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Oxyhydrative Scission of Olefins

III. An Extension to Various Olefins and Ketones

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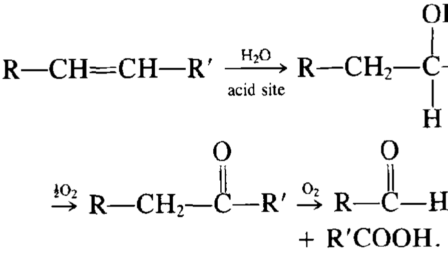
In an attempt to extend the oxyhydrative scission reaction which is typical with *n*-olefins, three olefins and four ketones with various structures have been subjected to oxidation over a V_2O_5–MoO_3 (V/Mo = 9/1) catalyst in the presence of water vapor. Styrene was selectively oxidized at 453–533 K to benzaldehyde and benzoic acid in conformity with the proposed scission scheme. Cyclohexene and 1-chloro-2-butene, however, were subjected to dehydrogenation and dehydrochlorination, respectively, at 423–533 K in preference to the scission reaction. Methylvinylketone underwent scission reaction to form acetic acid and carbon oxides at 423–473 K. 2-Chloro-3-butanone showed high reactivity even at 393 K and produced acetic acid very selectively; one of the expected scission products, acetylchloride, was hydrolyzed to acetic acid. Cycloketones, i.e., cyclopentanone and cyclohexanone, however, were oxidized only to carbon oxides. On the basis of these results the oxyhydrative scission mechanism and the requirements of reactants for it are discussed. © 1987 Academic Press, Inc.

INTRODUCTION

n-Butenes over binary oxide catalysts containing vanadium such as V_2O_5–MoO_3 (V/Mo = 9/1), can be oxidized to acetic acid very selectively at about 473 K in the presence of water vapor (*1*). Such oxidative C–C bond scission is not specific to *n*-butenes but also is applicable to other C_3–C_5 olefins, and the following reaction mechanism termed "oxyhydrative scission" has been proposed (*1*, *2*):



$$\mathrm{R{-}CH{=}CH{-}R'} \xrightarrow[\text{acid site}]{H_2O} \mathrm{R{-}CH_2{-}}\overset{\displaystyle OH}{\underset{\displaystyle H}{\mathrm{C}}}\mathrm{{-}R'} \xrightarrow{\frac{1}{2}O_2} \mathrm{R{-}CH_2{-}}\overset{\displaystyle O}{\overset{\|}{\mathrm{C}}}\mathrm{{-}R'} \xrightarrow{O_2} \mathrm{R{-}}\overset{\displaystyle O}{\overset{\|}{\mathrm{C}}}\mathrm{{-}H} + \mathrm{R'COOH}. \quad (1)$$

This reaction belongs to a type of heterogeneous oxidation reactions in which water molecules participate as a reactant: so far the heterogenized Wacker reaction (*3*, *4*), the olefin oxidation over Pd (*5*, *6*), and the oxyhydration of olefins over oxide catalysts (*7–9*) have been reported to belong to this type. The uniqueness of the present reaction is that carbon skeletons are split oxidatively. It is of interest to know how far this reaction can be extended to various reactants. This paper deals with the oxidation of various types of olefins and ketones over V_2O_5–MoO_3 to examine the applicability of the oxidative scission reaction.

EXPERIMENTAL

The binary oxide catalyst V_2O_5–MoO_3 (V/Mo = 9/1, apparent density 1.05 g/cm^3), used in this work was the same as that described in a previous paper (*1*) and was prepared from aqueous solutions of ammonium metavanadate and ammonium molybdate by the wet and dry methods (calcined at 823 K for 5 h in air). Oxidation reactions were carried out by using a con-

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TABLE 1

Oxidation of Cyclohexene

Temperature (K)	Conversion (%)	Selectivity (%)				
		Benzene	CH_3CHO	CH_3COOH	$CO + CO_2$	Others[a]
443	1.05	50.1	1.36	17.4	12.3	18.8
473	1.98	52.2	0.91	13.5	24.4	9.0
503	7.54	56.6	0.82	6.1	34.5	2.0
533	36.6	59.9	trace	3.3	36.6	0.2

Note. Catalyst: V_2O_5–MoO_3 (V/Mo = 9/1) 2.38 g; GHSV: 1700 h^{-1}; Feed gas (vol%): cyclohexene 5.0, N_2 28.5, O_2 28.5, H_2O 38.0.

[a] Acrylic acid, propionic acid, ethanol, methylethyl ketone, propionaldehyde.

ventional flow reactor with a fixed catalyst bed. Liquid reactants and water were fed with separate liquid microfeeders to the glass wool bed which was located at the entrance of the reactor where the liquids were evaporated and mixed with other gases before entering the reactor. Reaction products were analyzed by gas chromatography in the same way as described elsewhere (*1*). Dicarboxylic acids were analyzed after esterification with dimethylformamide dimethylacetyl. The selectivity of the reaction was defined on the basis of the reactant.

RESULTS

I. Oxidation of Cyclo- and Substituted Olefins

(*a*) *Cyclohexene.* Cyclohexene was oxidized in the presence of water vapor (Table 1). A main reaction was the oxidative dehydrogenation to benzene with selectivity greater than 50% at 443–533 K. The selectivity to acetic acid (AcOH) was ca. 20% at 443 K, but it decreased with a raise in temperature. Small amounts of carboxylic acids and aldehydes (C_2–C_4) were formed at higher temperatures.

(*b*) *Styrene.* The result of styrene oxidation is shown in Fig. 1. Styrene was far more reactive than ethylene but less reactive than the other *n*-olefins previously examined. Benzaldehyde and benzoic acid were obtained as major scission products. Acetophenone was also detected to ca. 10% selectivity at 453 K. Other minor partial oxidation products included acetic and acrylic acids. With increasing temperature, the selectivity to benzaldehyde decreased slightly while that to benzoic acid increased appreciably, suggesting that benzaldehyde is the primary product from styrene. The sum of the selectivities to benzaldehyde and benzoic acid increased from 45% at 453 K to 63% at 533 K.

(*c*) *1-Chloro-2-butene.* Figure 2 shows the result of the oxidation of 1-chloro-2-bu-

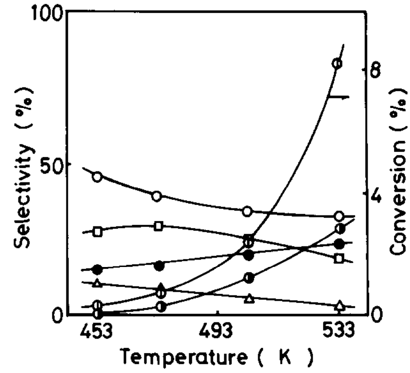


FIG. 1. Oxidation of styrene. Catalyst: V_2O_5–MoO_3 (V/Mo = 9/1) 2 g, GHSV 1774 h^{-1}. Feed gas (vol%): styrene 4.6, each of N_2, O_2, and H_2O 31.8. ◑, benzaldehyde; ⦶, benzoic acid; △, acetophenone; ● $CO + CO_2$; □ others (C_2–C_4 carboxylic acids and aldehydes) and unidentified products; ○, conversion.

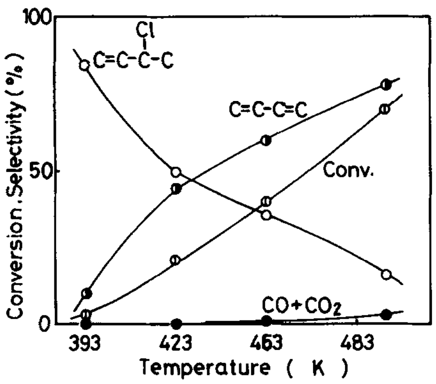


FIG. 2. Oxidation of *trans*-1-chloro-2-butene. Catalyst: V_2O_5–MoO_3 (V/Mo = 9/1) 2 g, GHSV 1763 h^{-1}. Feed gas (vol%): reactant 4.0, each of N_2, O_2, and H_2O 32.0.

tene, a halogen-containing olefin. In this case, isomerization to 3-chloro-1-butene took place at lower temperatures. With increasing temperature, dehydrochlorination to 1,3-butadiene became increasingly dominant and the selectivity to butadiene went beyond 50% at 453 K. Although complete oxidation to CO + CO_2 was noticeable above 423 K, the consecutive oxidation products of butadiene such as furan and crotonaldehyde were not detected up to 493 K.

II. Oxidation of Ketones

Previously it was reported that the apparent rate constants of the oxidation of *sec*-butyl alcohol and methylethyl ketone (MEK) (*1*), which are the primary and secondary intermediate products of *n*-butenes, are larger than the rate constant of butene oxidation by a factor of 1 and 2, respectively. This suggests that secondary alcohols and ketones are easily and selectively oxidized to the scission products. Here, the oxidation of some ketones was examined.

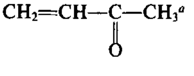
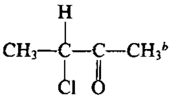
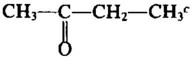
(*a*) *Methylvinyl ketone* (*MVK*). In the case of MVK oxidation (Table 2), acetic acid and CO + CO_2 were formed at nearly equal selectivities at 473 K, although it was estimated that considerable polymerization of MVK proceeded simultaneously. The conversion of MVK remained fairly low compared to that of MEK. Poisoning of the active sites by the polymerization products may be responsible for this.

(*b*) *2-Chloro-3-butanone*. The oxidation of 2-chloro-3-butanone gave acetic acid with selectivity more than 90% (Table 2). The conversion level was only slightly higher than that of MEK.

(*c*) *Cycloketones*. Cyclopentanone and cyclohexanone were far less reactive than MVK or 2-chloro-3-butanone, attaining con-

TABLE 2

Oxidation of Various Ketones

Reactant	Temperature (K)	Conversion (%)	Selectivity (%)				GHSV (h^{-1})
			CH_3CHO	CH_3COOH	CO + CO_2	Polymer	
 $CH_2{=}CH{-}\underset{\underset{O}{\Vert}}{C}{-}CH_3$[a]	423	2.30	0.80	47.0	34.2	17.0	1776
	443	3.83	1.23	46.6	39.5	12.7	
	473	6.51	0.40	40.5	45.0	13.0	
 $CH_3{-}\overset{H}{\underset{Cl}{C}}{-}\underset{\underset{O}{\Vert}}{C}{-}CH_3$[b]	393	31.5	0.73	95.0	trace		1744
	443	63.4	0.58	93.3	1.0		
	473	79.0	0.64	90.1	2.1		
 $CH_3{-}\underset{\underset{O}{\Vert}}{C}{-}CH_2{-}CH_3$[c]	443	56.0	25.0	74.2	0.8		1753

Note. Catalyst: V_2O_5–MoO_3 (V/Mo = 9/1) 2 g, Feed gas (vol%): [a] reactant 2.92, each of N_2, O_2, and H_2O 32.4, [b] reactant 4.69, each of N_2, O_2, and H_2O 31.8, [c] reactant 3.08, each of N_2, O_2, and H_2O 32.3.

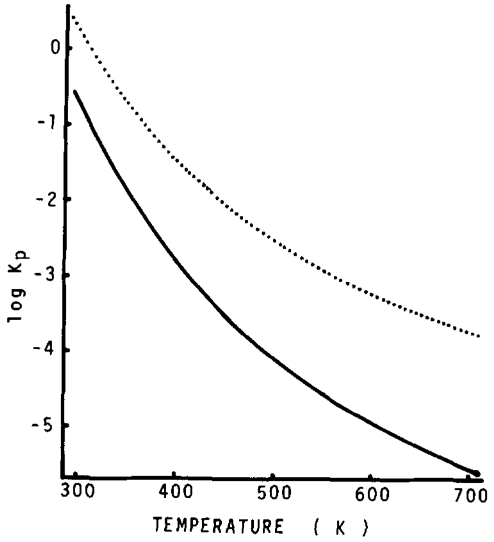


FIG. 3. Equilibrium constants for hydration as a function of temperature. · · ·, *trans*-2-butene; ——, cyclohexene.

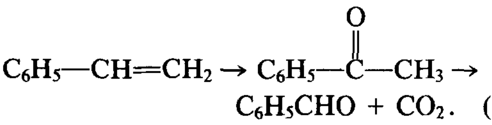
version levels of only a few percent at 430–510 K. The dominant reaction was the formation of CO + CO_2.

DISCUSSION

1. Oxyhydrative Scission of Olefins

As reported previously, *n*-olefins undergo oxidative scission reactions according to the common scheme in Eq. (1). An anomaly has been seen only in the case of ethylene, which is far more stable than larger olefins. In the present study on different types of olefins, only styrene underwent the scission reaction to benzaldehyde, while cyclohexene and 1-chloro-2-butene were directed to other competing reactions.

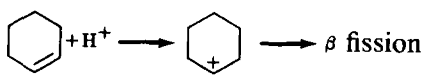
In the oxidation of styrene, acetophenone was also produced. As this compound is expected to be a reaction intermediate, according to the oxyhydrative scission, the following reaction path may be suggested:



$$C_6H_5{-}CH{=}CH_2 \rightarrow C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 \rightarrow C_6H_5CHO + CO_2. \quad (2)$$

However, this scission pattern of the ketone intermediate is different from that observed in the *n*-olefin oxidation in which the carbonyl group should be converted to -COOH, but not to -CHO. This may be a substituent effect of the phenyl group but it remains still possible that benzaldehyde is formed from different intermediates such as styrene oxide.

Cyclohexene should be converted to adipic acid via cyclohexanol and cyclohexanone if the oxyhydrative scission mechanism is operative. However, the experiments showed that oxidative dehydrogenation to benzene was predominant, being accompanied by the formation of considerable amounts of various fission compounds of C_2–C_4. It is of interest to compare the reactivities of cyclohexene and *n*-butenes. Figure 3 shows the equilibrium constants for the hydration of cyclohexene to cyclohexanol and of *trans*-2-butene to *sec*-butyl alcohol as a function of temperature (*10*). Thermodynamically the hydration of *trans*-2-butene is more favorable than that of cyclohexene at all temperatures at which the experiments were carried out. When the hydration of cyclohexene established equilibrium, the formation rate of cyclohexanol is calculated to be 0.022 μmol/min at 443 K, which is comparable to that of acetaldehyde. In practice, however, cyclohexanol was detected only in trace amounts, while *sec*-butyl alcohol formed in the *n*-butene oxidation amounted to about 50% of the equilibrium concentration. One of the reasons for this difference is that cyclohexene can be easily dehydrogenated to benzene. However, an another reason is also be conceivable; i.e., the carbonium ion derived from cyclohexene, a precursor of cyclohexanol, tends to undergo β fission.



(3)

Hindin *et al.* reported such fission reactions of iso-hexane and *n*-hexane at 373 and 523 K, respectively (*11*). The various fission products obtained in the present study may have been produced in this way.

In the reaction of 1-chloro-2-bentene, only isomerization to 3-chloro-1-butene took place at lower temperatures. According to Dittmer and Marcantonio (*12*), the equilibrium constant of this isomerization in toluene is 2.19–2.34 at 353.2 K. With increasing temperature, dehydrochlorination to butadiene increased gradually as has been found over acidic catalysts. It is noted that the formed butadiene was not further oxidized to furan, though V_2O_5–MoO_3 catalysts have been claimed to be effective for the formation of furan from butadiene. It is likely that the furan formation was poisoned by the chloride ions which were liberated.

On the basis of these results, the following requirements are suggested for the oxyhydrative scission reaction:

(1) Reactant olefins must be sufficiently stable against other competing reactions. Cycloolefins and halogen-containing olefins are often too unstable.

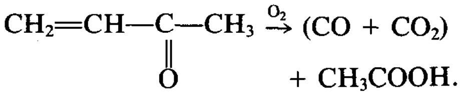
(2) Reactant olefins should preferably have hydrogen to avoid epoxide formation.

(3) The scission products must be relatively volatile. Otherwise they may be consecutively oxidized further.

II. Oxidation of Ketones

The results on MVK, MEK, and chlorobutanone are summarized in Table 2. In each case, acetic acid is a main product, suggesting that the oxidative cleavage of the central C–C bond is the major reaction. From the reactivity order MVK < MEK < chlorobutanone, it seems that scission becomes easier with an increase in inductive effects of the substituents.

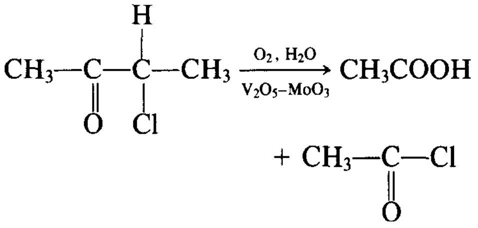
When saturated ketones like MEK are oxidatively cleaved, one of hydrogen atoms of the ketone shifts to the carbonyl portion as showed in Eq. (1). The same scheme is probably applicable to MVK, which gave acetic acid and CO + CO_2 at 47 and 40% selectivities at 443 K, respectively.



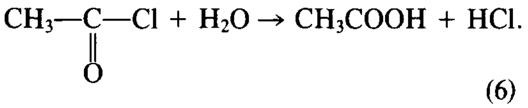
$$CH_2{=}CH{-}\underset{\substack{\|\\ O}}{C}{-}CH_3 \xrightarrow{O_2} (CO + CO_2) + CH_3COOH. \quad (4)$$

It is possible that the shift of a hydrogen atom from the vinyl group leaves a product with a highly carbonaceous composition (C_2H_2) which tends to be completely oxidized to CO and CO_2.

As for the oxidation of chlorobutanone, acetic acid is almost the sole product, without the formation of any chlorine-containing products. This is probably because acetyl chloride is easily hydrolyzed to acetic acid.



$$CH_3{-}\underset{\substack{\|\\ O}}{C}{-}\overset{H}{\underset{Cl}{C}}{-}CH_3 \xrightarrow[V_2O_5-MoO_3]{O_2,\ H_2O} CH_3COOH + CH_3{-}\underset{\substack{\|\\ O}}{C}{-}Cl \quad (5)$$



$$CH_3{-}\underset{\substack{\|\\ O}}{C}{-}Cl + H_2O \rightarrow CH_3COOH + HCl. \quad (6)$$

It should be noted that dehydrochlorination from the reactant gives rise to the formation of MVK. Accordingly, if the dehydrochlorination were to precede oxidative scission, the selectivity to acetic acid would have been less than 20%. The occurrence of C–C bond scission in preference to dehydrochlorination is worth noting. In contrast to these ketones, cyclohexanone and cyclopentanone were far less reactive and selective.

Schriesheim *et al.* (*13*) studied base-catalyzed bromination of C_4–C_8 cycloketones and found that the relative rates decreased with increase of ring size from C_4 to C_6 and as ring size increased above C_6 the rates again increased. The direct comparison with our work is thought to be impertinent since the V_2O_5–MoO_3 catalyst shows typical acidic character. The oxidation of cycloheptanone, however, might be expected to generate very different reaction chemistry from that of cyclopentanone or cyclohexanone because of the widely different conformations of intermediates derived from those. Oxyhydrative scission is not applicable to C_5–C_6 cycloketones.

As illustrated above, the C–C bond adjacent to the carbonyl group of a ketone can be oxidatively cleaved highly selectively unless it is a cycloketone. Introduction of electronegative substituents such as –Cl into a reactant ketone greatly facilitates the scission reaction. As the reaction can be obtained at temperatures as low as 443 K or below, this type of ketone oxidation over V_2O_5–MoO_3 may be important in developing new catalytic oxidation processes.

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