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Oxyhydrative Scission of *trans*-2-Butene in the Liquid Phase under Pressure

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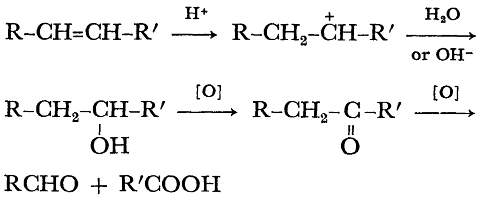
Synopsis. The liquid phase oxidation of *trans*-2-butene under pressure using a V_2O_5–MoO_3 catalyst suspended in water has been proved to yield acetic acid and aldehyde selectively at 170 °C. Taking into account the results of the oxidation of intermediate compounds, it is suggested that the reaction follows the same oxyhydrative scission mechanism as has been proposed for the gas phase oxidation.

The authors have reported the partial oxidation of lower olefins over V_2O_5–MoO_3 catalyst in the presence of water vapor at 160—290 °C.[1,2] The reaction is unique in that the carbon skeletons are oxidatively cleaved into smaller aldehydes and/or carboxylic acids. The following "Oxyhydrative Scission" mechanism has been proposed.[3]



$$\text{R-CH=CH-R}' \xrightarrow{H^+} \text{R-CH}_2\text{-}\overset{+}{\text{C}}\text{H-R}' \xrightarrow[\text{or OH}^-]{H_2O} \underset{\text{OH}}{\text{R-CH}_2\text{-CH-R}'} \xrightarrow{[O]} \underset{\text{O}}{\overset{}{\text{R-CH}_2\text{-C-R}'}} \xrightarrow{[O]} \text{RCHO} + \text{R}'\text{COOH} \qquad (1)$$

In the oxidation of higher olefins, however, desorption of acidic products from the catalyst surface requires higher reaction temperatures, which are less favorable for the hydration process involved in Eq. 1. Too great a rise in temperature is also undesirable for the selectivity of the reaction. This dilemma may be solved if the same reaction can be carried out effectively in the liquid phase. Therefore, oxidation of *trans*-2-butene and the proposed intermediate products has been examined in various solvents by using a V_2O_5–MoO_3 catalyst suspension.

Experimental

The V_2O_5–MoO_3 (V/Mo=9/1) catalyst was prepared from aqueous solutions of ammonium methavanadate and ammonium paramolybdate. The powder obtained was calcined at 550 °C for 5 h in air, and sieved to 30—40 mesh.

The liquid phase oxidation under atmospheric pressure was examined in a closed gas-liquid reactor equipped with a gas burette. The catalyst (2 g) was suspended in water or other solvents (30 cm^3) in the reactor. After degassing the reactor briefly, a gaseous reactant (*trans*-2-butene) was introduced as a mixture with oxygen, while the liquid reactants (10—50 mmol) were injected into the reactor through a sampling port. Oxidation under pressure was carried out in a SUS autoclave with an internal volume of 300 cm^3. After introduction of 3 g of catalyst and 60 g of water, *trans*-2-butene (38.57 mmol) and oxygen were introduced to a total pressure of 20 kg/cm^2 at 0 °C. After the reaction, the liquid and gas phases were separately subjected to gas chromatographic analyses.

Results and Discussion

In the gas phase oxidation, butenes are oxidized to acetic acid and acetaldehyde *via* *s*-butyl alcohol (*s*-BuOH) and ethyl methyl ketone (EMK).

1) Liquid Phase Oxidation under Ordinary Pressure. Gaseous mixtures of *trans*-2-butene and oxygen with the butene/O_2 ratios of 1/9 and 9/1 were brought into contact with the V_2O_5–MoO_3 catalyst suspended in water at 50, 70, and 90 °C, but no oxidation products could be detected. This appears to be due to insufficient reaction conditions. For the oxidation of *trans*-2-butene, solvents other than water were not examined, because the first step of the reaction (Eq. 1) necessitates the presence of water.

The liquid phase oxidation of *s*-BuOH was examined in various solvents. As a result, while no reaction occurred in water, benzene, or chlorobenzene, EMK was selectively obtained in dimethyl sulfoxide (DMSO). For example, the oxidation in DMSO at 125 °C for 13 h converted 10.8% of *s*-BuOH and the selectivity to EMK was 89%. No reaction of *s*-BuOH took place in DMSO without catalyst. In contrast to the gas phase oxidation of *s*-BuOH over the same catalyst, where considerable amounts of butenes are co-produced, no butenes were detected. The role of DMSO is not clear.

Liquid EMK could be oxidized at a considerable

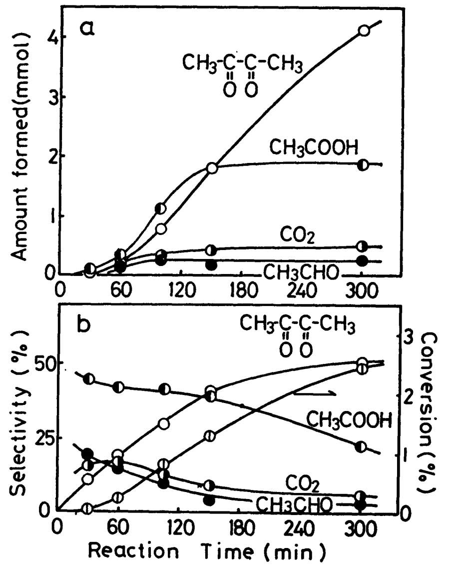
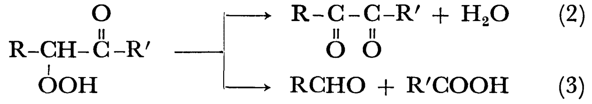


Fig. 1. Liquid phase oxidation of ethyl methyl ketone (EMK). Catalyst: V_2O_5–MoO_3 (V/Mo=9/1) 2 g, EMK: 335.4 mmol, 55 °C, 1 atm.

rate even at 55 °C without the addition of any other solvents (Fig. 1). Acetic acid, acetaldehyde, and CO_2 were formed only in the earlier periods up to 150 min, while the formation of biacetyl continued over the whole reaction period. It is known that the autoxidation of ketone in a homogeneous liquid phase proceeds *via* a hydroperoxide intermediate which is formed by the abstraction of a hydrogen atom at the α-position, followed by the addition of an oxygen molecule there.4—6) The hydroperoxide intermediate then decomposes in the following two ways.7)



$$R\text{-}\underset{OOH}{CH}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R' \longrightarrow \begin{cases} R\text{-}\underset{O}{\underset{\|}{C}}\text{-}\underset{O}{\underset{\|}{C}}\text{-}R' + H_2O & (2) \\ RCHO + R'COOH & (3) \end{cases}$$

This mechanism can account for the main products in the present reaction. However, the time course of the reaction does not seem to be fully consistent with this mechanism. It is known that the latter reaction (Eq. 3) is accelerated in the presence of carboxylic acids owing to the intervention of a carbonium ion mechanism, and the formation of acetic acid should then increase with time in an autocatalytic manner, provided that a hydroperoxide is a substantial intermediate. This is not the case in the present reaction, suggesting an intermediate other than a hydroperoxide. A surface complex between molecular oxygen adsorbed on the catalyst and EMK might be suggested as the intermediate by analogy with the gas phase oxidation.

2) Liquid Phase Oxidation of trans-*2-Butene under Pressure.* As described above, neither the hydration of *trans*-2-butene nor the oxidative dehydrogenation of *s*-BuOH could be attained in the liquid phase under atmospheric pressure below 90 °C. Accordingly, the liquid phase oxidation of *trans*-2-butene was examined at temperatures above 100 °C under pressure.

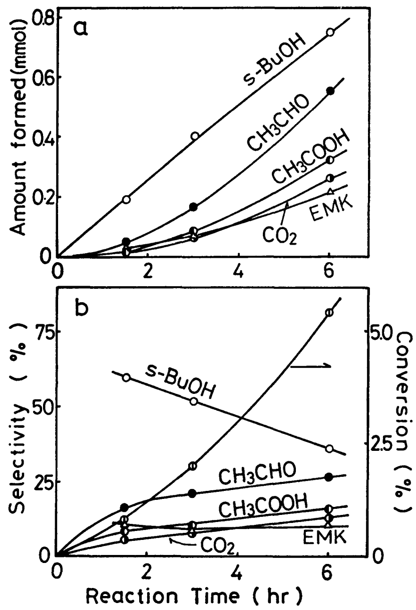


Fig. 2. Oxidation of *trans*-2-butene.
Catalyst; V_2O_5–MoO_3 (V/Mo=9/1) 3.0 g *trans*-2-butene 38.57 mmol, H_2O 60 cm^3, O_2 20 kg/cm^2, 170 °C, total pressure 36 kg/cm^2.

Figure 2 shows the results of the oxidation at 170 °C under pressure of 36 kg/cm^2. *s*-BuOH, EMK, acetaldehyde, acetic acid, and CO_2 were obtained, together with small amounts of propionic and butyric acids.

In the homogeneous oxidation of paraffins in nonaqueous solvents in the presence of soluble metal naphthenate catalysts, it has been reported that the formation of hydroperoxides (HPO) and their decomposition to alcohols, ketones, and acids proceed *via* the Haber-Weiss mechanism.8) In the autoxidation of lower olefins, however, it is known that the product distributions are different. Imamura *et al.*9) have investigated the oxidation of butenes in benzene at 145 and 175 °C under a pressure of 45 atm with a homogeneous catalyst of manganese naphthenate, and obtained butene oxides (19—26% selectivity), butanediol esters (≈15.8%), and a residue with higher boiling points (41—48%), together with small amounts of aldehydes, ketones, and carboxylic acids.

In the present heterogeneous reaction, the product distribution was similar to that in the catalytic oxidation of butenes in the gas phase, and did not include products characteristic of autoxidation, such as epoxides and glycol esters. While the yields of all the products increased with time, the selectivity to *s*-BuOH was relatively high in the initial stage. This fact suggests that *s*-BuOH is a primary product from the starting olefin, as in the gas phase catalytic oxidation. The *s*-BuOH formed is likely to be oxidized to EMK and then to acetaldehyde and acetic acid, as in the gas phase oxidation. It seems reasonable to assume that these oxidation processes also take place on the catalyst surface, though further experiments are needed to verify this assumption. We consider that the mechanism of the liquid phase oxidation of *trans*-2-butene over the suspended V_2O_5–MoO_3 catalyst would be similar to that of the gas phase oxidation over the same catalyst.

References

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