

Oxyhydrative Scission of Olefins

I. Oxidation of Lower Olefins

T. SEIYAMA, K. NITA, T. MAEHARA, N. YAMAZOE, AND Y. TAKITA

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

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A new type of oxidation of C_2 - C_5 olefins leading to the oxidative scissions of carbon skeletons was examined on the V_2O_5 - MoO_3 catalyst in the presence of water vapor. Acetic acid and acetaldehyde and acetic acid and propionic acid were selectively formed from C_2 - C_4 and C_5 olefins, respectively. The reaction was found to go through consecutive multisteps. Taking into account the similarities between the present oxidation and the oxyhydration reaction, it was concluded that the reaction comprises the oxyhydration of olefins to form ketones and the subsequent oxidative scission of the ketones to acids and aldehydes, thus best being named "oxyhydrative scission." The reaction scheme was discussed in comparison with mechanisms for other types of olefin oxidation reactions.

INTRODUCTION

Catalytic oxidation of olefins has been studied very extensively as an important branch of petrochemistry. To date, several types of olefin oxidations have been classified, such as allylic oxidation (1-3), carboxylic anhydride synthesis (4-6), oxyhydration (7-11), oxidative dehydroaromatization (12-14), and so on. In all these oxidations, the carbon skeletons of reactant olefins are preserved into main products, and other products with smaller carbon skeletons or scission products, like acetic acid from propylene, are regarded as undesirable byproducts. If such products can be yielded selectively, however, scission reactions would also be very important in view of the effective utilization of carbon resources as well as the usefulness of the products themselves. In practice, one can find many patents concerning effective catalysts for acetic acid formation from n -butenes; primarily, these are vanadium-

containing oxide catalysts such as V_2O_5 - Sb_2O_3 - SiO_2 (15), V_2O_5 - TiO_2 (16), or V_2O_5 - SnO_2 (17), with only the exception of SnO_2 - MoO_3 (18). However, few studies on this reaction have been reported (19).

It is well known that vanadium oxide is an effective catalyst for the oxidations of benzene to maleic anhydride and o -xylene to phthalic anhydride. Allylic oxidation also proceeds over vanadium oxide to yield acrolein from propylene and maleic anhydride from n -butenes via butadiene (20). These oxidations are usually achieved at temperatures above 300°C and do not require the presence of water vapor. In the presence of water vapor, however, a new type of catalytic oxidation of lower olefins takes place over vanadium-containing oxide catalysts at temperatures as low as 150-250°C. For instance, propylene and n -butenes can be selectively scissioned to form acetic acid and acetaldehyde. As suggested by the substantial importance of water

vapor for the reaction, this reaction is apparently different from the allylic oxidation or the carboxylic anhydride formation. Rather, the reaction conditions and the products suggest its relationship to the oxyhydration reaction. In the present paper, we examined this new type of oxidation using lower *n*-olefins with C₂-C₅ in order to establish the reaction type. We also attempted to elucidate the reaction mechanism.

EXPERIMENTAL

Catalysts. V₂O₅-MoO₃ (V/Mo = 9/1) catalyst was prepared as follows. Aqueous solutions of ammonium metavanadate and ammonium paramolybdate were mixed to an adequate composition, followed by evaporation to dryness on a water bath under violent stirring. The precipitate obtained was decomposed to binary oxide at 400°C for 2 hr, then the powder of the oxide was pressed into pellets and was calcined at 550°C for 5 hr in the air. Granules of 20-40 mesh were used.

Apparatus and method. The oxidation reaction was carried out in a conventional flow system using a 16-mm-i.d. Pyrex glass tube reactor with a fixed-catalyst bed inside. All gases used in this experiment were of commercial origin and were used without purification. The typical feed gas contained 7.5 mol% of a reactant olefin and 30.8 mol% each of nitrogen, oxygen, and water vapor. For the supply of water vapor, water was introduced at measured rates, by means of a microliquid feeder, to a heated glass-wool bed, located at the entrance to the reactor, where it was evaporated and mixed with other gases.

The effluent gas was led into a condenser kept at ca. 15°C, in which high boiling point products were separated by condensation along with water vapor. Products were identified by a mass spectrometer. All components in feed and effluent gases were analyzed by means of gas chromatography

using the following column packings: ODPN for olefins and carbon dioxide, DOS for free carboxylic acids, TCP or PEG No. 1000 for other partial oxidation products, and MS 5A for nitrogen, oxygen, and carbon monoxide. In the following sections, the selectivity to a product A is defined by:

$$\frac{\text{Moles of a reactant olefin converted to A}}{\text{total moles of a reactant olefin consumed}} \times 100\%$$

Data were taken under the steady state after oxidation at 200°C for 2 hr.

No oxidation product was detected in the oxidation of olefins over glass wool at temperatures up to 350°C, except for the formation of trace amounts of CO₂ at 300-350°C.

RESULTS

(a) Oxidation of Lower *n*-Olefins

n-Olefins with C₂-C₅ were subjected to the catalytic oxidation over V₂O₅-MoO₃ (V/Mo = 9/1) catalyst in the presence of water vapor. The results are shown in Tables 1 and 2 and in Figs. 1 and 2.

Ethylene was oxidized significantly only above ca. 200°C. Acetic acid (AcOH), acetaldehyde (AcH), and ethanol were produced from ethylene at a total conversion level less than 0.5% at 200°C, while, at higher temperatures, the deep oxidation of ethylene to CO or CO₂ was steeply accelerated with increasing temperature (Table 1). In contrast, propylene was oxidized more easily, as shown in Fig. 1. The oxidation was detectable at 120°C, a temperature 80°C lower than that for the ethylene oxidation. The product distribution changed rather markedly with temperature. Acetone was selectively formed up to about 200°C, with its formation rate reaching a maximum at ca. 180°C, whereas, at higher temperatures, scission products such as AcOH, formic acid, and AcH, increased, accompanied by the formation of a small amount

TABLE 1
Oxidation of Olefins over V_2O_5 - MoO_3 Catalyst^a

Olefin	Temperature (°C)	Conversion (%)	Selectivity (%)										Recovered butene (%)						
			CH_3CHO	CH_3COOH	C_2H_5COOH	sec -BuOH	MEK	Buta- diene	CO	CO ₂	Unknown	1-C ₄ '	<i>t</i> -2-C ₄ '	<i>c</i> -2-C ₄ '					
(A) Feed gas; standard composition																			
C ₂ H ₄	250	1.92	0.2	6.7									88.9	4.2					
	300	18.1	tr	5.5									85.3	9.2					
C ₃ H ₆	151	6.5	0.5	3.4		7.6 ^b	85.9 ^c						0.8	1.9					
	212	22.1	15.6	23.3		0.8 ^b	43.1 ^c						0.7	6.4	10.1				
1-C ₄ '	170	10.9	31.5	58.2	0.9	tr	1.5							4.5		55.6	19.4	25.0	
	230	39.6	14.0	53.7	0.9	tr	2.5		3.4				12.4	13.1		20.1	47.7	32.2	
	290	88.2	2.2	44.0	0.6	tr	0.7		0.6				33.1	18.9		18.9	49.9	31.2	
<i>c</i> -2-C ₄ '	170	2.8	44.1	44.1	tr									11.7		2.2	5.2	92.6	
	230	27.9	14.1	57.8		tr	1.9		4.5				4.9	16.8		14.4	45.6	40.1	
	290	83.2	1.8	35.1		tr	0.5		0.8				35.3	26.6		18.1	47.5	34.5	
<i>t</i> -2-C ₄ '	170	2.3	30.8	45.3	tr									21.7		9.8	87.8	2.5	
	230	11.2	7.7	23.0		tr	6.6		9.0				13.8	40.0		15.3	57.8	26.8	
	260	40.9	8.8	25.0		tr	2.45		4.8				24.0	34.9		19.4	48.4	32.1	
(B) Feed gas; without oxygen																			
1-C ₄ '	283		7.9	47.8		8.1	36.2										97.8	0.8	1.3
	330		2.6	26.0		0.7	9.8	53.7						0.8		6.4	91.1	3.9	5.1
	403		17.2	42.9			0.9	14.7					9.8	6.0	8.5	65.6	17.3	17.1	

^a Abbreviations used: BuOH, butanol; MEK, methyl ethyl ketone; C₄', butene; tr, trace amount.

^b Isopropyl alcohol.

^c Acetone.

of formaldehyde. Isopropyl alcohol (IPA), the hydration product of propylene, was also obtained as a minor product over the entire temperature range; its formation was found to amount to 40–60% of the equilibrium conversion, as calculated from the partial pressures of propylene and water vapor in the feed.

1-Butene was oxidizable at ca. 150°C as shown in Fig. 2. The formation of AcOH showed a monotonous increase with increasing temperature, while the breakdown to CO or CO₂ was so steeply enhanced at the high-temperature side that the reaction was no longer controllable at 300°C or above, due to the evolved heat of reaction. Therefore, the scission reaction to AcOH or AcH was more selective at lower temperatures. The sum of the selectivities to the two products amounted to ca. 90% at 170°C (Table 1). Small amounts of sec-butyl alcohol (sec-BuOH), methyl ethyl ketone (MEK), and butadiene were also obtained as well as traces of propionaldehyde and *n*-butanol. Ethylene, propylene, or epoxide was not detected even in traces.

The same products were also obtained from 2-butenes. The conversions and the product distributions were similar for all *n*-butene isomers at temperatures above 250°C because of the rapid double-bond isomerization. The rates of AcOH and AcH

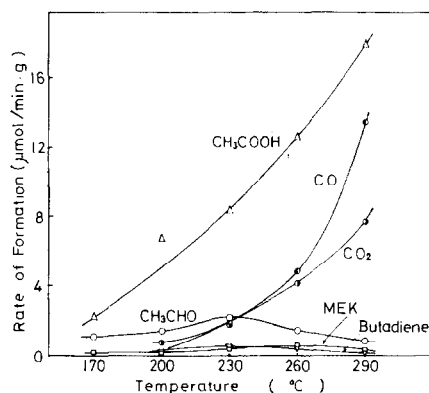


FIG. 2. Oxidation of 1-butene. Reaction conditions are the same as in Fig. 1.

formation at lower temperatures gave the following order of reactivity for butene isomers: 1-butene > *cis*-2-butene > *trans*-2-butene.

As shown in Table 2, *n*-pentenes were oxidized to a wide variety of products, such as carboxylic acids, aldehydes, alcohols, and ketones in addition to CO and CO₂. The main products were AcOH, propionic acid, *n*-butyric acid, methyl propyl ketone (MPK), and diethyl ketone (DEK). Selectivities to acids decreased monotonously as the temperature increased due to breakdown to CO and CO₂. It is seen in the table that far more 2-pentanol than 3-pentanol is obtained in the oxidation of 1-pentene, while both are comparable in the *cis*-2-pentene oxidation. It is also noted that 1-pentene is somewhat more reactive than *cis*-2-pentene.

(b) Oxidation of Butadiene and Isobutene

The reactivities of butadiene and isobutene were examined under the same reaction conditions for comparison with the above oxidations of *n*-olefins. Figure 3 represents the results of butadiene oxidation over a V₂O₅-MoO₃ catalyst. Clearly, butadiene is more resistant to oxidation than *n*-olefins; the conversion is only 2.8%, even at 200°C. One can see from the figure that butadiene is largely converted to CO

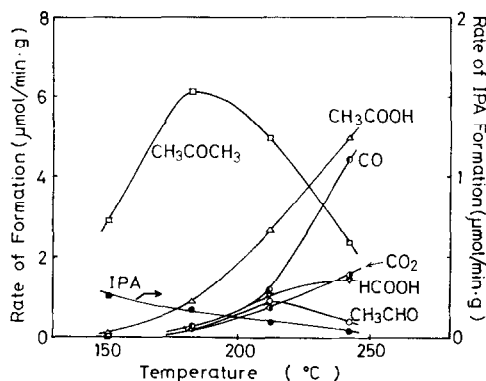


FIG. 1. Oxidation of propylene. Catalyst: V₂O₅-MoO₃ (V/Mo = 9/1) 4.30 g. Feed gas (cm³/min): olefin, 5.0; N₂, O₂, and H₂O (g), 20.6 each.

TABLE 2
 Oxidation of Pentenes

Olefin	Temperature (°C)	Conversion (%)	Selectivity (%)										Recovered pentene (%)			
			CH ₃ CHO	CH ₃ COOH	C ₂ H ₅ COOH	CH ₂ =CH-COOH	C ₃ H ₇ COOH	C ₃ -2-ol	C ₃ -3-ol	Ketone ^a	CO ₂	Unknown	1-C ₃ '	t-2-C ₃ '	c-2-C ₃ '	
1-C ₃ '	170	1.79	2.5	30.0	11.1	—	—	6.9	2.7	0.2	9.3	30.8	6.5	88.4	8.3	8.3
	250	2.50	2.3	30.2	5.9	1.3	7.8	0.4	0.1	7.8	40.7	3.4	3.4	46.6	30.0	23.4
	280	9.05	1.6	22.3	3.3	2.6	11.5	0.05	0.05	1.7	49.8	7.1	7.1	24.7	47.2	28.2
c-2-C ₃ '	170	1.67	5.6	34.4	15.5	—	—	—	3.7	2.5	11.0	21.5	5.8	2.4	6.4	91.1
	230	—	4.1	26.5	7.3	1.1	3.7	0.4	0.2	6.8	42.4	7.5	7.5	7.0	30.0	63.0
	280	8.53	2.3	24.4	5.0	1.2	9.8	0.04	0.04	2.9	50.7	3.6	3.6	11.0	44.8	44.2

^a Ketone: methyl propyl ketone + diethyl ketone; C₃: pentane; C₃': pentene.

and CO₂ and that the partial oxidation takes place to a limited extent, accounting for only 40% of the total conversion at the greatest extent. The main partial oxidation products are acrylic acid, acrolein, and furan. The formation of AcOH and AcH was very small below 200°C.

Oxidation of isobutene is shown in Fig. 4. Isobutene was unreactive up to 140°C. Acetone (~30%), AcH (20%), tert-butanol (~20%), and CO₂ (30%) were formed with selectivities shown in parentheses at 165°C. The formation of all products except AcH increased with increasing temperature, resulting in a level of isobutene conversion which corresponds to about one-fourth of that achieved in *n*-butene oxidation at the same temperature.

(c) Reaction Path from 1-Butene up to AcOH

Presuming that AcOH formation from olefins in the present oxidation consists of consecutive reactions of multiple steps, we pursued the reaction path, choosing 1-butene oxidation as an example. Figure 5a shows the influence of contact time upon product distribution at 150°C. The selectivity to sec-BuOH is seen to increase with the decrease of contact time, approaching nearly 100% at contact time 0, while the selectivities to other products exhibit the opposite tendency. This indicates that sec-BuOH, the hydration product, is the sole primary product from 1-butene in the oxidation reaction.

When being started with sec-BuOH instead of 1-butene, the reaction gave MEK and *n*-butenes along with small amounts of AcH and AcOH as shown in Fig. 5b. The selectivity to each (AcH, AcOH, and butenes) decreased monotonously with decreasing contact time, in marked contrast to the concomitant increase in MEK. The selectivities at contact time 0 were extrapolated as 80 and 20%, respectively, for MEK and *n*-butenes. This shows that the oxidative dehydrogenation of sec-BuOH to MEK

takes place in parallel with the dehydration to *n*-butenes, and that the former reaction is about four times faster than the latter.

DISCUSSION

(a) Pattern and Mechanism of Oxidative Scission of Olefins

As mentioned above, oxidation of lower olefins over V_2O_5 - MoO_3 catalysts in the presence of water vapor eventually results in the formation of acids and/or aldehydes with carbon skeletons smaller than those of reactant olefins. The reaction is thus characterized by the oxidative scission of carbon skeletons, different in type from any of the olefin oxidations which, so far, have been rather well established. Hereafter, we shall discuss the pattern and mechanism of this scission reaction as well as its relevance to other known oxidation reactions.

First, let us consider the scissioning pattern of olefins. Table 3 lists the major oxidation products from *n*-olefins with C_2 - C_5 in the present experiments. There are many intermediate and final products reflecting the consecutive nature of the reaction. However, it is evident that lower olefins are selectively converted to acids and aldehydes with smaller carbon skeletons, except for the case of ethylene, which

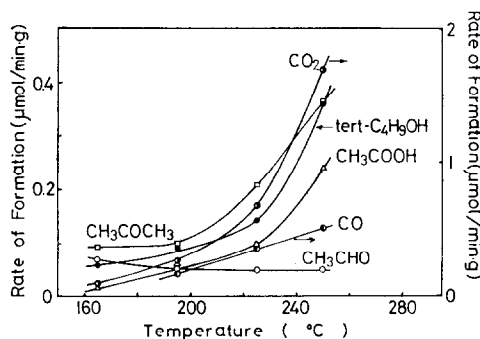


FIG. 3. Oxidation of butadiene. Reaction conditions are the same as in Fig. 1.

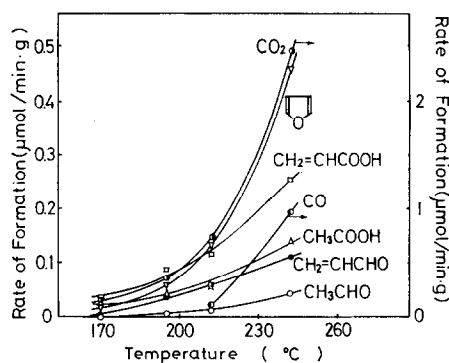


FIG. 4. Oxidation of isobutene. Reaction conditions are the same as in Fig. 1.

is simply oxidized to AcOH or to the total breakdown products, CO and CO_2 , depending on the reaction temperature. Then, what happens to the remaining parts of the carbon skeletons of C_3 - C_5 olefins? The situation is quite straightforward in the oxidation of *n*-butene. In this case, the sum of the selectivities to AcOH and AcH amounts to over 90% at temperatures below $160^\circ C$. This indicates that an *n*-butene molecule is selectively split into just two halves to yield AcOH and/or AcH. Even in the *n*-pentene oxidation in which total breakdown takes place to a greater extent, the quantity of CO and CO_2 formed is far less than that calculated from the scission products with C_2 and C_3 , based on the assumption that the remaining parts of the carbon skeleton are exclusively converted to CO or CO_2 . More interesting, in the case of propylene oxidation below $260^\circ C$, the selectivity ratio of C_2 products (AcOH and AcH) to C_1 products is nearly 2:1, and the C_1 products contain comparable amounts of formic acid and CO_2 (see Table 1). This indicates that the propylene skeleton is selectively scissioned into C_2 and C_1 fragments, and that CO_2 is probably formed consecutively from formic acid. These results clearly show that the formation of acids or aldehydes from *n*-olefins in these cases is associated with direct scission of the carbon skeleton. CO

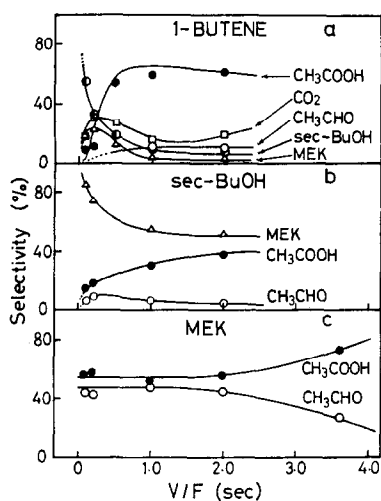


FIG. 5. Effect of contact time on the selectivities in the oxidation of 1-butene, sec-butanol, and MEK. Temperature: (a) 150, (b) 120, and (c) 100°C. Feed gas (cm³/min): (a) 1-butene, 4.47; O₂, 17.8; H₂O, 17.8; N₂, 18.5. (b) sec-butanol, 1.39; O₂, 17.8; H₂O, 17.8; N₂, 21.6. (c) MEK, 1.81; O₂, 17.8; H₂O, 17.8; N₂, 21.2.

and CO₂ are considered to form via consecutive oxidation of the acids and aldehydes formed or via simultaneous reactions.

Furthermore, considering the equilibration of the isomer distributions of *n*-butenes and *n*-pentenes during oxidation, it is noted that oxidative scission occurs at the olefinic carbons. This rejects the concept postulated earlier that acetic acid formation from *n*-butenes is attained by splitting off the terminal carbons consecutively.

Now, we will consider the reaction mechanism. The oxidative scission of olefins exhibits many similarities to the oxyhydration of olefins previously reported by one of the present authors, as presented below. In the oxyhydration, olefins are converted to the corresponding saturated ketones over catalysts such as SnO₂-MoO₃ and Co₃O₄-MoO₃, and the reaction has been shown to proceed via two consecutive steps of hydration of olefins to form alcoholic intermediates and succeeding oxidative de-

TABLE 3

Major Products from Olefins	
Olefin	Product
CH ₂ =CH ₂	CO ₂ (CH ₃ COOH)
CH ₂ =CH-CH ₃	CH ₃ COOH
{ CH ₂ =CH-CH ₂ -CH ₃	{ CH ₃ CHO
{ CH ₃ -CH=CH-CH ₃	{ CH ₃ COOH
{ CH ₂ =CH-CH ₂ -C ₂ H ₅	{ CH ₃ COOH
{ CH ₃ -CH=CH-C ₂ H ₅	{ C ₂ H ₅ COOH

hydrogenation of the intermediates to ketones.

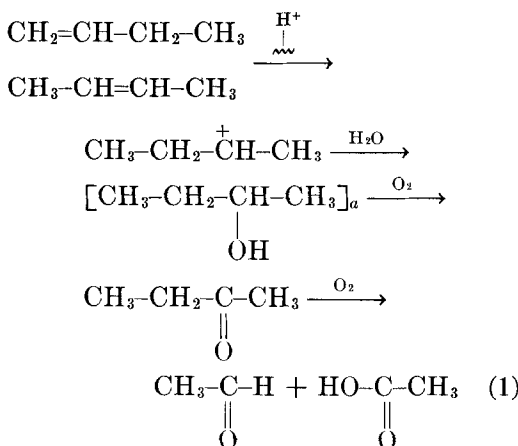
(i) Both the oxidative scission and the oxyhydration reactions occur under similar conditions and require the presence of water vapor. (In the absence of water vapor, oxidation of 1-butene takes place significantly only above 280°C over V₂O₅-MoO₃.)

(ii) Alcohols and ketones corresponding to reactant olefins are formed as intermediates or final products.

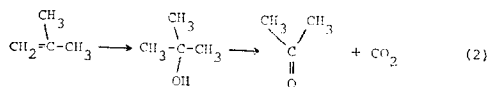
(iii) The reactions are accompanied by rapid double-bond isomerization of olefins.

These similarities strongly suggest that both reactions are closely related to each other in that they possess several reaction steps in common. In fact, in the case of 1-butene oxidation, for instance, the oxyhydration reaction over SnO₂-MoO₃ gives MEK, whereas further oxidation of MEK results in the formation of AcOH and AcH in the oxidative scission reaction (Fig. 5). One of the authors reported the oxidation of propylene over V₂O₅-MoO₃ (V/Mo = 9/1) in the presence of water vapor (9). Figure 4 in Ref. (9) strongly suggests that acetic acid is formed by successive oxidation of the acetone formed at higher temperatures. Thus, the oxidative scission reaction is considered to comprise ketone formation via the oxyhydration mechanism, coupled with oxidative scission of the produced ketones to equimolar acids and aldehydes. The reaction mechanism is represented by

Eq. (1) for the butene oxidation.



It is understood that the most remarkable feature of this reaction is the selective scission of intermediate ketones. This type of reaction is best named "oxyhydrative scission." This mechanism reasonably explains the main products in Tables 1 and 2. The low reactivity of ethylene is interpreted to be due to the difficulty in forming the primary carbonium ion. In the oxidation of isobutene, small amounts of unsaturated compounds were obtained, though their formation is expected according to other oxidation mechanisms. It is considered that isobutene is hydrated to tert-butanol, which is successively oxidized to acetone, while being accompanied by C-C bond scission.



(b) Comparison of Oxyhydrative Scission with other Oxidations

A great deal of study has been devoted to the catalytic oxidation of lower olefins, and the reaction mechanisms have been elucidated or postulated for some characteristic oxidations. It would be worthwhile to compare the oxidative or more precisely oxyhydrative scission reaction with these oxidations. In the first place, the comparison is made with the allylic oxidation, the oxidation which proceeds over various metal oxide catalysts, includ-

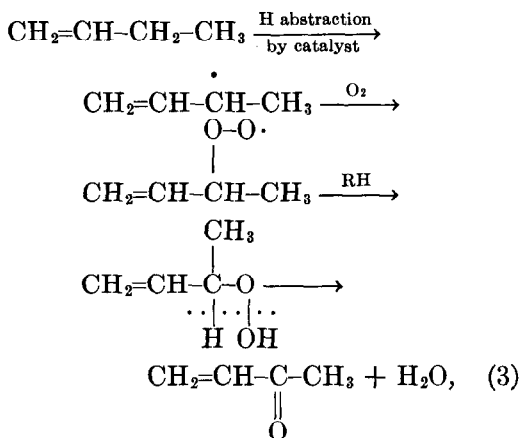
ing the well-known "SOHIO" catalyst $\text{Bi}_2\text{O}_3-\text{MoO}_3$. According to the allylic oxidation, lower olefins are dehydrogenated to form allylic intermediates, which are then oxidized consecutively to the final products. Thus, propylene and *n*-butenes are usually oxidized to acrolein and butadiene, respectively. Over vanadium oxide catalysts, butadiene is further oxidized to maleic anhydride. This allylic oxidation, however, usually takes place at temperatures above 350°C , well above the optimum temperature for the oxyhydrative scission reaction. In fact, only a limited amount of butadiene was formed from *n*-butenes in the present oxidation over $\text{V}_2\text{O}_5-\text{MoO}_3$ catalysts, as shown in Table 1. Further, when the reaction was started from butadiene, the products were largely CO and CO_2 , along with small or insignificant amounts of furan, acrolein, acrylic acid, and AcOH (Fig. 3). These facts show that the allylic oxidation mechanism cannot dominate in the present oxidation. It may be needless to say that acrolein and acrylic acid are ruled out as reaction intermediates, because, if so, the sum of selectivities to AcOH and AcH should not exceed 50% in contradiction to the experimental fact. Similarly, the very small conversion of pentenes to unsaturated compounds also denies the significance of the allylic oxidation (Table 2).

It has been confirmed by D and ^{14}C tracer studies that the hydrogen abstraction from olefins is the rate-determining step in the allylic oxidation (1, 2, 21). This suggests slow double-bond isomerization of olefins, unless other mechanisms are involved. During oxyhydrative scission, however, rapid isomerization was observed, due to the acidic property of the catalysts. This is another piece of evidence for rejecting the allylic oxidation mechanism.

It might be possible to obtain acids and/or aldehydes from olefins if the double bonds could be directly cleaved by the attack of excited oxygen. However, it is difficult to obtain excited oxygen thermally

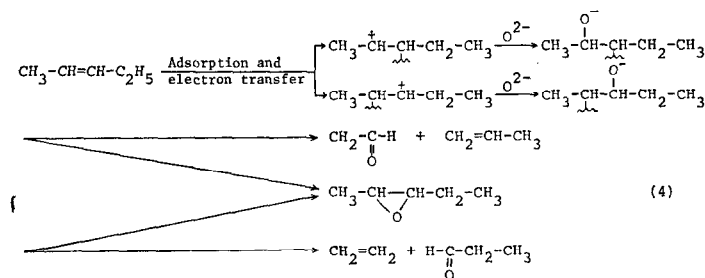
on the catalyst surface. In addition, while the olefin oxidation with excited oxygen usually gives epoxides, ethers, or stripped olefins, none of these characteristic products was obtained in the present oxidation. These exclude the importance of such a mechanism in the scission reaction.

Bretton *et al.* (22) obtained methyl vinyl ketone (MVK) in addition to acids and aldehydes in the oxidation of 1-butene over V_2O_5 -Alfrax catalysts and proposed the following autoxidation-like mechanism.



where RH is an olefin molecule from which the peroxy radical abstracts hydrogen atom. However, it is highly unlikely that such a mechanism contributes significantly to oxyhydrative scission, because only a small amount of MVK was formed from *n*-butenes in our case, and no corresponding products were produced from *n*-pentenes.

Butt and Fish (23) reported the oxidation of *n*-pentenes over pumice-supported V_2O_5 catalysts in the absence of water vapor. According to their results, *n*-pentenes were principally oxidized to AcH at 250–350°C and to *n*-butyraldehyde, propionaldehyde, ethylene, propylene, methanol, and epoxy-pentenes at 350–400°C. The absence of AcOH from products is a special feature of the reaction. It should be noted that the contact time used by Butt and Fish is strikingly long (33.6 sec), so that oxidation can proceed in substantial quantity without catalysts. Butt and Fish proposed a mechanism represented by Eq. (4).



This mechanism postulates a carbonium-ion formation different in type from that proposed in Eq. (3). However, that no epoxides, ethylene, or propylene were obtained in the present pentene oxidations (Table 1) makes this mechanism unlikely in oxyhydrative scission.

Concerning the heterogeneous catalytic oxidation of olefins in which the water molecule participated significantly, the

oxyhydration (7–11), the heterogenized Wacker reaction (24), and the allylic type of oxidation over metallic palladium (25–28) have so far been developed. All these reactions convert olefins to the corresponding aldehydes or ketones without scissioning carbon skeletons. The oxyhydrative scission reaction of olefins studied here would add one special example to this reaction group. Further elucidation of its mechanism seems

very important for a systematization of olefin oxidation. Verification of the proposed mechanism is in progress.

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