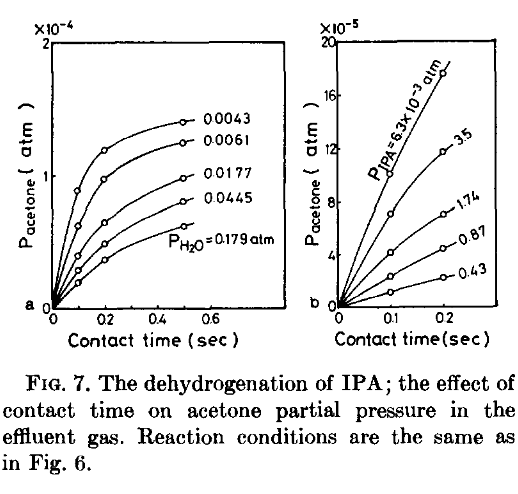


FIG. 7. The dehydrogenation of IPA; the effect of contact time on acetone partial pressure in the effluent gas. Reaction conditions are the same as in Fig. 6.

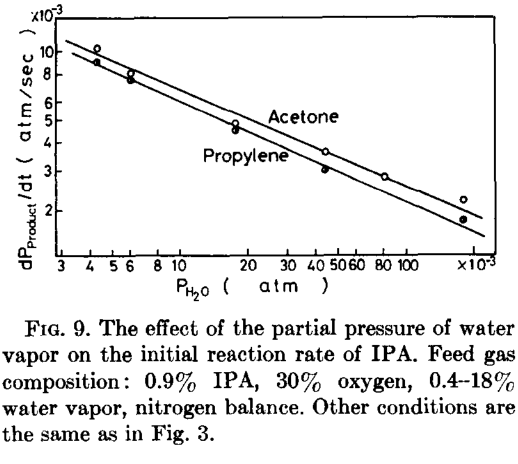


FIG. 9. The effect of the partial pressure of water vapor on the initial reaction rate of IPA. Feed gas composition: 0.9% IPA, 30% oxygen, 0.4–18% water vapor, nitrogen balance. Other conditions are the same as in Fig. 3.

same slope for both reactions. The effect of ketone was also studied. The rates were nearly independent of P_{MEK} as shown in Fig. 10. These results are expressed by power rate equations for dehydration ($dP_{C_3H_6}/dt$) and dehydrogenation to acetone (dP_A/dt):

$$\frac{dP_{C_3H_6}}{dt} = k_{-1}^0\cdot P_{IPA}^1\cdot P_{O_2}^0 \cdot P_{H_2O}^{-0.43}\cdot P_K^0, \qquad (5)$$

$$\frac{dP_A}{dt} = k_2^0\cdot P_{IPA}^1\cdot P_{O_2}^0 \cdot P_{H_2O}^{-0.43}\cdot P_K^0, \qquad (6)$$

where k_{-1}^0 and k_2^0 are apparent rate constants, and estimated to be 0.124 and 0.151, respectively, for a fixed value of $P_{H_2O} = 0.3$ atm.

DISCUSSION

(*i*) *Reaction Scheme to Produce Acetone*

The intermediate nature of IPA is clear from the high selectivity to IPA in the initial stage of reaction as shown in Fig. 2. The variation of IPA concentration with contact time shown in Fig. 1 is, in appearance, a typical behavior of an intermediate. However, the conversion of propylene was less than 5% even when the IPA concentration decreased with the increase in contact time. The decrease in IPA concentration cannot be ascribed to the decrease in propylene. It must be due to the retardation by acetone as shown in Fig. 4 for MEK.

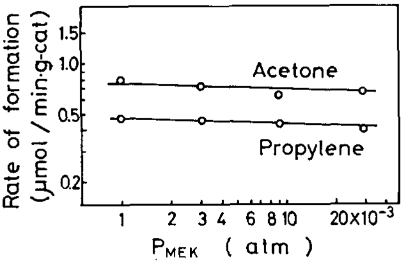
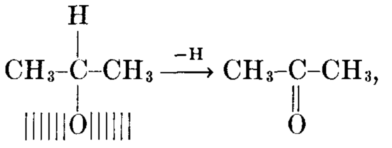


FIG. 10. The effect of the partial pressure of methylethyl ketone on the reaction of IPA. Feed gas composition: 0.8% IPA, 30% oxygen, 30% water vapor, nitrogen balance. Other conditions are the same as in Fig. 3.

The intermediate formation of IPA is consistent with the previous results that acid sites are responsible for the acetone formation (*7*) and that the ^{18}O of $H_2{}^{18}O$ is incorporated into the product acetone (*4*). The first-order kinetics with respect to propylene for the initial rate of propylene consumption is reasonable as the rate of hydration. In this way, all the results are fully consistent with the reaction scheme represented by Eqs. (1)–(3).

Buiten proposed a scheme for acetone formation from propylene over an SnO_2 covered with MoO_3 catalyst which is essentially the same as ours (*12*, *13*). His scheme assumes an adsorbed isopropoxy intermediate:



$$CH_3\text{-}\underset{\overset{|}{||||||O||||||}}{\overset{\overset{H}{|}}{C}}\text{-}CH_3 \xrightarrow{-H} CH_3\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH_3,$$

where oxygen comes from a hydroxyl group on the catalyst surface. It should be mentioned that this mechanism would be indistinguishable from ours if the oxygen exchange of the surface hydroxyl group with water were rapid, as was probably expected, and if the exchange of isopropoxy intermediate with IPA were rapid.

Buiten made an argument against our scheme (*13*) which consisted essentially of two remarks. (i) The amount of acetone formed from propylene was larger than that formed from IPA under identical conditions, on the basis of our previous results (*2*). (ii) The equilibrium concentration of IPA at higher temperatures, where he observed the oxidation to acetone, is extremely small, so that the conversion of IPA goes predominantly toward propylene.

The second remark is reasonable at higher temperatures where his studies were made but by no means rules out the possibility of an IPA intermediate. The first remark was based on our experiment for qualitative study of products. Thus the rates of acetone formation obtained by the separate oxidation of propylene and IPA are estimated and shown in Table 1. The comparison was made with a similar amount of acetone in the effluent gas to avoid the effect of acetone. On the basis of Eq. (6) the comparison should be made on the observed rate of acetone formation divided by IPA pressure. As shown in the last column of Table 1, both rates are similar in magnitude, in conformity with the present scheme.

(*ii*) *Relative Rates of Elementary Steps*

The oxidation to acetone is made up of at least two elementary steps: hydration and oxidative dehydrogenation. A rough estimate of the relative rates of these two steps may be made on the basis of the stationary concentration of IPA relative to equilibrium. The equilibrium concentration of IPA with respect to the hydration of propylene is calculated by the following equations (*12*, *14*):

(Stanley's equation)

$$\log K_p = 1950/T - 6.060, \qquad (7)$$

(Buiten's equation)

$$\log 1/K_p = 7.52 - (2614/T). \qquad (8)$$

It is also shown in Fig. 1 by broken lines for the experimental condition. It is obvious that the IPA concentration reaches about 50–75% of the equilibrium value for each equation at the maximum. This seems to suggest that the rate of the first step, the hydration of propylene, is comparable to that of the second step, the oxidative dehydrogenation of IPA formed at 130°C.

However, as is clear from Fig. 4, the rate of propylene consumption is strongly retarded by MEK, while acetone shows no retarding effect on the dehydrogenation of IPA, as shown in Fig. 10. It was previously demonstrated that acid sites are responsible for acetone formation (*7*). Giordano *et al.* ascribed this acidity to Mo^{5+} (*15*). The retarding effect of ketone seems to be caused by interaction of ketone with the acid site. This is reasonable in view of the electron-donating nature of ketone and of the well-known acid-catalyzed hydration of propylene. In this respect, IPA has an ionization potential similar to that of acetone and is also likely to give a similar retarding effect.

Thus the rate of propylene hydration seems to be significantly reduced in the presence of acetone and IPA. In fact, the stationary concentration of IPA passes through a maximum as acetone concentration increases. This seems to be caused by the reduction of the hydration rate as described before. The authors had con-

TABLE 1

The Rate of Acetone Formation in the Oxidations of Propylene and IPA[a]

Reactant	Concentration in the effluent gas (mol%)		Rate of dehydrogenation of IPA (atm sec^{-1})	Apparent rate constant (rate/P_{IPA}) (sec^{-1})
	IPA	Acetone		
Propylene[b]	15.4×10^{-3}	1.92×10^{-3}	4.6×10^{-5}	0.30
IPA[c]	38.0×10^{-3}	2.20×10^{-3}	11.0×10^{-5}	0.29

[a] Common condition; contact time, 0.2 sec.

[b] Inlet concentration of propylene; 8%.

[c] Taken from Fig. 7.

sidered that the hydration step of olefin is rate determining (*2*, *5*); however, from the results presented in this paper, it is estimated that there is no single rate-determining step under the reaction condition of substantial conversion to acetone. This conclusion is supported by the ratio k_2^0/k_{-1}^0 estimated to be 1.2; if the hydration of propylene is rate determining, the ratio should be much larger than unity. In this respect, the observed rate constant ratio ($k_2^0/k_{-1}^0 = 1.2$) is reasonable as the rate ratio of dehydrogenation to dehydration. The steady-rate Vs should be related with those elementary rates by

$$Vs = V_1 - V_{-1} = V_2, \qquad (8)$$

where V_1, V_{-1}, and V_2 denote the rates of hydration, dehydration, and dehydrogenation, respectively. If $V_2/V_{-1} = 1.2$, then $V_1 = 1.8V_2$, while the difference between V_1 and V_2 would be smaller in the presence of acetone.

The situation would be different at higher temperature where the interaction between the acid site and acetone would be weaker so that the inhibitive effect of acetone would be less extensive. Indeed, Buiten observed a kinetic isotope effect of $V_H/V_D \simeq 2$ comparing the rates of oxidation of $CH_2{=}CD{-}CH_3$ and $CH_2{=}CH{-}CH_3$ over $SnO_2{-}MoO_3$ at 370°C (*13*). Since the methine hydrogen is eliminated only in the dehydrogenation step, this result seems to suggest oxidative dehydrogenation of IPA to be rate determining at higher temperature.

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