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MEERWEIN-PONNDORF-VERLEY REACTION OVER MAGNESIUM OXIDE

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The hydrogen transfer reaction between ethanol and acetone $CH_3CH_2OH + (CH_3)_2CO \longrightarrow CH_3CHO + (CH_3)_2CHOH$ was studied over magnesium oxide by use of deuterium tracer. Ethanol transfered its hydrogen of CH bond to carbonyl carbon atom, suggesting that the hydride ion transfer from surface ethoxide anion is involved in the reaction. On the other hand, methyl hydrogens in acetone were rapidly exchanged with hydroxyl in ethanol.

Adsorbed species on magnesium oxide is, in general, anionic in feature compared to that on less ionic oxides such as alumina and silica.1-5) In the present communication, the hydrogen transfer reaction $CH_3CH_2OH + (CH_3)_2CO \longrightarrow CH_3CHO + (CH_3)_2CHOH$ was studied over magnesium oxide by use of deuterium tracer. The reaction proceeded by a mechanism similar to that of the Meerwein-Ponndorf-Verley reaction which occurs in homogeneous phase,6) suggesting that surface ethoxide anion formed on magnesium oxide donates hydride ion to carbonyl carbon in acetone.

The reactions between d_6-ethanol and d_0-acetone, and d_1-ethanol-OD and d_0-acetone were studied in a flow system. The deuterium distribution in the reactants and the products in the outflow was determined by the mass spectrometric method. The partial pressures of the reactants and the products were determined by gas chromatography. Prior to the experiments, magnesium oxide (10.2 gr. : Kishida Chemical Co., extra pure grade) was heated in an oxgen stream at 500°C for 3 hrs.

When a gaseous mixture of ethanol and acetone was passed over the catalyst with a nitrogen stream, the hydrogen transfer reaction occurred above 170°C. Under the present experimental conditions, the conversion is always less than 7 %, so that the backward reaction is practically negligible. No reaction occurred when either ethanol or acetone alone was admitted through the catalyst bed.

When the reaction between d_6-ethanol and d_0-acetone was carried out, the peaks were observed at m/e=58, 59 and 61 in the mass spectrum of acetone in the outflow. Since the strong peak at m/e= 58 is assigned to the parent peak for d_0-acetone,7) it is concluded that d_1- and d_2-acetones are formed in appreciable amounts during the course of the reaction. The hydroxyl group of ethanol in the outflow was examined by the infrared spectrophotometric method, and it was found to be markedly diluted with protium in the course of the reaction. However, the mass spectrometric analysis revealed that both α- and β-hydrogen atoms in ethanol molecule were practically unexchanged with protium in acetone. Since the amount of the products is negligible compared with that of the reactants, acetone molecule is exchanged its hydrogen atoms practically with hydroxyl group in ethanol. From the atomic fraction of deuterium in acetone as well as the mole fraction of d_n-acetones obtained, it is concluded that the exchange of hydrogen between hydroxyl group and acetone is practically at equilibrium, indicating that it occurs readily compared with the hydrogen transfer reaction. As in the case of base catalyzed reaction in homogeneous phase,[6,8] the exchange possibly proceeds through acetone in the enolic form. Figure 1 shows the mass spectra obtained for acetaldehyde together with the assignments of its fragment ions.[9] The atomic fraction of deuterium in aldehyde group is estimated from the peaks at m/e = 29 and 30 to be 0.9. Acetaldehyde with -CDO group is selectively formed in the reaction. However, methyl group is diluted with protium to appreciable extent as was found for acetone. Figure 2 shows the results obtained for isopropanol.

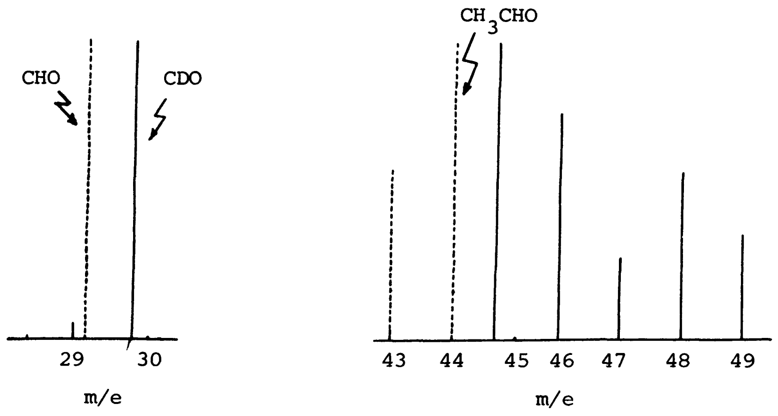

Figure 1. The Mass Spectra of Acetaldehyde.
Solid lines: Acetaldehyde in the outflow.
Dotted lines: d_o- Acetaldehyde.

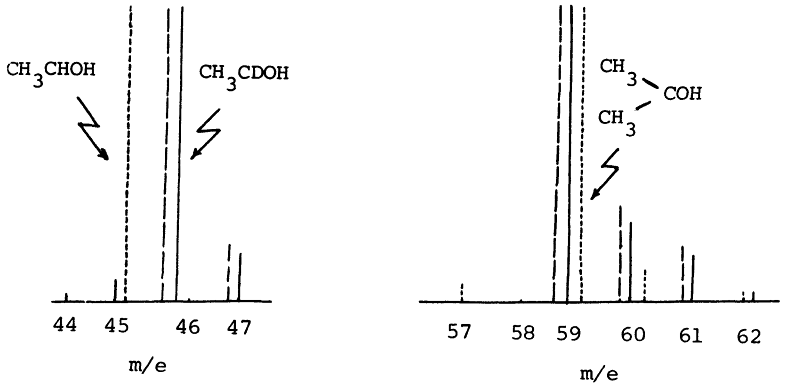

Figure 2. The Mass Spectra of Isopropanol.
Solid lines: Isopropanol in the outflow.
Dotted lines: d_0-isopropanol.
Broken lines: The spectra estimated.

Prior to the analysis, hydroxyl deuterium was replaced by protium. The relative heights of the peaks are shown in the mass ranges where both the parent and (M-15) peaks are found (M designates the mass of the parent species). Dotted lines are the spectra for isopropanol-d_o for which the intense peaks at 45 and 59 are assigned respectively to the fragments CH_3CHOH and $(CH_3)_2COH$.[10] The solid lines represent the spectra of isopropanol obtained in the tranfer reaction. It is evidently seen that the peak at m/e = 46 is intense in one mass range, suggesting that d_1-fragment either CH_3CDOH or CH_2DCHOH is predominant. However, in another range, the peak at m/e = 59 is intense so that d_o-fragment $(CH_3)_2COH$ is predominant. Isopropanol with $(CH_3)_2CD$-group is preferentially formed in the reaction between d_6-ethanol and d_o-acetone. When d_1-ethanol-OD is allowed to react with d_o-acetone, deuteroxyl group is readily diluted with hydrogen in acetone molecule. Substantially, no deuterium was bound to α-carbon of isopropanol. In this respect, it is concluded that hydrogen of CH bond in the ethanol molecule, possibly α-hydrogen, is transfered almost exclusively to the carbonyl carbon atom. In view of the facts that small amounts of d_n-acetones are formed in the course of the reaction between d_6-ethanol and d_o-acetone, isopropanols formed are slightly deuterated on its β-carbon. On these bases, the relative heights of the peaks are estimated in more detail on the assumption that no isotope effect is exerted upon the fragmentation of d_n-isopropanol. The broken lines in Figure 2 represent the peaks thus estimated and are fairly in accord with the observed spectra. From those features of the results, it is evident that the reaction proceeds through a mechanism similar to that in the homogeneous phase.[6,8,11] Because of anionic nature of ethoxide formed on magnesium oxide,[1-3] its α-hydrogen would be easily removed as hydride ion. With the aid of an infrared spectrophotometric method, it was further found that the transfer reaction under the steady state proceeds in proportion to the amount of adsorbed acetone and ethoxide anion. Therefore, these results lead to the conclusion that the hydride ion transfer step is rate determining. This is somewhat different from the results obtained in homogeneous phase.[12,13] The details of the work will be published elsewhere.

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