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Hydrogen-transfer Reaction between Ketones and Alcohols over Metal Oxide Catalysts

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Intermolecular hydrogen-transfer reactions have been studied by many workers. According to Schächter and Pines,[1] when a mixture of isopropyl alcohol and 2-butanone was passed over calcium oxide at about 320°C, both acetone and butanol were produced. Niiyama *et al.*[2] have reported the hydrogen-transfer reaction between alcohol and ketone over silica-magnesia catalysts and proposed a mechanism similar to that of the Meerwein-Ponndorf reduction. In our preceding papers,[3] it was found that the reactions between allyl alcohol and propionaldehyde or propylene oxide are accelerated by silica-magnesia and metal oxide catalysts. In this paper, the mechanism of the hydrogen-transfer reaction on metal oxides was studied using a conventional pulse reactor (carrier gas: He) at 260°C.

Materials. The metal oxides used were MgO, CaO, SrO, and BaO of a commercial grade. The properties of the metal oxides used are given in Table 1.

TABLE 1. THE PROPERTIES OF METAL OXIDE CATALYSTS AND THE REACTIVITIES OF THE HYDROGEN TRANSFER REACTION BETWEEN METHYL ETHYL KETONE AND 2-PROPANOL OVER THESE OXIDES AT 260°C

Catalyst	Surface area (m^2/g)	Basicity[a] (mmol/g)	Activity/g[b] (arbitrary unit)
MgO	55.6	0.288	65.5
CaO	13.3	0.014	62.6
SrO	5.3	0.004_5	1.6
BaO	1.9	0.005_3	3.4

a) Measured at $H_0=+7.2$.
b) Obtained from the formation of *sec*-butyl alcohol.

Results and Discussion

The hydrogen-transfer reaction was carried out over metal oxides using an equimolar mixture of alcohol and ketone. Under our reaction conditions, the reactivity of the dehydrogenation of alcohol was very small. In all cases, the dehydrogenated product of alcohol and the hydrogenated product of ketone were obtained. Table 1 shows the reactivities of the reaction between 2-propanol and methyl ethyl ketone (MEK) over several metal oxides. The reactivities were calculated from the formation of 2-butanol. The reactions are poisoned by dichloroacetic acid. Though the basicity[4] (measured at $H_0=+7.2$) of magnesium oxide is much larger than that of calcium oxide, the activities of these metal oxides are almost the same. According to Take *et al.*[5] these metal oxides have the same amount of a strong base, which is stronger than $H_0=+24$, but strontium oxide has only a small amount of the strong base. Therefore, it is considered that the strong base is favorable for the reaction.

Table 2 gives the reactivities of the reaction between

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[1] Y. Schächter and H. Pines, *J. Catal.*, **11**, 147 (1968).

[2] H. Niiyama and E. Echigoya, The 23rd Annual Meating of Chemical Society of Japan, Preprints of papers, No. 1 p. 51 (1970).

[3] Y. Okamoto, T. Imanaka, and S. Teranishi, This Bulletin, in press.

[4] K. Tanabe and T. Yamaguchi, *J. Res. Inst. Catal., Hokkaido Univ.*, **11**, 179 (1964).

[5] J. Take, N. Kikuchi, and Y. Yoneda, *J. Catal.*, **21**, 164 (1971).

Table 2. The reactivities of hydrogen transfer reactions between methyl ethyl ketone and several alcohols on MgO at 260°C

Alcohol	Reactivity/g[a] (arbitrary unit)	$D_r^{(R)}$ [b]
Methanol	9.94	1.0523
Ethanol	32.9	1.0699
2-propanol	68.1	1.0896
n-Butanol	37.5	——
t-Butanol	8.44	——

a) Obtained from the formation of *sec*-butyl alcohol.
b) The delocalizability for radical reaction of α-hydrogen of alcohol.

Table 3. Kinetic isotope effect of hydrogen transfer reactions between methyl ethyl ketone and deuterated alcohols over MgO at 260°C

Alcohol	k_D/k_H [a]
C_2H_5OD	1.04
CD_3OD	0.722

a) The ratio of reactivity of deuterated alcohol to non-deuterated one.

MEK and several alcohols, while Table 3 shows the kinetic isotope effects on the reaction. Fig. 1 shows the relation between the reactivity and the delocalizability, $D_r^{(R)}$, of the hydrogen attached to the α-carbon of alcohol.[6] On the basis of these fact, it may be concluded that the rate-determining step is the hydrogen-abstraction process from the α-carbon, not from the hydroxyl group. When intermolecular hydrogen-tansfer reactions between 2-propanol and several ketones were carried out, a good parallel relation between the reactivity and the electron-donating power of ketone ($\Delta\nu_D$; cm^{-1}) was found, as was revealed in a preceding paper.[3] The electron-donating power of a compound is defined[7] as the relative difference (countered as wave numbers) of the O–D adsorption band of methanol-*d* observed in the compound from that in benzene.

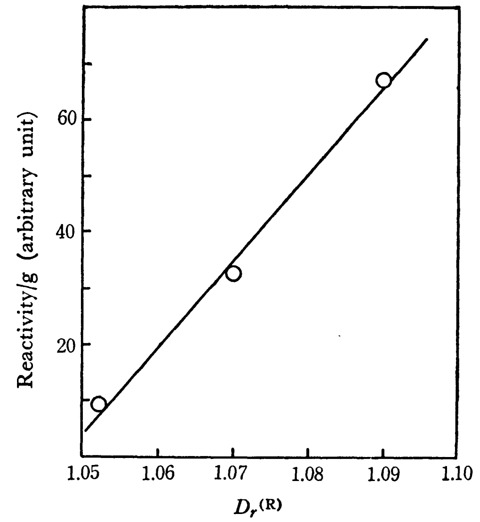
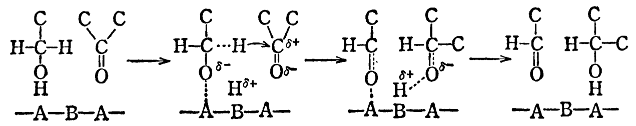


Fig. 1. Correlation between the reactivity of the hydrogen transfer reaction and $D_r^{(R)}$ of α-hydrogen of alcohol.

The poisoning effect of pyridine on the reaction was studied over a magnesium-oxide catalyst in order to make it clear which were the active centeres, but pyridine has no effect on the reaction, whereas magnesium oxide is considered to have a very weak acid site.[3,8] It is considered that alcohol is adsorbed on a strong basic site, thus dissociating the hydroxyl group, and that the basic strength of the anion formed is stronger than that of pyridine. As the electron-donating power of pyridine ($\Delta\nu_D$; 128 cm^{-1}) is much larger than those of the ketones used, the reaction must be poisoned, if the weak acid site also favorable for the adsorption of ketones. Therefore, it is considered that ketone is not adsorbed and not activated by the acid site on metal oxide. Taking these facts into consideration, the reaction mechansim on metal oxides is deduced to be as follows:



A: Weak acid site
B: Strong basic site

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[6] K. Morokuma "Organic Quantum Chemistry" Kagaku-dozin, Kyoto (1966), p. 90.

[7] T. Kagiya, Y. Sumida, and T. Inoue, This Bulletin, **41**, 767 (1968).

[8] St. Malinowski, S. Szczepaniska, A. Bielanski, and J Sloczynski, *J. Catal.*, **4**, 324 (1965).