JOURNAL OF CATALYSIS 50, 364–372 (1977)

Oxyhydrative Scission of Olefins

II. Examination of Reaction Mechanism

YUSAKU TAKITA, KENJI NITA, TAKASHI MAEHARA,
NOBORU YAMAZOE, AND TETSURO SEIYAMA

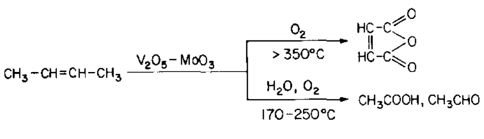
*Department of Materials Science and Technology, Faculty of Engineering,
Kyushu University, Higashi-ku, Fukuoka 812, Japan*

Received April 4, 1977; revised July 25, 1977

In the presence of water vapor and gaseous oxygen, lower olefins such as *n*-butenes are subject to oxidative scission over V_2O_5–MoO_3 catalysts at 170–250°C to form carboxylic acids and/or aldehydes. To examine the mechanism of this reaction, the effects of the acid–base character of catalysts and the feed of water vapor and gaseous oxygen on the reaction were investigated. The results show that, while acidic sites of catalysts, water vapor, and gaseous oxygen are all necessary for the reaction, water vapor in particular plays an important role, the cut of its feed causing a total loss of reactivity of olefins at temperatures below 250°C. Results also show that the reaction proceeds consecutively through the oxyhydrative scission mechanism previously proposed; an olefin is hydrated on an acidic site of the catalyst to form an alcohol followed by oxidation to a ketone and oxidative scission to the final products. The oxidation of C_5 ketone isomers indicates that the last step, the oxidative scission of ketones, follows Popoff's law. In addition, reactivity orders of assumed intermediates show that, of the multiple reaction steps, the oxidative scission step is rate determining in propylene oxidation, while this step is faster than others in butene oxidation.

INTRODUCTION

In the catalytic oxidation of *n*-butenes, dehydrogenation to 1,3-butadiene and oxidation to maleic anhydride are particularly important (*1*). For the latter catalysis, V_2O_5–P_2O_5, V_2O_5–TiO_2, and V_2O_5–MoO_3 are effective (*2*, *3*). In the presence of water vapor, however, *n*-butenes are selectively oxidized to acetic acid and/or acetaldehyde with C–C bond scission over the same catalysts at temperatures of 200–250°C much lower than that for the maleic anhydride formation (*4*–*6*).



In a previous paper (7), we reported the selective formation of acetic acid and both acetic and propionic acids from propylene and *n*-pentenes, respectively, over V_2O_5–MoO_3 (V/Mo = 9/1) catalysts. Butadiene and isobutene were similarly oxidized to acrylic acid and acetone, respectively, though less selectively. From these results, we proposed an "oxyhydrative scission" mechanism in which ketones initially formed by the oxyhydration (*8*–*11*) of olefins are consecutively subjected to oxidative C–C bond scission. However, there are very few papers concerning the mechanism of this reaction. Kaneko *et al.* (*12*, *13*) have proposed a different mechanism free from the participation of water vapor, in disagreement with our mechanism. This

ISSN 0021-9517

TABLE 1

Oxidation of *cis*-2-Butene over Various Catalysts[a]

Catalyst	Surface area (m^2/g)	Conversion (%)	Selectivity (%)				Recovered butene (%)		
			CH_3CHO	CH_3COOH	$CO + CO_2$	C''_4[b]	1-C'_4[b]	*t*-2-C'_4[b]	*c*-2-C'_4
V_2O_5–MoO_3[c]	6.68	39.5	14	54	26	3	20	48	32
V_2O_5	2.78	31.5	11	38	44	5	17	43	40
V_2O_5–P_2O_5[c]	1.72	2.5	13	18	22	47	15	33	52
V_2O_5–Na_2O[c]	1.26	6.2	34	29	14	17	9	15	76

[a] Catalyst, 4.3 g; reaction temperature, 230°C; feed gas (cm^3/min): butene, 5; N_2, O_2, and H_2O, 20.6 each.

[b] C''_4, butadiene; C'_4, butene.

[c] MoO_3, 10 atomic%; P_2O_5, Na_2O, 2 atomic% each.

paper deals with further verification of the oxyhydrative scission mechanism.

EXPERIMENTAL

V_2O_5–Na_2O (V/Na = 98/2) and V_2O_5–P_2O_5 (V/P = 98/2) catalysts were prepared from appropriate compositions of ammonium metavanadate, sodium carbonate, and diammonium hydrogenphosphate by the wet and dry method as mentioned in a previous paper (*7*). V_2O_5–MoO_3 (V/Mo = 9/1) catalysts were from the same origin as in that previous paper (*7*). Experiments were carried out in a conventional flow system using a 16-mm-i.d. Pyrex glass tube reactor with a fixed catalyst bed inside. Liquid reactants were fed to an evaporator located just before the catalyst bed by a microfeeder, to be evaporated and mixed with the other gases there. Products were analyzed by gas chromatography except for maleic anhydride which was subjected to a neutralization analysis.

RESULTS

The Effects of Acid–Base Character of Catalysts

The oxidation of *cis*-2-butene was carried out over vanadium oxide catalysts with or without additives such as P_2O_5 and Na_2O to examine the effects of the acid–base character of catalysts. BET surface area and the performance of the catalysts obtained are shown in Table 1. The addition of 2% P_2O_5 or Na_2O to V_2O_5 brought about a decrease in surface area, in contrast to the opposite trend exerted by the addition of MoO_3. However, more pronounced effects of P_2O_5 or Na_2O addition are discerned in the marked depression of conversion and the alteration of the product distribution, while the effects of MoO_3 addition are modest in these respects. The addition of P_2O_5 causes an extreme increase in selectivity to butadiene. As can be seen from Table 1, the rate of butadiene formation per unit surface area slightly increases from 1.26 to 1.52 $\mu mol/min \cdot m^2$ with the addition of P_2O_5. It is also noted that the recovered olefins have been subjected to double bond isomerization to considerable extents even at lower conversion levels in oxidation. It is thus concluded that the addition of P_2O_5 modifies the character of the V_2O_5 catalyst in such a way as to decelerate the oxyhydrative scission reaction without a significant change in activity for the allylic oxidation. In the case of the addition of Na_2O, the observed reduction of olefin isomerization reflects a decrease in acidity of the catalyst. The selectivity to butadiene in this case remains intermediate between those obtained over V_2O_5–P_2O_5 and V_2O_5–MoO_3. We believe that the decrease of butene conversion with the addition of Na_2O suggests the participation of surface acidic sites to the scission reaction. The decrease in conversion with P_2O_5 addition, on the other hand, may be caused by increased difficulty in supplying

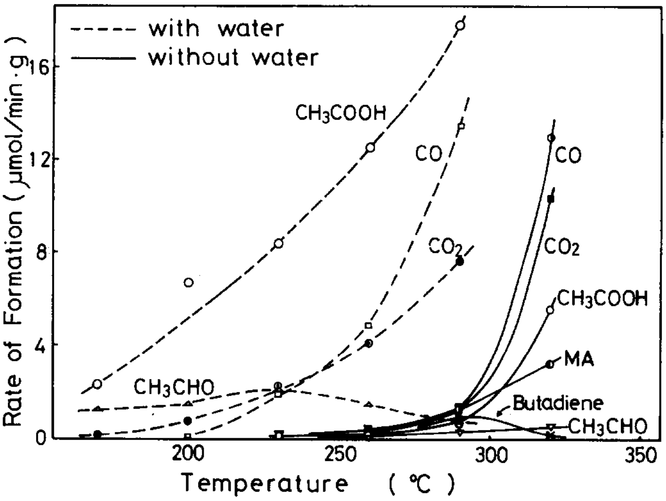


FIG. 1. Effect of water vapor on oxidation of 1-butene. Catalyst: V_2O_5–MoO_3 (V/Mo = 9/1), 4.3 g. Feed gas (cm^3/min): 1-butene, 5.0; O_2, 20.7; solid line, N_2, 41.4; broken line, H_2O, 20.7; N_2, 20.7.

active oxygen necessary in the subsequent reaction steps.

The Effect of Water Vapor

1-Butene oxidation was carried out in the absence of the feed of water vapor over the V_2O_5–MoO_3 catalyst outgassed beforehand (10^{-3} Torr) at 130°C for 2 hr. The result is compared with that obtained under the feed of water vapor (broken line) in Fig. 1. Clearly, reactivity is much lowered in the absence of water vapor, so that oxidation of 1-butene becomes significant only above 250°C. At 290°C, butene conversion was less than one-sixth of that reached in the presence of water vapor. While selectivity to acetic acid is reduced particularly at lower temperatures, butadiene and maleic anhydride (MA), which are insignificant products in the presence of water vapor, form with significant selectivities of 15 and 18% at 290°C, respectively, together with smaller amounts of acetone, *n*-butyraldehyde, acrylic acid, and methyl vinyl ketone. Although the formation of these products is steeply accelerated above 300°C except for butadiene, selectivities to acetic acid and acetaldehyde remain low at 15.7 and 1.6%, respectively, at 320°C. The drastic acceleration of the oxyhydrative scission reaction in the presence of water vapor as shown in Fig. 1 provides strong evidence for the participation of water vapor in the reaction.

The Effect of Oxygen

To know the effect of oxygen on the scission reaction, oxidation of *cis*-2-butene was examined over the V_2O_5–MoO_3 catalyst in the presence of water vapor but no added gaseous oxygen. The feed in this case, however, actually contained about 800 ppm of oxygen as an impurity in the nitrogen carrier used. The results are shown in Fig. 2a. Naturally, reactivity of butene was drastically depressed compared with that under the normal oxidation condition. Butene conversion was only about 1% at 170°C and was only 1/25 of that attained under the normal conditions at 290°C. The rate of oxygen consumption necessary to account for the oxidation products up to 230°C was smaller than could be supplied by the impurity oxygen in the carrier, but at 290°C oxygen was apparently supplied by the reduction of catalyst. In accordance

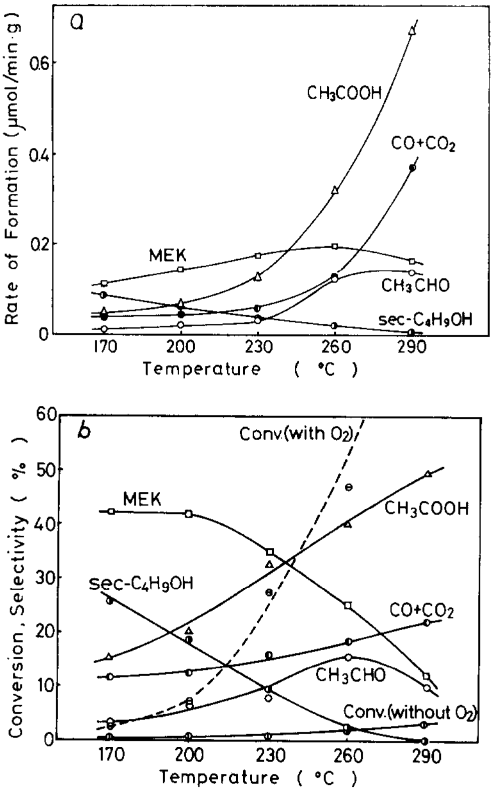


FIG. 2. Effect of oxygen on oxidation of *cis*-2-butene. Catalyst: V_2O_5–MoO_3 (V/Mo = 9/1), 4.3 g. Feed gas (cm^3/min): *cis*-2-butene, 5.0; H_2O, 20.7; N_2, 41.4.

with this, X-ray powder patterns of the catalyst after use at 290°C showed the existence of a part of reduced phase $V_2O_{4.33}$. Because of such a reduction of the catalyst, the experiments shown in Fig. 2a were carried out by increasing the temperature stepwise.

The corresponding selectivities are summarized in Fig. 2b. Clearly, s-butanol (sec-C_4H_9OH) and methyl ethyl ketone (MEK), which are the hydration product of butene and its primary oxidation product, respectively, assumed much higher selectivities than under the normal conditions and reached a sum of about 70% at temperatures below 200°C. With an increase in temperature, these selectivities were reduced to be replaced by selectivities to other products, AcOH, AcH, and $CO + CO_2$. These facts support the contention that the alcohol and the ketone are intermediates of the scission reaction.

Oxidative Scission of Methyl Propyl Ketone and Diethyl Ketone

In order to know how ketone intermediates undergo the C–C bond scission, catalytic oxidations of methyl propyl ketone (MPK) and diethyl ketone (DEK) were carried out over the V_2O_5–MoO_3 catalyst (Fig. 3). These ketones were easily oxidized and reached conversion levels of 20–30% at 130°C.

In the former oxidation, MPK was selectively converted to equimolar amounts of acetic acid and propionaldehyde at 130°C. With an increase in reaction temperature up to 190°C, selectivities to acetaldehyde, CO_2, and propionic acid increased at the expense of selectivity to

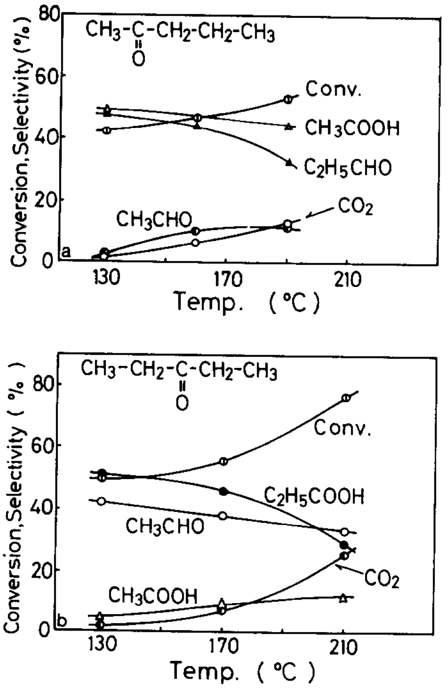


FIG. 3. Oxidation of C_5 ketone isomers. Catalyst: V_2O_5–MoO_3 (V/Mo = 9/1), 3.0 g. Feed gas (cm^3/min): ketone, 3.0; O_2, 18.0; H_2O, 18.0; N_2, 21.0.

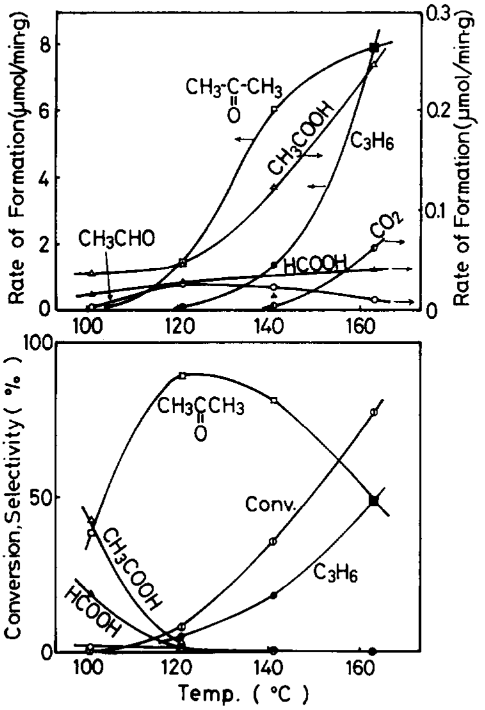


FIG. 4. Oxidation of isopropyl alcohol (IPA). Catalyst: V_2O_5–MoO_3 (V/Mo = 9/1), 4.3 g. Feed gas (cm^3/min): IPA, 2.04; O_2, 20.7; H_2O, 19.5; N_2, 23.7.

propionaldehyde, while the selectivity to acetic acid remained almost unchanged.

On the other hand, DEK was oxidized to almost equimolar amounts of propionic acid and acetaldehyde at 130°C. The selectivities to these diminished with increasing temperature due to the increase in CO_2 and acetic acid formation. It is noted in Fig. 3b that the sum of the selectivities to propionic acid and CO_2 and that to acetaldehyde and acetic acid both amount to about 50% at 210°C. This indicates that acetaldehyde is successively oxidized to acetic acid and that propionic acid is deeply oxidized to CO_2 at higher temperatures.

Comparison of these two oxidations shows that a ketone is oxidatively split into two parts in such a way that the portion containing the original carbonyl group is converted to carboxylic acid and the remaining portion to aldehyde, as is discussed later.

Oxidation of Assumed Intermediates

According to the proposed reaction mechanism, oxyhydrative scission of propylene proceeds through isopropyl alcohol (IPA) and acetone. Therefore, the oxidations of isopropyl alcohol and acetone were examined here over the V_2O_5–MoO_3 catalyst. In the former case (Fig. 4), IPA showed significant reactivity at temperatures above 100°C. Acetone was a major product in the lower temperature region, while the dehydration of IPA to propylene and the oxidation to acetic acid became considerable with increasing temperature.

From acetone (Fig. 5), acetic and formic acids were selectively formed. Below 150°C, the ratio of the selectivity to AcOH and to HCOOH + CO_2 + HCHO was near 2:1, suggesting the oxidative scission of acetone to AcOH and the remaining products.

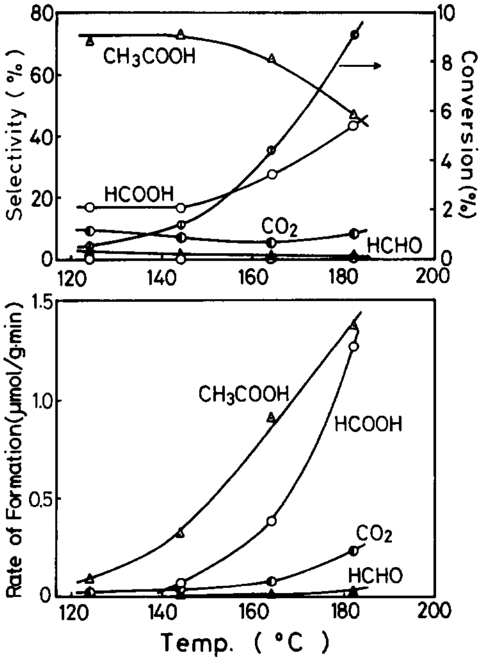
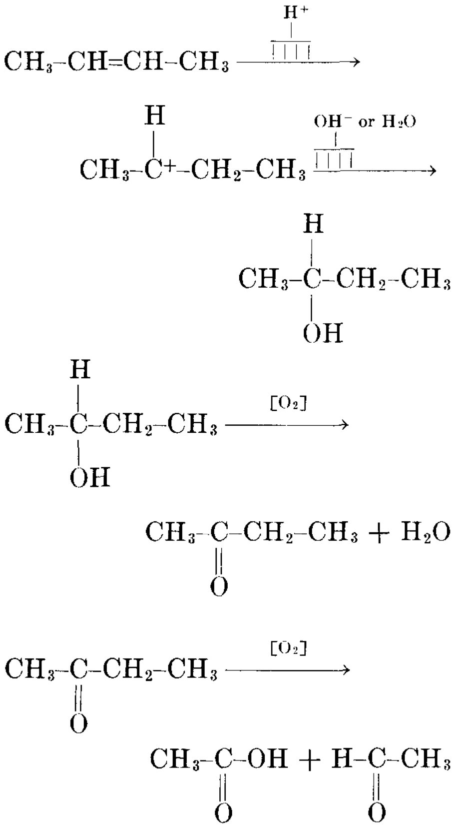


FIG. 5. Oxidation of acetone. Catalyst: V_2O_5–MoO_3 (V/Mo = 9/1), 4.3 g. Feed gas (cm^3/min): acetone, 2.03; O_2, 20.7; H_2O, 19.8; N_2, 23.7.

DISCUSSION

Examination of Reaction Mechanism

In a previous paper (7), we proposed the following reaction mechanism for the oxyhydrative scission of C_3–C_5 olefins:



$$CH_3\text{-}CH{=}CH\text{-}CH_3 \xrightarrow{H^+} CH_3\text{-}\overset{H}{\overset{|}{C^+}}\text{-}CH_2\text{-}CH_3 \xrightarrow{OH^- \text{ or } H_2O} CH_3\text{-}\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}\text{-}CH_2\text{-}CH_3 \quad (1)$$

$$CH_3\text{-}\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}\text{-}CH_2\text{-}CH_3 \xrightarrow{[O_2]} CH_3\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_2\text{-}CH_3 + H_2O \quad (2)$$

$$CH_3\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_2\text{-}CH_3 \xrightarrow{[O_2]} CH_3\text{-}\underset{O}{\underset{\|}{C}}\text{-}OH + H\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3 \quad (3)$$

The first step is an acid-catalyzed hydration reaction, for which acidic properties of catalysts and the existence of water vapor are of inevitable importance.

As for the acid–base character, V_2O_5 itself has acidic sites stronger than $pK_a = 3.3$ which are detectable by the dimethyl yellow indicator. However, such qualifications with Hammett indicators are not suitable for binary oxide catalysts containing vanadium with colors of orange to grayish green. Instead, the acidities of catalysts in the present case were estimated from the catalytic activity for the olefinic isomerization which is known to be promoted by acidic sites of catalysts.

The catalysts listed in Table 1 show a wide variety of isomer distributions of recovered butenes. While it is not possible to give quantitative comparisons of specific rates of isomerization between catalysts, it is apparent that isomerization of *n*-butenes is slowest over V_2O_5–Na_2O, indicating a decreased acidity compared with the others. This is considered to be connected with the depression of scission reaction over that catalyst. Specific rates of butene consumption, and of AcOH and AcH formations, are shown in Table 2 together with the relative rates normalized to unit surface vanadium atoms. Specific activity is seen to be highest at V_2O_5 in both butene consumption and oxygenated compound formation. The high reaction rate exerted by V_2O_5–MoO_3 is mainly associated with the magnification of surface area by the addition of MoO_3. In the case of V_2O_5–P_2O_5, however, isomerization takes place rapidly while acetic acid formation

TABLE 2

Effect of Additives on Specific Rates[a]

Catalyst	Rate of butene consumption (μmol/m$^2\cdot$min)	Rate of formation (μmol/m$^2\cdot$min)			Specific rate	
		CH_3CHO	CH_3COOH	CH_3CHO $+CH_3COOH$	Butene consumption	CH_3CHO $+CH_3COOH$ formation
V_2O_5–MoO_3	3.48	0.48	1.84	2.32	0.58	0.81
V_2O_5	5.88	0.65	2.23	2.88	1.00	1.00
V_2O_5–P_2O_5	0.77	0.10	0.14	0.24	0.13	0.08
V_2O_5–Na_2O	2.60	0.89	0.75	1.64	0.44	0.57

[a] Data are taken from Table 1.

is reduced, the situation appearing to be complex as mentioned earlier.

As the proposed mechanism involves a nucleophilic reaction of H_2O or OH^- with the carbonium ion formed, the overall rate of reaction will be decreased when no water vapor is fed to the reaction system. Actually, as can be seen from Fig. 1, reactivity is depressed so much without the feed of water vapor that neither the oxyhydrative scission nor the complete oxidation takes place below 250°C. It was also noted that the rate of butene isomerization was almost halved in this case compared with the reaction under the normal condition. Kaneko *et al.* (*14*) proposed that the carbonium ion reacts with oxygen over a V_2O_5–SnO_2–WO_3 (1:1:0.5)/SiO_2 (33.7 wt%) catalyst. They observed the promotion effect of water vapor but accounted for it by the selective retardation of the allylic type oxidation, a reaction competitive with the scission reaction. However, our results strongly suggest that water molecules not only favor the formation of Brönsted acid sites but also appear to participate in Eq. (1) as reactants. This will be clearer from the fact that hydration or oxyhydration products such as *s*-butanol *s*-BuOH and MEK increase when oxygen feed is stopped, as mentioned below. In this regard, it is thought that the complete oxidation to CO and CO_2 at temperatures below 290°C in these cases was brought about mainly by successive oxidation of the intermediate products of the scission reaction.

The subsequent steps represented by Eqs. (2) and (3) in the proposed mechanism necessitate the supply of oxygen; otherwise s-BuOH has to be obtained selectively. In practice, with the feed of oxygen gas cut off, the formation of s-BuOH and MEK was certainly enhanced, reaching amounts far exceeding those obtained under the usual conditions over the whole temperature range examined. As for s-BuOH formation, it reached 91% of the equilibrium conversion calculated from the initial partial pressures of butene and water vapor using the following equations (*15*):

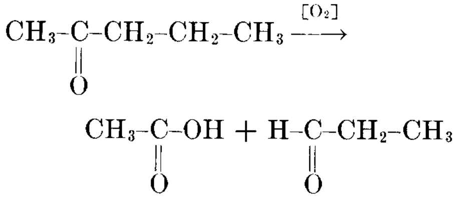
$$\begin{aligned} &n\text{-butene} + H_2O \overset{K_p}{\rightarrow} \text{s-BuOH} \\ &\log K_p = 1845/T - 6.935. \end{aligned} \tag{4}$$

It is concluded that the hydration of butenes is nearly in equilibrium under such a condition. The formation of MEK from s-BuOH under the same condition takes place consuming the impurity oxygen (800 ppm) in the carrier and a part of the lattice oxygen of the catalyst, as stated before. Such reduction of the catalyst is not unusual because Tarama *et al.* (*15*) reported that V_2O_5 was reduced by cyclohexane even at 81°C in a static method. The fact that s-BuOH can be oxidized to MEK with catalyst oxygen suggests the involvement of a redox mechanism in the oxidation steps.

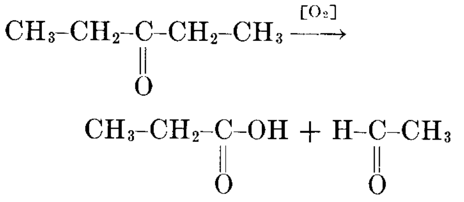
As mentioned above, the effects of water vapor and oxygen on the scission reaction are consistently explained in terms of the proposed mechanism by which olefins are first hydrated on the acidic sites of catalysts to form alcoholic intermediates followed by their oxidation to ketones and further oxygenated compounds.

Reaction Mechanism of Ketone Oxidation

It is known that ketones, though relatively resistant to usual oxidizing agents, can be oxidized with strong oxidants such as chromic acid to give 2 mol of carboxylic acids (*16*). In the oxidation of an unsymmetrical ketone R–CO–R′ where R and R′ are primary alkyl groups, the scission occurs in such a way that the original carbonyl group remains attached to the smaller alkyl group (*17*). In the present catalytic oxidation over the oxide catalysts containing vanadium, equimolar amounts of acids and aldehydes were obtained from lower *n*-olefins via ketone intermediates. In this case, the carbonyls of unsymmetrical ketone intermediates such as MEK are retained by the smaller alkyl groups as above. This may suggest simply that the weakest C–C bond which has the smallest dissociation energy of a ketone molecule is subjected to oxidative scission. However, a problem arises as to which portion of the two fragments from a ketone molecule is converted to an acid. This problem can be solved by comparing the oxidations of two C_5 ketone isomers as follows. Assuming that the fragment containing the carbonyl group is oxidized to a carboxylic acid, the following products have to be obtained from methyl propyl ketone and diethyl ketone provided that the formed aldehydes are not oxidized further.



$$\mathrm{CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow{[O_2]} CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH + H\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}CH_3} \quad (5)$$



$$\mathrm{CH_3\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}CH_3 \xrightarrow{[O_2]} CH_3\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH + H\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3} \quad (6)$$

In fact, acetic acid and propionaldehyde were formed in equimolar amounts from MPK at low temperatures, as shown in Fig. 3. Similarly, the expected products from DEK were also obtained, verifying the above scheme. Such a scissioning pattern coincides with Popoff's law (*17*). Best *et al.* (*18*) showed a high kinetic isotope effect in the homogeneous oxidation of cyclohexanone by chromic acid and suggested the presence of an enol intermediate. However, it is not clear whether oxyhydrative scission over heterogeneous catalysts proceeds via the same enol intermediate as in the homogeneous oxidation.

On the basis of these results, one can in general estimate scission products from a given reactant olefin. That is, an olefin is first hydrated according to Markovnikov's law and the resulting alcohol is oxidized to a corresponding ketone, which is oxidatively scissioned into an aldehyde and an acid in accordance with Popoff's law.

The Slowest Step of the Scission Reaction

As mentioned above, the oxyhydrative scission of olefins is composed of multiple steps of consecutive reactions. Which step is slowest or rate controlling, then? This question was studied for the reactions starting from propylene and *trans*-2-butene. Table 3 summarizes the results on the separate oxidations of propylene, IPA, and acetone at 160°C and of *trans*-2-butene, s-BuOH, and MEK at 180°C. The apparent

TABLE 3

Comparison of Apparent Rate Constants[a]

Reactant	P^O_{reactant} (atm)	P_{products} (atm)	Contact time (s)	Apparent rate constant, k (s^{-1})
(a) C_3H_6	0.0745	0.0065	4.02	0.023
(b) $CH_3CH(OH)CH_3$	0.0310	0.0217	4.10	0.294
(c) CH_3COCH_3	0.0310	0.0021	4.10	0.017
(d) t-2-C_4H_8	0.0745	0.0019	4.02	0.0064
(e) s-BuOH	0.0221	0.0057	4.15	0.072
(f) MEK	0.0308	0.0175	4.15	0.202

[a] Catalyst: V_2O_5–MoO_3(V/Mo = 9/1), 4.3 g; temperature: (a) 160°C, (b) 180°C. Feed gas (reactant, O_2, N_2, H_2O; cm^3/min): (a) 5.6, 20.7, 20.2, 21.3; (b) 2.04, 20.7, 23.7, 19.5; (c) 2.03, 20.7, 23.7, 19.8; (d) 5.0, 20.7, 20.7, 20.7; (e) and (f) 2.0, 21.0, 21.0, 21.0.

rate constants were calculated assuming a first-order dependence of the rates on the partial pressures of reactants. In the case of the C_3 series the oxidation of acetone is slowest. This explains the high selectivity to acetone observed in the stationary oxidation of propylene at low temperatures. The large rate constant for IPA is partly contributed to by a dehydration reaction. It is concluded that the slowest step of the oxyhydrative scission of propylene is the oxidation step of acetone.

As for the C_4 series, the rate constants increase by an order of magnitude in going from butene to MEK. The ease of the oxidation of MEK compared with acetone is accounted for by the possession of a relatively weak internal C–C bond. Because of such a reactivity order, the steady concentration of s-BuOH in the oxyhydrative scission of *trans*-2-butene amounts to only 30–40% of the equilibrium conversion, whereas that of MEK is very low. The rate-determining step of the steady reaction in this case is not yet clear. The detailed investigation based on the kinetic method is in progress.

REFERENCES

1. Bond, G. C., "Heterogeneous Catalysis," p. 93. Oxford University Press, London/New York, 1974.

2. B. P. 1,070,642 (1967); G. P. 1,951,537 (1970); Belg. P. 666, 519 (1965); G. P. 1,443,452 (1970).

3. Voge, H. H., *Advan. Catal.* **17**, 203 (1967).

4. Japan. P. 67 ~ 9,173.

5. Brockhans, R., *Chem. Ing. Tech.* **38**, 1039 (1966).

6. B. P. 1,234,896.

7. Seiyama, T., Nita, K., Maehara, T., Yamazoe, N., and Takita, Y., *J. Catal.*, in press.

8. Moro-oka, Y., Tan, S., Takita, Y., and Ozaki, A., *Bull. Chem. Soc. Japan* **41**, 2820 (1968).

9. Moro-oka, Y., Takita, Y., and Ozaki, A., *J. Catal.* **23**, 183 (1971).

10. Takita, Y., Ozaki, A., and Moro-oka, Y., *J. Catal.* **27**, 185 (1972).

11. Moro-oka, Y., Takita, Y., and Ozaki, A., *J. Catal.* **27**, 177 (1972).

12. Kaneko, K., Koyama, T., and Wada, S., *Bull. Japan. Petrol. Inst.* **16**, 17 (1974).

13. Kaneko, K., Koyama, T., Hurukawa, H., and Wada, S., *Nippon Kagaku Kaishi*, 1105 (1974).

14. Kaneko, K., Hoshino, Y., and Wada, S., *Bull. Japan. Petrol. Inst.* **16**, 24 (1974).

15. Tarama, K., Teranishi, S., Yoshida, S., and Tamura, N., *in* "Proceedings of the 3rd International Congress on Catalysis (Amsterdam)," p. 282, North-Holland, Amsterdam, 1965.

16. Hercz, N., *Ann.* **186**, 257 (1877); Wagner, G., *Ber.* **15**, 1194 (1882).

17. Popoff, A., *Ann.* **161**, 275 (1872).

18. Best, P. A., Littler, J. S., and Waters, W. A., *J. Chem. Soc.*, 822 (1962).