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ORIENTATION OF BENZOIC ACID AND TEREPHTHALIC ACID ON AN ALUMINA SURFACE AND THEIR REACTIVITIES OBSERVED BY INFRARED SPECTROSCOPY

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The orientation of benzoic acid and terephthalic acid on alumina was ascertained by IR measurements. Benzoic acid was chemisorbed as a carboxylate anion with a vertical conformation of the benzene ring ($0 < \theta < 1\cdot0$) and as a mixture of the anion and the acid ($1\cdot0 < \theta$). Terephthalic acid was chemisorbed as a mixture of monocarboxylate anion (hydrogenterephthalate) and dicarboxylate anion ($0 < \theta < 0\cdot3$), as the monocarboxylate anion with a vertical conformation of benzene ring ($0\cdot3 < \theta < 1\cdot0$) and a mixture of the monocarboxylate anion and terephthalic acid ($1\cdot0 < \theta$). The carboxyl group of expected hydrogenterephthalate adsorbed through the carboxylate anion on alumina ($\theta = 0\cdot8 : 0\cdot37$ mmol g^{-1} alumina) readily reacted with dimethyl sulphate to form monomethyl terephthalate selectively.

INTRODUCTION

The application of adsorbents such as alumina and silica gel as solid supports in organic synthesis affords a new procedure for selective reactions; they are used deliberately as the reaction medium for substrate orientation with suppression of translational movement. This gives the possibility of highly selective reactions, e.g. ozonolysis of aliphatic esters,[1] terminal chlorination of octanoic acid,[2] enone photocycloaddition,[3] selective synthesis of crown ethers,[4] O-methylation of alcohols,[5] monomethyl esterification of dicarboxylic acids[6,7] and selective preferential monoesterification of the longer carbon chain in a mixture of dicarboxylic acids.[8,9] However, the mechanisms of the selective reactions have not been interpreted satisfactorily so far.

It is known from IR[10–13] and inelastic electron tunnelling spectroscopy (IETS)[14] measurements that carboxylic acids chemisorb on alumina as symmetrical bidentate carboxylate anions, and the remainder of the molecule is remote from the alumina surface under certain conditions. Recently, isomeric phthalic acids on alumina or an aluminium mirror have been measured by IR or IETS, terephthalic acid being adsorbed as a monocarboxylate anion[15,16] or dicarboxylate anion[17] under different preparation conditions. Higo *et al.* has reported the orientation of adsorbed terephthalic acid as a monocarboxylate anion irrespective of whether the sample of the acid was adsorbed on alumina from an ethanolic solution[18] or by evaporation.[19]

We have previously reported the successful monesterification of dicarboxylic acids where the monomethyl esters were obtained quantitatively by use of alumina as a reaction medium.[6–9] The results of the monomethyl esterification implied that discarboxylic acids are chemisorbed on alumina as monocarboxylate anions under certain conditions. However, it is unsatisfactory to interpret the relationship between orientation and reactivity of dicarboxylic acids as giving unambiguous information about adsorption phenomena. The characteristics of a selective reaction are attributed to the state of adsorption of a dicarboxylic acid in an actual reaction system. This explains why the selective monoesterification of dicarboxylic acids occurs on the alumina surface.

This paper reports an investigation of the relationship between the orientations of terephthalic acid and benzoic acid on alumina and the reactivity towards methylating reagents on the basis of IR measurements.

RESULTS AND DISCUSSION

Absorption spectrum of benzoic acid adsorbed on alumina

The IR spectrum of alumina as an adsorbent exhibited a broad absorption at about 3450 cm^{-1} and a weak band at about 1630 cm^{-1} due to stretching and bending vibrations, respectively, of the OH groups of the

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alumina. These OH bands were negligible when the IR absorption of benzoic acid adsorbed on alumina was measured using almost the same amount of alumina at the reference beam side.

The spectrum of the adsorbed sample of benzoic acid ($\theta = 0{\cdot}8$) is illustrated in Figure 1(d). The amount sufficient for surface coverage ($\theta = 1$) was set at $0{\cdot}58\ \mathrm{mmol\,g^{-1}}$ alumina, i.e. the same value as for terephthalic acid.[6] A new band at $1550\ \mathrm{cm^{-1}}$ due to the stretching vibration of the carboxylate anion of sodium benzoate [ν_{as} (COO^-) (as = asymmetric vibration)], indicated by the triangle, appeared with concomitant disappearance of the characteristic band at $1695\ \mathrm{cm^{-1}}$ due to the stretching vibration of C=O of benzoic acid [ν(C=O)]. In contrast, in the spectrum of the excess amount of the acid for surface saturation (Figure 1(e), $\theta = 5{\cdot}0$] the ν(C=O) band appeared accompanying the $\nu_{as}(COO^-)$ band. The characteristic band at $1602\ \mathrm{cm^{-1}}$ of the benzene ring [ν(benzene)] was detected in the spectra of both samples.

These results indicate that benzoic acid was chemisorbed on alumina as the carboxylate anion, and the acid in excess of that required for surface coverage was physisorbed on alumina.

Dependence of surface coverages (θ) on orientation of benzoic acid

Molar amounts of benzoate anion and benzoic acid in the adsorbed sample were evaluated on the basis of the intensities of the IR absorption of the bands at $1550\ \mathrm{cm^{-1}}$ due to $\nu_{as}(COO^-)$ and at $1602\ \mathrm{cm^{-1}}$ due to ν(benzene) followed by the calibration as described under Experimental.

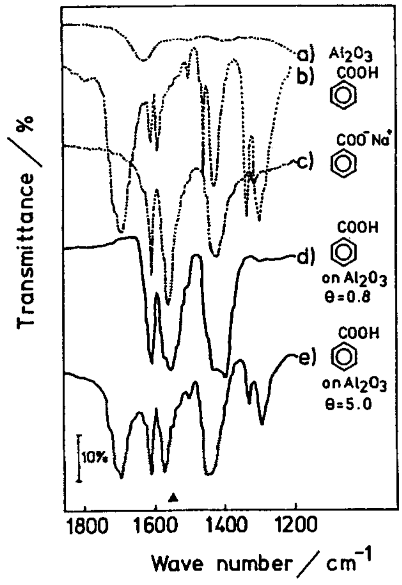

Figure 1. IR spectra of (a) alumina, (b) benzoic acid, (c) sodium benzoate and (d) and (e) benzoic acid adsorbed on alumina

Figure 2 shows the molar ratio of the carboxylate anion to the benzene ring contained in the adsorbed sample vs θ. Until $\theta \approx 1{\cdot}0$, the ratio shows constant value of *ca* 0·95, but at $\theta > 1{\cdot}0$ the ratio decreased drastically. The shape of the pattern of the line is similar to that for calculated values (dotted line) based on the assumption that the acid forms a monomolecular layer as carboxylate anions over the alumina until the $\theta \approx 1{\cdot}0$.

From the results, it is reasonable to conclude that benzoic acid is chemisorbed on alumina as carboxylate anions and that the excess of the acid is adsorbed as acid-holding carboxyl groups for $\theta > 1{\cdot}0$. A schematic representation is shown in Figure 3. The anion probably has a symmetrical bidentate structure with equivalent oxygen atoms with its benzene ring perpendicular to the surface, as reported by Hall and Hansma.[14] This vertical conformation of the benzene ring is also acceptable from consideration of the fairly good agreement of the values of the cross-section of a single molecule over an alumina surface with a micropore structure ($0{\cdot}45\ \mathrm{nm^2}$) and the critical cross-section of an aliphatic carboxylic acid over a flat surface of water ($0{\cdot}205\ \mathrm{nm^2}$),[20] taking into account the difference in the experimental conditions of the surfaces. Generally, the molecules of fatty acids over a flat surface of water are arranged almost vertically, irrespective of their chain

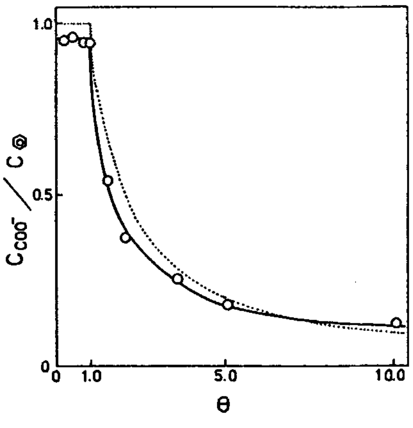

Figure 2. Ratio of concentration of the carboxylate anion to that of the benzene ring contained in the adsorbed sample on the basis of the IR absorption. Solid line: experimental data from the IR absorption by comparison of the band at $1550\ \mathrm{cm^{-1}}$ due to $\nu_{as}(COO^-)$ of the carboxylate anion with that at $1602\ \mathrm{cm^{-1}}$ due to ν(benzene). Dotted line: calculated values based on the assumption that the acid is chemisorbed on alumina forming a monomolecular layer over the alumina as a carboxylate anion in the θ range 0–1·0

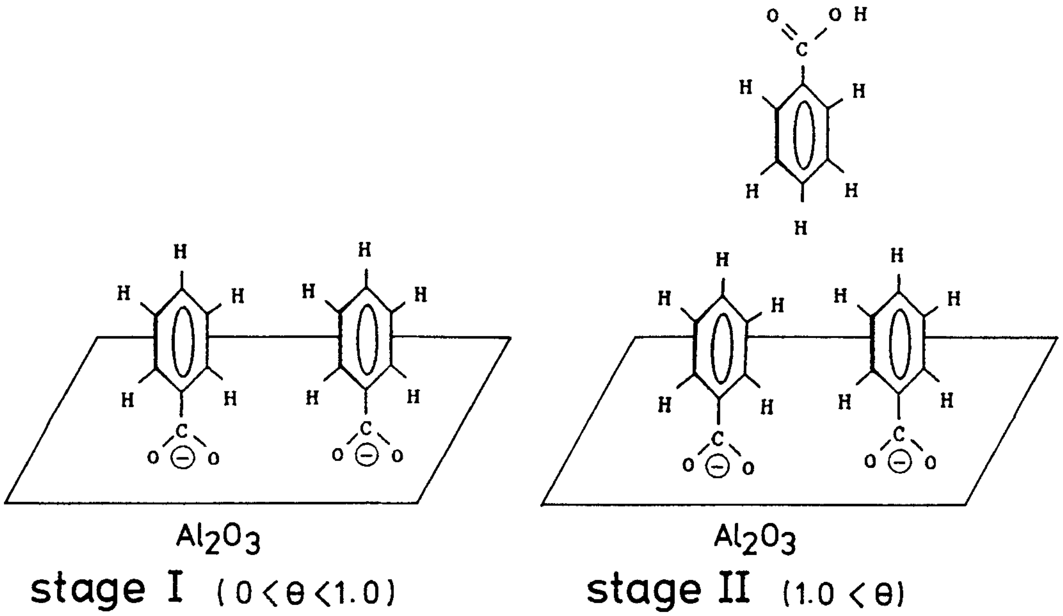

Figure 3. Proposed models for the orientation of benzoic acid on alumina

length. The value of 0·45 nm^2 was found from the amount sufficient for surface coverage (0·58 mmol g^{-1} alumina) and the relative surface area of the alumina (158 m^2 g^{-1}) by BET measurement.

Absorption spectrum of terephthalic acid adsorbed on alumina

The IR absorption of an adsorbed sample of terephthalic acid was measured. A spectrum of the absorption is shown in Figure 4(c). The broad absorption included the new bands, indicated by triangles, due to carboxylate anion [Figure 4(b)], in addition to bands similar to those for terephthalic acid [Figure 4(a)]. The characteristic bands resulting from the carboxylate anion in sodium hydrogenterephthalate [Figure 4(b)] and terephthalic acid [Figure 4(a)] were as follows: the bands at 1560 and 1395 cm^{-1} were due to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, respectively, in sodium hydrogenterephthalate, and the bands at 1685 and 1420 cm^{-1} were due to $\nu(C{=}O)$ and the coupling band of $\nu(C{=}O)$ and the bending vibration of OH, respectively, in terephthalic acid.

The results imply that the hydrogenterephthalate anion is present in the adsorbed sample from consideration of the orientation of benzoic acid. The anion probably has its benzene ring perpendicular to the surface, as suggested previously from selective monomethyl esterification with diazomethane[6] and as Higo *et al.*[18,19] mentioned from IETS measurements.

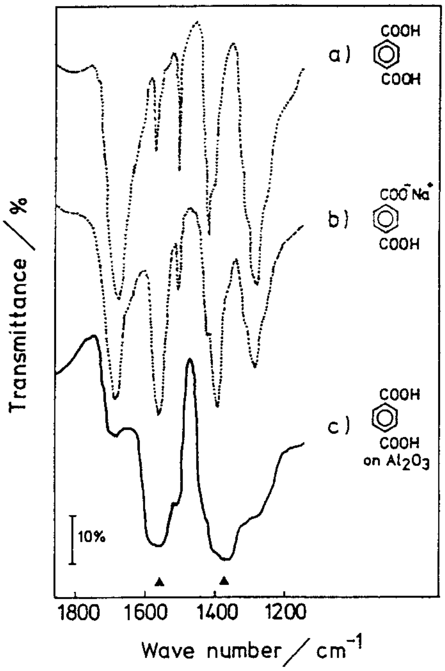

Figure 4. IR spectra of (a) terephthalic acid, (b) sodiu hydrogenterephthalate and (c) terephthalic acid adsorbed o alumina ($\theta = 0{\cdot}8$)

Dependence of θ on orientation of terephthalic acid

Terephthalic acid was present at a concentration of 0·58 mmol g^{-1} alumina, in sufficient amount for surface coverage.[6] Molar amounts of carboxylate anion and carboxyl group in the adsorbed sample of the acid were evaluated on the basis of the intensities of the IR absorption of the bands at 1685 cm^{-1} due to $\nu(C{=}O)$ and at 1560 cm^{-1} due to $\nu_{as}(COO^-)$. There was some interference with the evaluation of the amount of COO^- ion, attributed to overlapping with a weak band at 1570 cm^{-1} due to ν(benzene). Figure 5 shows the molar ratio of the carboxylate anion to the carboxylate anion plus terephthalic acid contained in the adsorbed samples vs θ. The ratio decreased with increase in θ and became constant in the range $0{\cdot}3 < \theta < 1{\cdot}0$, and at $\theta > 1.0$ the ratio decreased drastically. The dotted line in Figure 5 was calculated on the basis of the assumption that the acid was chemisorbed on alumina forming a monomolecular layer over the alumina as monocarboxylate anions in the range $0 < \theta < 1$. The deviation of the solid line from the dotted line is probably due to the excess evaluation of the intensity of the $\nu_{as}(COO^-)$ band due to some overlapping with the relatively broad band at 1685 cm^{-1} of $\nu(C{=}O)$ and due to an overlapping with a weak band at 1570 cm^{-1}due to ν(benzene).

It can be assumed that three adsorption stages for the acid conformation on alumina exist. A schematic representation is shown in Figure 6. In stage I, where θ is $<0{\cdot}3$, the acid was chemisorbed as a mixture of monocarboxylate and dicarboxylate anions. In stage II, where θ is in the range 0·3–1·0, the acid was chemisorbed mainly as monocarboxylate anion. In stage III, where the θ exceeds 1·0, the acid in excess of that required for surface coverage was adsorbed via the remaining two carboxyl groups in the molecule.

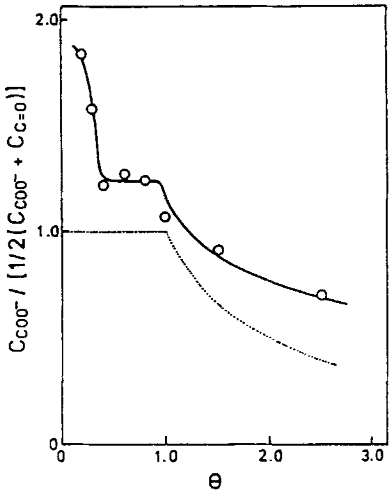

Figure 5. Ratio of concentration of the carboxylate anion to that of the carboxylate anion plus terephthalic acid contained in the adsorbed sample on the basis of the IR absorption. Solid line: experimental data from the IR absorption by comparison of the band at 1560 cm^{-1} due to $\nu_{as}(COO^-)$ of the carboxylate anion and that at 1685 cm^{-1} due to $\nu(C{=}O)$ of the carboxyl group. Dotted line: calculated values based on the assumption that the acid is chemisorbed on alumina forming a monomolecular layer over the alumina as a monocarboxylate anion in the θ range 0–1·0

Higo *et al.*[18,19] studied the orientation of the acid by IETS measurement and reported that the acid was adsorbed as the hydrogenterephthalate anion on alumina. In our study by IR measurement, the orientation of the acid on alumina was attributable to the surface coverage θ. Probably the hydrogenterephthalate reported by Higo *et al.* was detected under empirical conditions in the neighbourhood of surface saturation ($\theta = 1$) of the acid on alumina.

The monocarboxylate anion probably has a symmetrical bidentate structure with equivalent oxygen atoms with its benzene ring perpendicular to the surface, as in the case of the benzoate anion. This vertical conformation is acceptable from consideration of the selective formation of monomethyl terephthalate.[6,7] This might lead to a change in the inherent reactivities of the two carboxyl groups in the acid.

Production of monomethyl terephthalate anion after methylation

The IR spectrum of the reaction mixture of the adsorbed sample of terephthalic acid after monomethyl esterification with dimethyl sulphate was measured. The reaction conditions are detailed under Experimental. The spectrum reflected the monomethyl terephthalate anion produced on alumina, i.e. a broad absorption spectrum [Figure 7(c)] was observed with a similar absorption to that of monomethyl terephthalate adsorbed on alumina [Figure 7(b)]. The spectrum included new bands at 1724, 1430–1450 and 1260–1280 cm^{-1}, indicated by triangles, in addition to the bands due to terephthalic acid adsorbed on alumina accompanying the decrease in the absorption of the band at *ca* 1685 cm^{-1} due to $\nu(C{=}O)$ of a carboxyl group. These new bands are characteristic of a methyl ester due to $\nu(C{=}O)$, asymmetric bending vibration of CH_3 and asymmetric stretching vibration of C—O—C, respectively. These data reveal the formation of the monomethyl terephthalate anion accompanying the decrease in IR absorption of the hydrogenterephthalate anion.

Furthermore, gas–solid (GSC) and high-performance liquid chromatographic (HPLC) analyses of the sample after the methyl esterification showed that monomethyl terephthalate was formed to the extent of about 72% and dimethyl terephthalate about 12%. In the case of

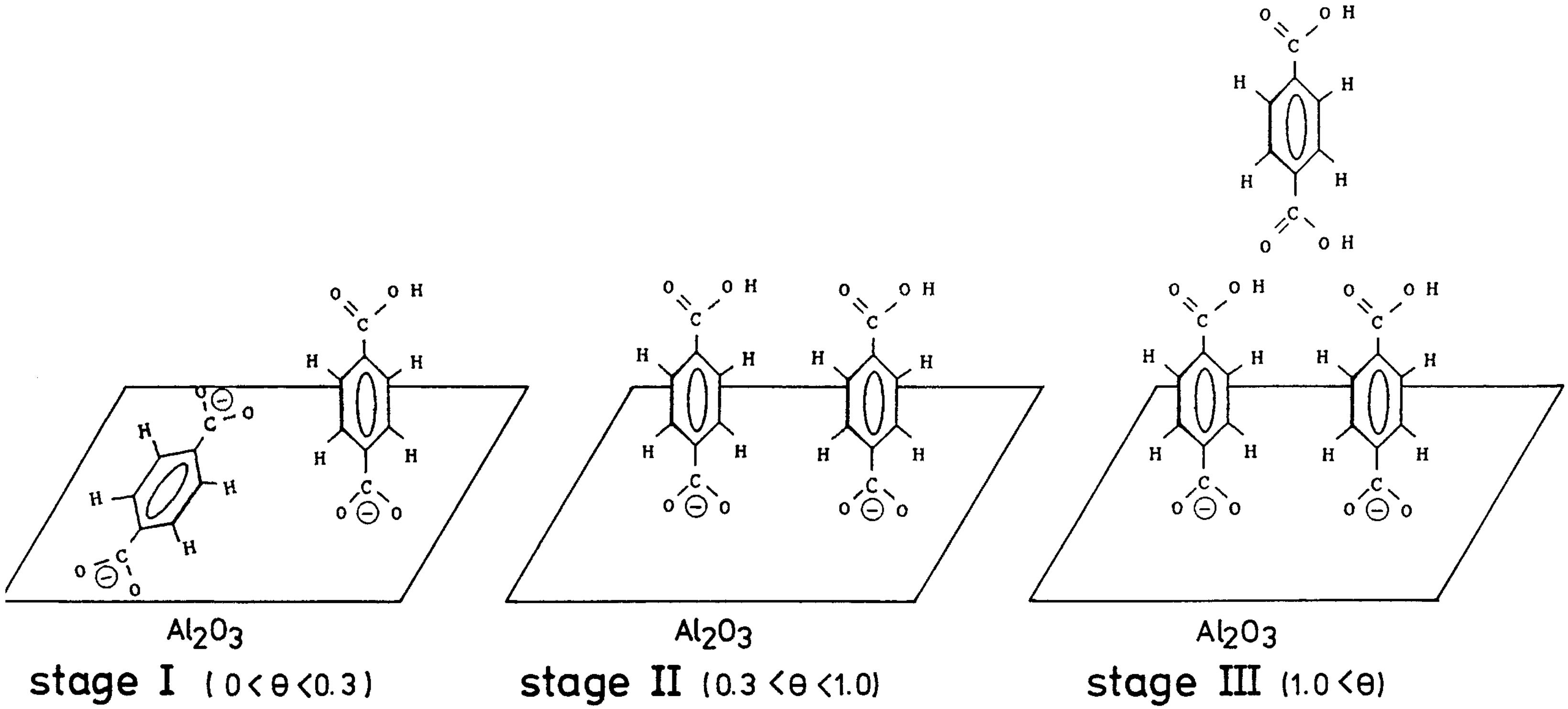

Figure 6. Proposed models for the orientation of terephtahlic acid on alumina

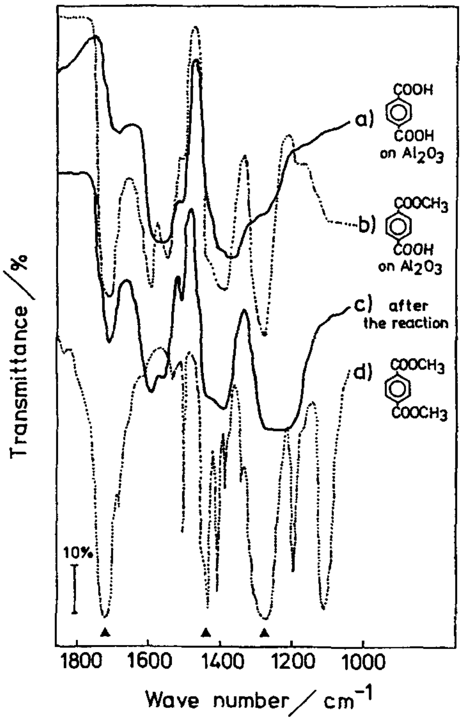

Figure 7. IR spectra of (a) terephthalic acid adsorbed on alumina ($\theta = 0{\cdot}8$), (b) monomethyl terephthalate adsorbed on alumina ($\theta = 0{\cdot}8$), (c) the reaction mixture of the adsorbed sample of (a) after monomethyl esterification with dimethyl sulphate (see Experimental) and (d) dimethyl terephthalate

benzoic acid adsorbed on alumina, methyl benzoate was formed to the extent of about 12%. This means that about 84% of the carboxyl group of hydrogenterephthalate adsorbing on alumina reacts preferentially with dimethyl sulphate.

These results led to the conclusion that terephthalic acid was chemisorbed on alumina as hydrogenterephthalate anion, where its orientation was taken to be perpendicular conformation as shown in the stage II in Figure 6. This vertical conformation leads to changes in the inherent reactivities of two carboxyl groups of terephthalic acid, and then the carboxyl group of the hydrogenterephthalate anion can react preferentially with dimethyl sulphate to form the monomethyl terephthalate anion on alumina.

EXPERIMENTAL

Materials. Alumina reference catalyst of the Catalysis Society of Japan; JRC-ALO-5) of surface area 158 $m^2 g^{-1}$ determined by BET measurement was dried at 110 °C for several days and stored in a desiccator. Cyclohexane was dried by refluxing with calcium hydride and distilled. Sodium hydrogenterephthalate was synthesized from terephthalic acid with 0·5 molar equivalent of metallic sodium. Other materials were commercially available and used as received.

Preparation of adsorbed sample. An adsorbed sample of terephthalic acid was prepared as follows. The alumina powder was added to an ethanolic solution of a certain amount of terephthalic acid. The mixture was allowed to stand for 8 h at 30 °C with occasional shaking. The ethanol was then slowly removed under reduced pressure. The amount of terephthalic acid required for surface saturation (0·58 mmol g^{-1} alumina) was determined previously from the adsorption isotherm.[6] An adsorbed sample of benzoic acid was prepared in the same manner except that dichloroethane was used as the solvent.

Monomethyl esterification of terephthalic acid adsorbed on alumina. About 6·4 ml (5 g) of cyclohexane and 0·5 g of the adsorbed sample were placed in a reaction vessel, 1·5 molar equivalents of dimethyl sulphate were introduced and the reaction was started with vigorous stirring at room temperature for 2 h. The alumina was then filtered off and eluted with ethyl acetate. After the eluate had been concentrated, the product was analysed by GSC with a Chromosorb 101 column and HPLC with a C_{18} column.

The sample after monomethyl esterification for IR measurement was prepared as follows: after the termination of the reaction the alumina was filtered off, then washed with water and dried under reduced pressure in order to remove excess of dimethyl sulphate and derivatives.

IR measurements. The spectra were measured on a JASCO infrared spectrometer. The pressed-disc technique was adopted with dry, powdered potassium bromide. A disc of the alumina sample was prepared by grinding in a smooth agate mortar with a small amount of potassium bromide.

The amounts of carboxylate anion and carboxylic acid contained in the adsorbed sample can be determined from the absorption intensities for each characteristic band. The intensity was converted into molarity by determining the relative ratio of absorption coefficients, ε. With benzoic acid, the ratio of the absorption coefficients of the band at 1550 cm^{-1} due to $\nu_{as}(COO^-)$ to that at 1602 cm^{-1} due to ν(benzene) of sodium benzoate was equal to 1·2. The ratio of the band at 1602 cm^{-1} due to ν(benzene) of benzoic acid to that of sodium benzoate was equal to 0·19. With terephthalic acid, the ratio of the band at 1685 cm^{-1} due to $\nu(C{=}O)$ of the acid to that at 1560 cm^{-1} due to $\nu_{as}(COO^-)$ of sodium hydrogenterephthalate was equal to 0·89.

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