

The Conversion of Benzaldehyde into Benzyl Benzoate with Alkaline Earth Metal Oxide Catalysts

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When benzaldehyde was treated at 120–200°C over alkaline earth metal oxides, a large amount of benzyl benzoate and a very small amount of benzyl alcohol were found as the reaction products. The time variation of the ester formation gave a S-shaped curve including an induction period. After the induction period, the reaction obeyed the first order rate equation with respect to the concentration of benzaldehyde. The catalytic activity increased in the order of $\text{MgO} < \text{CaO} \ll \text{SrO} \ll \text{BaO}$ and a very good correlation was found between the catalytic activity and surface basicity. The catalytic activity was decreased by the addition of phenol, benzoic acid or pyridine.

It was observed in the experiment using deuterated benzaldehyde that the two α -hydrogens of benzyl groups of benzyl benzoate and benzyl alcohol formed were deuterated and that there was no kinetic isotope effect for the ester formation ($k_H/k_D = 1.0 \pm 0.2$), whereas the induction period was prolonged. Infrared spectra of the adsorbed benzaldehyde showed the existence of the metal benzylate and benzoate on the surface.

It has been concluded that the active species of MgO and CaO for the ester formation are the metal benzylates whose formation is facilitated by both the basic sites (O^{2-}) and acidic sites (Me^{2+}) on the surface. The reaction mechanism was discussed in comparison with the homogeneous base-catalyzed reaction.

INTRODUCTION

It is well known that benzaldehyde is converted by disproportionation into benzoic acid and benzyl alcohol in aqueous alkali solution (Cannizzaro reaction) and also reacts with basic metal alcoholates to form benzyl benzoate (Tishchenko reaction). The mechanisms of the base-catalyzed reactions in homogeneous phase are well understood. However, since no work has been done on the reaction of benzaldehyde with solid bases, we have studied the heterogeneous base-catalyzed reaction.

Alkaline earth metal oxides, which were reported to have basic properties on the surface (1–6), were used as catalysts. Alumina, sodium hydroxide mounted on silica, solid sodium hydroxide, and strontium and barium peroxides were also used for comparison.

The present paper reports the correlation between the catalytic activity and the surface property, the nature of active sites and the reaction mechanism.

EXPERIMENTAL METHODS

1. Catalysts and Reagents

MgO, CaO and SrO were prepared by calcining their hydroxides (Kanto Chemical Co.) at 180–1000°C for 3 hr in air. In some cases, CaO and SrO were also prepared from the carbonate and the nitrate, respectively, by thermal decomposition. Nickel crucible was used for the preparation of SrO. Al_2O_3 (Kishida Chemicals Co.) was calcined at 500°C for 2 hr. These oxides were stored in sealed ampoules. BeO (Wako Pure Chemicals Co.) and BaO (Koso Chemicals Co.) were used as cata-

lysts without any pretreatment. Solid sodium hydroxide was dried at 110°C. NaOH/SiO₂ was prepared by immersing a silica gel in aqueous NaOH solution, filtering and heat-treating at 200°C for 3 hr; the amount of sodium was 2.26×10^{-3} mol/g. SrO₂ and BaO₂ were prepared by a precipitation method using hydrogen peroxide (7) and calcined at 200°C for 3 hr.

Benzaldehyde of reagent grade was distilled twice under reduced pressure and stored under nitrogen gas in a cold and dark place. Benzaldehyde- α -d₁ was synthesized and purified by Wiberg's method (8), the purity was confirmed to be the same as that reported by infrared and mass spectra. Benzyl alcohol used as an addition was purified by distillation under reduced pressure. Other various additions such as benzoic acid, phenol, cyclohexane, benzene, and pyridine were all commercial reagents.

2. Basic Property and Surface Area

The basicity of catalysts was measured by titrating with 0.10 *N* benzoic acid-benzene solution, using bromthymol blue ($pK_a = 7.1$) and phenolphthalein ($pK_a = 9.3$) as indicators (9). The specific surface area was determined by applying BET method to the adsorption isotherm of nitrogen at -196°C.

3. Reaction

About 30 ml of benzaldehyde was reacted over 1.0 g of solid catalysts under a

stream of dried nitrogen at $105\text{--}200 \pm 0.3^\circ\text{C}$; the reaction mixture was stirred by a magnetic stirrer. At appropriate time intervals, the sample was taken out and after the catalyst was separated, it was analyzed by a gas chromatograph with a column of silicone DC 550. Deuterated benzyl benzoate and benzyl alcohol were identified by infrared and mass spectra.

4. Measurement of Infrared Spectra

Thin discs of magnesium and calcium hydroxides prepared by pressing at 2 and 4 kg/cm², respectively, were mounted on a Nichrome wire holder placed in the heating zone of an infrared cell and decomposed to their oxides by evacuating at 700°C for 2 hr. The calcined discs were moved into the optical path with a magnet and evacuated to about 3×10^{-5} mm Hg at room temperature. Benzaldehyde was adsorbed on the oxides at room temperature. Desorption of benzaldehyde and products was carried out by evacuating samples at temperatures of 180–400°C for 15–75 min. Infrared spectra were measured at room temperature with a Hitachi Model 215 infrared spectrophotometer.

RESULTS

Reaction Products and Order of Reaction

Main reaction product was benzyl benzoate, a small amount of benzyl alcohol (below 1.0% usually and several percent

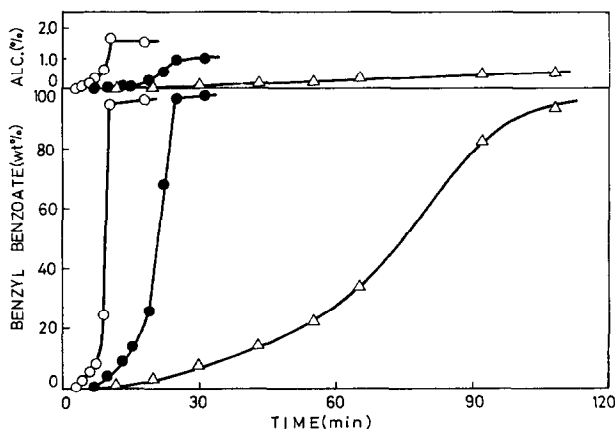


Fig. 1. Weight percent of benzyl benzoate and benzyl alcohol produced vs reaction time. Reaction over BaO at reaction temperatures: (○) 138.0; (●) 128.0; (△) $118.0 \pm 0.3^\circ\text{C}$.

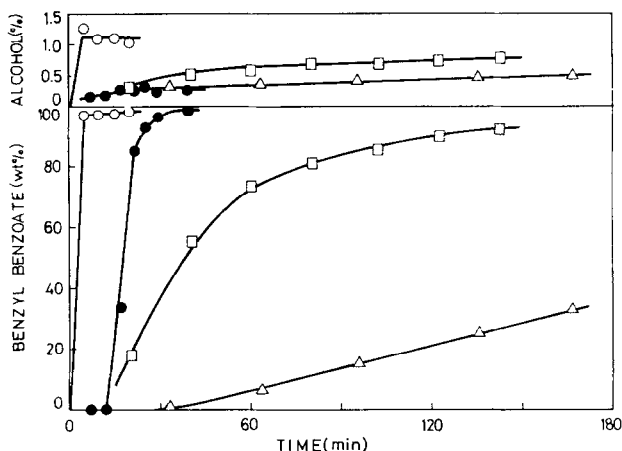


Fig. 2. Weight percent of benzyl benzoate and benzyl alcohol produced vs reaction time. Reaction at $180.0 \pm 0.3^\circ\text{C}$ over: (O) BaO without heat treatment; (●) $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ calcined at 600°C ; (□) $\text{Ca}(\text{OH})_2$ at 700°C ; (Δ) $\text{Mg}(\text{OH})_2$ at 500°C .

at most) being formed simultaneously. Plots of the weight percent of benzyl benzoate against reaction time gave S-type curves including induction periods as shown in Figs. 1 and 2. The amount of formed benzyl alcohol increased gradually as the reaction proceeded. Figures 1 and 2 show the temperature dependence of the reaction and the difference in catalytic activity of alkaline earth metal oxides, respectively. The reaction obeyed the first order rate

equation with respect to the concentration of benzaldehyde after induction period as shown in Fig. 3. The rate constant was taken as catalytic activity.

Catalytic Activity and Basicity

Table 1 shows the basicity and catalytic activity of alkaline earth metal oxides. The activity per unit surface area whose order was $\text{BeO} \ll \text{MgO} < \text{CaO} \ll \text{SrO} \ll \text{BaO}$ at the temperature range from 150 to 200°C increased with the increase of the basicity, though the basicities of SrO and BaO could not be determined because of their small surface areas. Strontium oxide prepared by calcining its nitrate at 800°C showed almost the same activity as that prepared from its hydroxide. A very good correlation was found between the activity and basicity per unit surface area of CaO obtained by calcining $\text{Ca}(\text{OH})_2$ at 300 – 800°C (Fig. 4). CaO obtained by thermal decomposition of CaCO_3 at 900°C showed a high activity, though CaO obtained by calcining $\text{Ca}(\text{OH})_2$ at 900°C showed little activity. The similar results were reported for the isomerization of olefins by Schächter and Pines (10). The activity of Al_2O_3 was very low, only 0.2 wt% of the ester being formed. Solid NaOH, NaOH/SiO₂, BeO, SrO₂ and BaO₂, which changed a colorless phenolphthalein to red, did not show any activity.

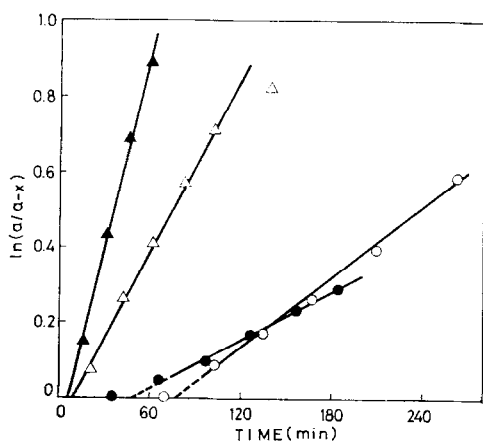


Fig. 3. Plots of first order rate equation. The a is the initial concentration of benzaldehyde and $a - x$ the concentration at given times. Reaction at $180.0 \pm 0.3^\circ\text{C}$ over $\text{Ca}(\text{OH})_2$ calcined at: (▲) 500°C and (Δ) 700°C ; (●) CaO at 600°C ; (○) $\text{Mg}(\text{OH})_2$ at 180°C .

TABLE 1
AMOUNT OF BASE AND CATALYTIC ACTIVITY OF ALKALINE EARTH METAL OXIDES

| Catalysts ^a | Specific surface area (m ² /g) | Amount of base (mmol/g) | Rate constants | |
|------------------------|---|-------------------------|--------------------------------------|--------------------------------------|
| | | | (min ⁻¹ g ⁻¹) | (min ⁻¹ m ⁻²) |
| BeO | — | — | 0 | 0 |
| MgO | 25 ^b | 7.5×10^{-3} | 2.9×10^{-3} | 1.2×10^{-4} |
| CaO | 16.1 | 5.7×10^{-1} | 4.3×10^{-2} | 2.7×10^{-3} |
| SrO | 0.4-0.6 | Basic ^c | 0.24 | 0.4-0.6 |
| BaO | 0.46 | Basic ^c | 0.29 | 0.63 |

^a MgO, CaO and SrO were obtained from their hydroxides by calcination at 400, 500 and 800°C, respectively. Reaction temperature was 180°C for BeO, MgO, CaO and SrO and 120°C for BaO.

^b Cited from Ref. (18).

^c It was impossible to measure the amounts of base because of their small surface areas. But the color of the surface of these catalysts turned pink by adsorption of phenolphthalein.

The Arrhenius plots, where CaO and SrO were used as catalysts, are shown in Fig. 5. The energy of activation was calculated to be 9.4 kcal/mol for CaO and 54 kcal/mol for SrO. The values for MgO and BaO were almost the same as those for CaO and SrO, respectively. Thus, the alkaline earth oxides can be classified into two groups: a group of MgO and CaO which showed low activation energy and another group of SrO and BaO which showed high activation energy.

Effect of Additions on Reaction

The effect of the addition of benzyl benzoate and benzyl alcohol is shown in Fig. 6, where the catalyst immersed in the liquids before the reaction at reaction temperature was contacted with benzaldehyde. Benzyl benzoate showed no effect on the reaction. However, the addition of benzyl alcohol caused the induction period to shorten remarkably, though the reaction rate was not changed. When calcium, strontium and barium benzylates, which were prepared by the reaction of the metals with benzyl al-

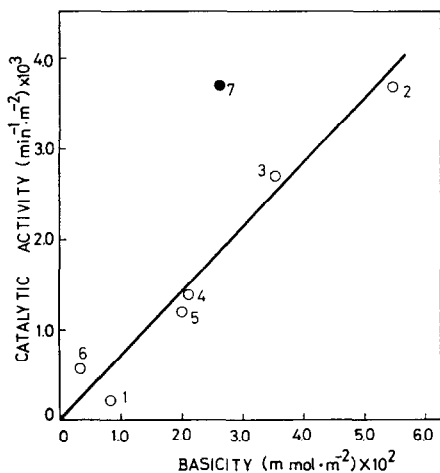


FIG. 4. Basicity and catalytic activity of $\text{Ca}(\text{OH})_2$ calcined at: (1) 300; (2) 400; (3) 500; (4) 600; (5) 700; (6) 800°C and of CaCO_3 decomposed at (7) 900°C.

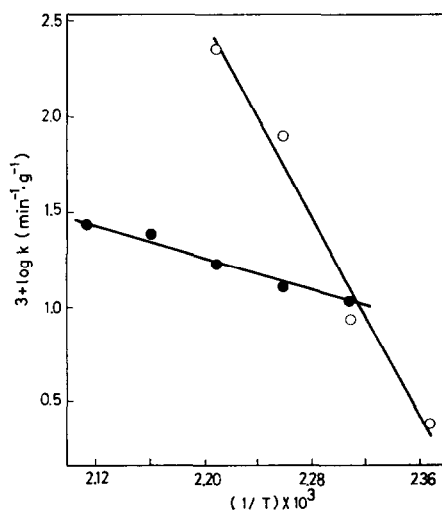


FIG. 5. Arrhenius plots: (●) $\text{Ca}(\text{OH})_2$ calcined at 500°C; (○) $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ at 600°C.

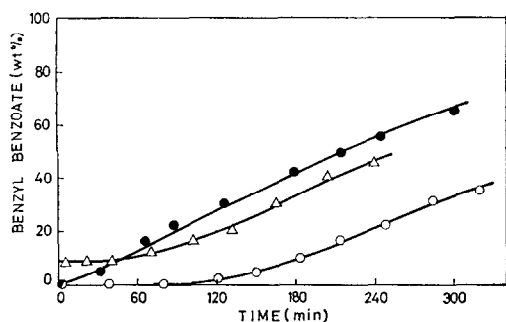


FIG. 6. Effect of addition of benzyl benzoate and benzyl alcohol on induction period. Reaction at $180.0 \pm 0.3^\circ\text{C}$ over CaO calcined at 600°C : (○) without addition; with addition of (△) benzyl benzoate and (●) benzyl alcohol.

cohol, were used as catalysts, the reaction proceeded without any induction period.

The catalytic activity was decreased by the addition of benzoic acid and almost entirely lost by the addition of phenol or pyridine. No effect was observed when aprotic reagents such as benzene and cyclohexane were added.

Isotope Effects

It was observed in the experiment using deuterated benzaldehyde that the two α -hydrogens of benzyl group of benzyl benzoate and benzyl alcohol formed were completely deuterated, all products being benzyl- α,α - d_2 -benzoate and benzyl- α,α - d_2 -alcohol. The first order rate constants, k_H

and k_D , of the reactions of benzaldehyde- α - d_0 and benzaldehyde- α - d_1 were 5.9 ± 0.8 and $5.9 \pm 0.6 \times 10^{-2} \text{ min}^{-1}\text{g}^{-1}$. There was no kinetic isotope effect ($k_H/k_D = 1.0 \pm 0.2$) as shown in Fig. 7. However, the induction period was found to be prolonged when deuterated benzaldehyde was used (Fig. 7).

Infrared Spectra of Adsorbed Benzaldehyde

Figure 8 shows the changes in the spectra of benzaldehyde adsorbed on MgO produced by evacuation at 25 – 400°C . The absorption bands at 1707 , 2747 and 2832 cm^{-1} due to the C=O and C—H stretching vibrations of the aldehyde group and the bands at 1112 , 1276 , 1720 , 2902 and 2958 cm^{-1} due to the O—C—O, C=O and C—H stretching vibrations of benzyl benzoate were observed for the sample on which benzaldehyde was adsorbed at room temperature. On evacuation at 180°C , the bands due to the aldehyde disappeared completely and the intensity of the bands due to the ester decreased, while new bands appeared at 2860 and 2940 cm^{-1} . On evacuation at 250°C , the bands of the ester disappeared completely, but the new bands remained, which almost disappeared by evacuation above 350°C . On the other hand, the bands at 1400 and 1567 cm^{-1} became broad and the intensity increased remarkably as evacuation temperature was raised. The

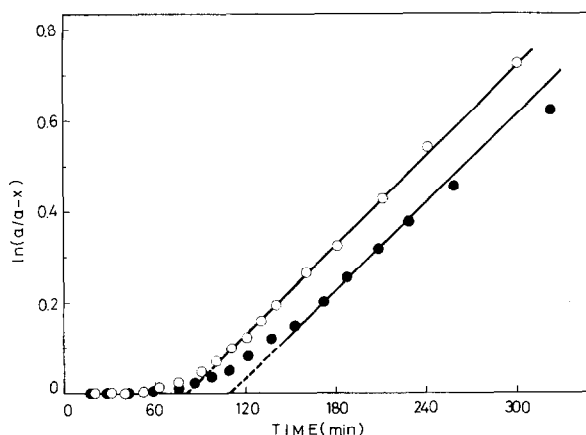


FIG. 7. Plots of first order rate equation. Reaction of: (○) benzaldehyde- α - d_0 ; (●) benzaldehyde- α - d_1 at $17.00 \pm 0.1^\circ\text{C}$.

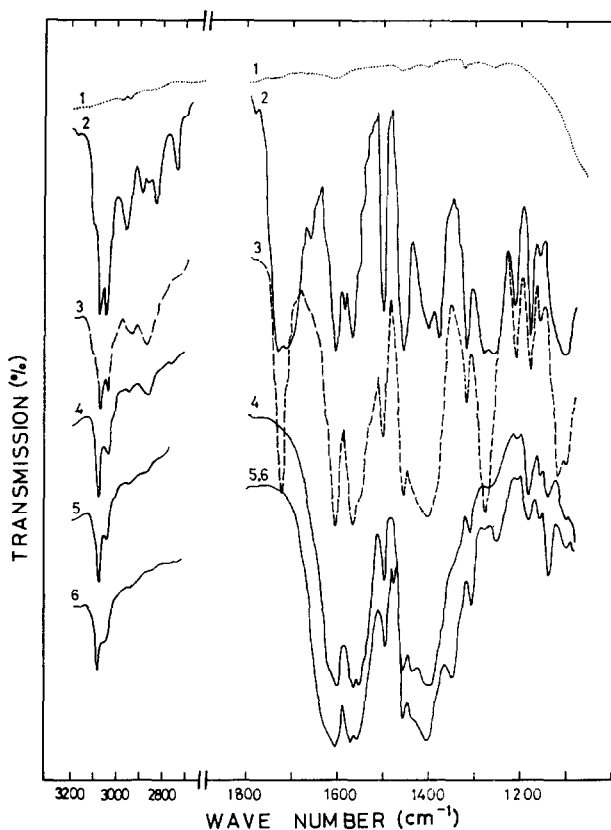


Fig. 8. Change in ir spectra of benzaldehyde adsorbed on MgO: (1) background; (2) adsorbed at room temperature for 11 min; (3) evacuated at 180°C for 35 min; (4) at 250°C for 13 min; (5) at 350°C for 40 min; (6) at 400°C for 20 min.

spectra of deuterated benzaldehyde adsorbed on MgO are shown in Fig. 9. In this case, the absorption bands at 2073 and 2112 cm^{-1} due to the C-D stretching band and the bands at 1115, 1240, 1290, 1720, 2186 and 2247 cm^{-1} due to the deuterated benzyl benzoate were observed for the sample on which deuterated benzaldehyde was adsorbed at room temperature. On evacuation at 150°C, those bands disappeared and new bands appeared at 2062 and 2176 cm^{-1} . The new bands disappeared on evacuation at 350°C. The changes in the spectra in the range of 1000–1800 cm^{-1} were the same as those in Fig. 8.

The spectral changes by desorption of benzaldehyde and deuterated benzaldehyde adsorbed on CaO were the same as those

on MgO, though the spectra were not so clear as for MgO.

DISCUSSION

Active Sites

The correlation of the basicity of MgO and CaO with the catalytic activity and the decrease in activity by the addition of acidic molecules such as benzoic acid and phenol seem to indicate that the active site is mainly basic. It was reported by several workers that the basic site is a surface lattice oxygen, O^{2-} (1-6). However, solid NaOH, NaOH/SiO₂, SrO₂ and BaO₂, which showed only basic property with phenolphthalein, did not show any catalytic activity and the catalytic activity of MgO and

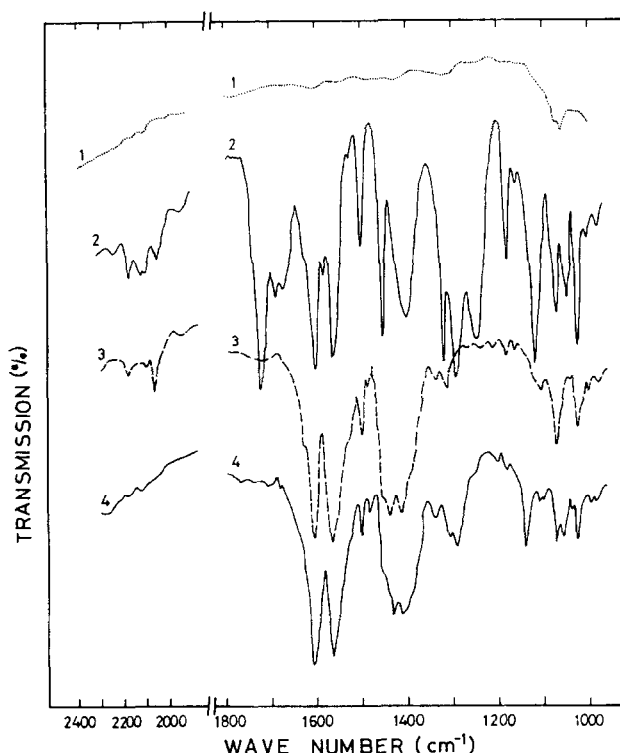


FIG. 9. Change in ir spectra of deuterated benzaldehyde adsorbed on MgO: (1) background; (2) adsorbed at room temperature for 10 min; (3) evacuated at 150°C for 75 min; (4) at 350°C for 30 min.

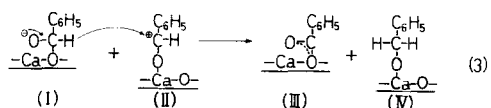
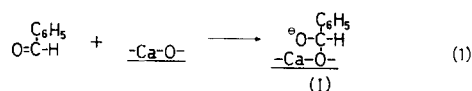
CaO was lost by the addition of pyridine. These results suggest that the Lewis acid site (metal ions of MgO and CaO) is considered to be also important as an active site.

Remarkable shortening or disappearance of the induction period observed when benzyl alcohol was added to MgO, CaO and SrO or when benzylates of Mg, Ca and Sr metals were used as catalysts indicates that the active species for the formation of benzyl benzoate are the metal benzylates, the induction period being the time required for the formation of the benzylates on catalyst surface. The active species are formed by the reaction of benzaldehyde with basic and acidic sites, as described below.

Mechanism of the Formation of Benzylate and Benzyl Alcohol

On the basis of the basic and acidic nature of CaO and the kinetic results, it is in-

ferred that calcium benzylate is formed over CaO according to the following reactions:



Benzaldehyde reacts with a basic site, O^{2-} , of CaO to form an intermediate (I), while it reacts with a Lewis acid site, Ca^{2+} , to form an intermediate (II). Calcium benzoate (III) and benzylate (IV) are formed by the hydride ion transfer from (I)

to (II). A small amount of benzyl alcohol is considered to be formed by a proton transfer from surface hydroxyl group to benzylate (IV). The fact that benzyl- α , α - d_2 -alcohol is formed from benzaldehyde- α - d_1 supports the validity of reactions (1)–(3) and the step of the alcohol formation.

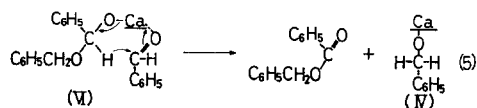
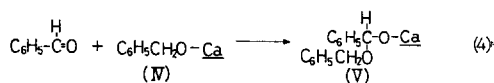
The prolongation of the induction period observed when deuterated benzaldehyde was used instead of benzaldehyde supports that the hydride ion transfer from (I) to (II) is the rate-determining step for the formation of surface benzylate and benzoate.

The existence of the benzylate (IV) and benzoate (III) on MgO and CaO was confirmed by infrared study. The absorption bands at 2860 and 2940 cm^{-1} in Fig. 8 can be assigned to those due to the CH_2 group of the magnesium benzylate formed on the surface, since the bands, which are different from those of free benzyl alcohol, appeared at 2845 and 2950 cm^{-1} when benzyl alcohol was adsorbed on MgO and evacuated at 250°C. In the case of the adsorption of benzaldehyde on Al_2O_3 , Kuiper, Medema and Van Bokhoven (11) attributed the band at 2850 cm^{-1} to aluminum benzylate. On the other hand, the bands at 1400 and 1567 cm^{-1} in Fig. 8 can be assigned to those due to symmetric and asymmetric stretching vibrations of the carbonate group of magnesium benzoate on the surface (12). On evacuation above 250°C, the intensity of these bands increased and that of the bands of surface benzylates decreased, suggesting that the benzylate changes to the benzoate. The bands at 2062 and 2176 cm^{-1} in Fig. 9 are also attributed to the deuterated benzylate formed on MgO.

The very low catalytic activity of Al_2O_3 for the formation of ester is considered to be due to the fact that the benzylate (active species) formed on the surface is easily oxidized (13).

Mechanism of the Formation of Benzyl Benzoate

Since the active species for the formation of benzyl benzoate are metal benzylates which are formed by reactions (1)–(3), the following mechanism seems to be probable:



In the Tishchenko reaction, the hydride ion transfer of step (5) is considered to be rate-determining (14), in accordance with the fact that the reaction is second order with respect to the concentration of benzaldehyde. However, since the reaction was first order in the present reaction system, the rate-determining step should be step (4). Moreover, the possibility that the hydride ion transfer is the rate-determining step is ruled out by the observed isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.0 \pm 0.2$).

The mechanism of the conversion of benzaldehyde into benzyl benzoate over SrO and BaO seems to be different from that over CaO and MgO, since the energy of activation observed for SrO and BaO was much higher than that observed for CaO and MgO.

Comparison with Homogeneous Base-Catalyzed Reaction

The well-known Cannizzaro and Tishchenko reactions in homogeneous phase are second order with respect to the concentration of benzaldehyde. The ratio of the reaction rate of benzaldehyde- α - d_0 (k_{H}) to that of benzaldehyde- α - d_1 (k_{D}) is $k_{\text{H}}/k_{\text{D}} = 1.8 \pm 0.2$ for hydroxyl ion-catalyzed Cannizzaro reaction (8) and $k_{\text{H}}/k_{\text{D}} = 6.8 \pm 0.5$ for metal silver catalyzed Cannizzaro reaction in aqueous sodium hydroxide solution (15). From these results, the rate-determining step of both reactions is considered to be the hydride ion transfer. However, the reaction of benzaldehyde catalyzed by solid base was first order and showed no isotope effect after induction period. The energy of activation for the hydroxyl ion-catalyzed Cannizzaro reaction is 13–14 kcal/mol (16, 17), which is different from those for the heterogeneous reaction in the present work. These results reveal that the mechanism for the forma-

tion of benzyl benzoate is different from those of the Canizzaro and Tishchenko reactions. On the other hand, the isotope effect was found for induction period or for the formation of metal benzylate on the surface. This indicates that the mechanism of the formation of benzylate is very similar to that of the Cannizzaro reaction, as shown in reaction (1)–(3). However, a Lewis acid site as well as a basic site plays an important role as an active site in heterogeneous reaction.

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