94751-76-5; (±)-**17a**, 94751-77-6; (±)-**17b**, 94751-78-7; (±)-**17c**, 94751-79-8; (±)-**18a**, 81908-03-4; (±)-**18b**, 81908-01-2; (±)-**19a**, 94751-80-1; (±)-**19b**, 94751-81-2; (±)-**20**, 94840-95-6; (±)-**21a**, 94751-82-3; (±)-**21b**, 94751-83-4; (±)-**22**, 94840-96-7; (±)-**23**, 94751-84-5; (±)-**24**, 94751-85-6; (±)-**25**, 94841-61-9; (±)-**26**, 94781-19-8; (±)-**27**, 94781-20-1; (±)-**28**, 94751-86-7; (±)-**29**, 94840-97-8; (±)-**30**, 94751-87-8; (±)-**31**, 94840-98-9; (±)-**32** (2α-Me), 94751-88-9; (±)-**32** (2β-Me), 94841-62-0; (±)-**33** (2α-Me), 94751-89-0; (±)-**33** (2β-Me), 94841-63-1; (±)-**34**, 94781-21-2; (±)-**35**, 94781-22-3; $EtOMgCH(CO_2Et)_2$, 35227-78-2.

Heterogeneous Catalysis of Glucose Mutarotation by Alumina in Dimethyl Sulfoxide. 2. Catalytic Activity of Various Aluminas, Effects of Inhibitors, and the Acid/Base Properties of the Active Sites

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The relative abilities of thermally treated aluminas to heterogeneously catalyze the mutarotaion of α-D-glucose have been studied in dimethyl sulfoxide at 25 °C. Heating of standard alumina to 150 °C, 600 °C, 800 °C, and 1100 °C results in reduced surface areas and catalytic activities. However, heating at 1250 °C produces a most effective, low surface area (6 M^2/g) alumina which, unlike the other aluminas, shows pseudo-first-order kinetics, does not become progressively deactivated, and irreversibly adsorbs little glucose. Kinetic inhibition of mutarotation is shown by added polyhydroxy compounds (e.g., inositol) but not by monohydroxylic (methanol) or aromatic additives. As shown by lack of an effect of added pyridine, and by the increased activity when the stronger base *n*-butylamine is added, the major catalytic sites on standard alumina are Brønsted acids rather than Lewis acids. However, the relative inhibition brought about when alumina is treated with carbon dioxide shows that the high catalytic activity of 1250 °C alumina is predominately due to basic sites produced by the thermal dehydration.

Although there are extensive and detailed kinetic studies of alumina as a catalyst for many reactions in the gas phase, few investigations of the kinetics of alumina-catalyzed reactions in liquid phases have been reported. Reports of the utility of solution reactions catalyzed by alumina,[1] together with interest in determining the general characteristics of some reactions using liquid suspensions of catalytic solids, have prompted this study of heterogenous catalysis by alumina.

For determination of the characteristics of a heterogeneous alumina reaction relative to homogeneous catalysis in solution, a reaction that is well established in a homogeneous liquid phase, i.e., the mutarotation of glucose, was chosen for study in dimethyl sulfoxide (Me_2SO). A first report[2] has presented results showing that there are three types of adsorption sites for glucose on alumina, that the catalytically active site density on a widely available "standard" alumina is 5.4×10^{13} per cm^2, and that these sites have an activity about 9 times greater than that of hydronium ions under homogeneous conditions in water. However, this standard alumina slowly deactivates during the reaction and adsorbs a significant fraction (about 14%) of the glucose substrate.

We report here studies to determine the relative catalytic activities of various thermally treated aluminas and to obtain catalysts with less adsorption but with high activity. The alumina surface possesses many types of Lewis and Brønsted acidic and basic functional groups (e.g., Al^{3+}, $OH^{\delta+}$, $-O^-$, $-O^{\delta-}H$, and "defect sites")[3,4] which are all potential catalysts for glucose mutarotation.[5] By means of inhibitors, we have determined the acid/base characteristics of the active sites, i.e., whether this heterogeneous mutarotation occurs at centers which are Lewis or Brønsted acids/bases.

Results and Discussion

Thermal Treatment of Alumina. On heating a sample of alumina which has water adsorbed on the surface, first, some of the water molecules are desorbed and some react with the surface to form OH groups. As the sample is heated further, acidic and basic hydroxyl groups eliminate to form Lewis base and acid sites respectively.[6] Above 300 °C "defect sites", consisting of clusters of vacancies (Lewis acids) and neighboring oxide ions (Lewis bases) which are catalytically active in most gas-phase reactions, are formed.[3] At greater than 1100 °C, α-alumina, which is normally considered to be catalytically inactive, is formed.[4] The change in activity per unit surface area as the alumina is heated can therefore give information on the nature of the active sites. If only Lewis acid or basic oxide sites are catalytically active, an increase in activity per area will be observed; if only Brønsted acid or basic hydroxyl groups are active, there should be a decrease in activity.

Standard alumina was heated and the weight loss, surface area, and catalytic activity were determined to investigate the effect of thermal dehydration (see Table I). The results show that with standard alumina heated at up to 600 °C the catalytic activity decreases with increase in temperature. The previously reported main characteristics of the heterogeneous catalytic mutarotation,[2] i.e., curved first-order plots due to significant initial adsorption fol-

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Table I. Effects of Dehydration on Catalytic Activity

no.	dehydratn condns	wt loss, %	surface area, M^2/g	rate constant, 10^4 s^{-1} g^{-1}	rate constant per unit area, 10^6 s^{-1} m^{-2}	glucose adsorbed, %
1	none		140	1.9 ± 0.1	1.4	14
2	24 °C, 4 days, 0.01 torr over P_2O_5	2.8	144	1.4 ± 0.2	1.0	14
3	150 ± 5 °C, 0.01 mm, 2 days	5.7	130	0.9 ± 0.1	0.7	14
4	600 ± 50 °C, under dry N_2, 4 h	6.2	116	0.5 ± 0.05	0.43	13
5	800 ± 50 °C, under dry N_2, 4 h	6.2	100	0.7 ± 0.1	0.7	10
6	1100 ± 50 °C, under dry N_2, 3 h	7.2	14	0.54 ± 0.02	3.9	3.5
7	1250 ± 50 °C, under dry N_2, 6 h	7.9	6.2	2.20 ± 0.05	36	3

[a] First-order rate constant obtained using 60 mL of 0.05 M glucose solution with 1.6 g of alumina at 25 °C. Errors were estimated from maximum and minimum slopes.

lowed by progressive deactivation of the catalyst, are retained with aluminas heated at up to 1100 °C. However at 1100 °C or above, where alumina undergoes extensive sintering and changes its crystal structure from the γ to α form, the catalyst shows a completely different behavior. The mutarotation catalyzed with "1250 °C alumina" showed high activity and strictly first-order kinetic plots with no deactivation of catalyst and with relatively little adsorption (3%) of glucose. With alumina heated to 1250 °C there is a great reduction in surface area and yet this catalyst gives an increased first-order rate constant. A considerable increase in specific activity (rate constant per unit area) therefore occurs and, contrary to the absence of activity for α-alumina for most reactions, this 1250 °C α-alumina is the most efficient catalyst for this heterogeneous mutarotation.

The decrease of specific activity with samples of alumina heated to 600 °C indicates that various types of defect sites,[3] produced by the thermal treatment of alumina at greater than 300 °C, cannot be the primary active agents in catalyzed glucose mutarotation in Me_2SO. This loss of specific activity when heated at temperatures below 800 °C, or even below 150° C, suggests that the catalytic sites exhibit Brønsted (rather than Lewis) properties, i.e., the catalytic properties arise from H^+ or OH^- ion activity from groups which are lost from the surface as water when alumina is heated.

The unusually high activity of α-alumina and the observed increase in activity, despite a reduced surface area, for samples heated above 800 °C are probably related to increased basicity (to which glucose mutarotation is very sensitive).[7] Changes in the pH values of aqueous alumina slurrys, before and after heating, show that there is an increase in the basicity of the aluminas when heating to 1250 °C. A development of basic oxide groups by general stripping of water molecules from the alumina can more easily occur above the Tammann temperature of 870 °C where ionic diffusion begins to occur at an appreciable rate.[8] A similar increased mobility of ions, allowing the reaction of initially separate OH groups to form water, is also expected during transition from the γ to the α form of alumina.

Adsorption at Active Sites. To investigate the specificity of adsorption at the catalytic sites, the inhibitory effects of a few organic compounds were studied. The adsorption of glucose on alumina likely occurs by the interaction of the polar hydroxyl groups on glucose with the polar groups (e.g., Al^{3+}, $-O^-$, $-O^{\delta-}H$, $-OH^{\delta+}$) on the surface. Many simple molecules, especially polar ones, would be expected to compete with glucose for adsorption sites. If these sites are also the active sites, on addition of compounds with the appropriate competing groups, the rate of mutarotation of glucose would decrease.

Table II. Effects of Inhibitors on the Catalytic Activity and on the Amount of Glucose Adsorbed[a]

inhib	concn of inhib, M	concn of glucose, M	inhibn, %	decrease in glucose adsorbed, %
benzene	0.05	0.05	0	0
naphthalene	0.05	0.05	0	0
methanol	0.15	0.03	0	0
	0.40	0.03	≃0	0
methyl α-D-glucoside	0.01	0.05	17	
	0.05	0.05	28	
iso-inositol	0.05	0.05	67	60
hexanal	0.01	0.05	17	5
	0.05	0.05	26	14
	0.25	0.05	95	60
DL-glyceraldehyde	0.05	0.05	50	54

[a] Using 1.6 g of alumina with 60 mL of glucose solution (Me_2SO) at 25 °C.

Somewhat surprisingly, water does not inhibit the mutarotation,[2] but, as shown in Table II, some other less polar compounds are effective inhibitors. Simple π-donors such as benzene or naphthalene are not inhibitors, and a monohydroxyl compound (methanol) is also ineffective even in high concentrations. However, the polyhydroxyl compounds, α-methyl glucoside and inositol, do compete well with glucose for both adsorption and active sites. Inositol (a conformational model for the cyclic form of glucose) and glyceraldehyde (a model for the open chain form of glucose) each give an equal decrease in percent of glucose adsorbed and percentage inhibition. Therefore these compounds show no special preference for adsorption on catalytically active, rather than inactive, sites on the surface.

However, the more interesting inhibitor is *n*-hexanal. It is less efficient than inositol or glyceraldehyde on a mole to mole basis, since it has only one polar group. But as shown in Table II, the percentage decrease in activity is higher at all concentrations than the percentage decrease in adsorption. This indicates that hexanal prefers catalytically active sites to other adsorption sites. From these inhibition results it may be concluded that the catalytically

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active sites are fairly specific for adsorption of polyhydroxy compounds and can, in addition, interact with an aldehyde group somewhat better than do other types of adsorption sites on alumina.

Acid/Base Functional Groups at the Active Sites. The acid/base character at the active sites can be investigated by use of more specific inhibitors such as carbon dioxide (which reacts with strongly basic functional groups ($-O^-$ and $-O^{\delta-}H$)) and pyridine (which reacts with Lewis acid sites and relatively strong Brønsted acid sites).[9a,10]

The standard alumina catalyst and the aluminas pyrolyzed to 800 °C and to 1250 °C were each treated with dry carbon dioxide for 24 h. They were then tested for activity toward mutarotation of glucose; these activities were reduced by 10 ± 5%, 27 ± 7%, and 85 ± 5%, respectively, relative to untreated catalysts. This partial inhibition of catalytic activity by CO_2 is likely due to the formation of carbonates (which are much less basic and therefore less active than oxide ions) on the surface. Consistent with this is that the original activity of the 85% deactivated 1250 °C alumina was completely regained simply by a relatively mild thermal treatment that should decompose such carbonates (650 °C for 3 h).

The results of the inhibition by carbon dioxide show that the fraction of activity due to basic sites increases with the greater dehydration that occurs at higher temperatures. This is consistent with suggestions made above concerning thermal dehydration of alumina, i.e., that the high specific activity of 1250 °C alumina results predominantly from basic sites. These are likely to be oxide ions produced by the loss of water from Brønsted acidic ($-OH^{\delta+}$) and Brønsted basic ($-O^{\delta-}H$) sites during the thermal treatment.

Like carbon dioxide, the size of pyridine is small enough so that all sites that are active toward glucose should be sterically accessible to pyridine. However, addition of pyridine would test for Lewis acid and relatively strong Brøsted acid sites at the active sites.[9] Measurement of the catalytic activity of standard alumina in the presence of pyridine in Me_2SO, or even added directly onto the alumina, showed only a negligible (4%) effect on the rate of mutarotation. Therefore strong Lewis acid sites on alumina are not involved in mutarotation of glucose, and any catalytically active Brønsted acid sites are too weak to be influenced by pyridine.

The inhibitory effect of a stronger base, *n*-butylamine, was then investigated.[10,11] When *n*-butylamine was added to a standard kinetic run for mutarotation (see Experimental Section for concentrations), part of the amine was adsorbed on alumina and part remained in solution. Unlike the similar test with pyridine, the *n*-butylamine left in solution caused a simultaneous homogeneous mutarotation. Subtraction of the rate constant for homogeneous catalysis (observed in filtered samples) from the observed first-order rate constant for simultaneous homo- and heterogeneous reaction gave the rate constant for catalysis by the *n*-butylamine treated alumina. This was 44% greater than that with untreated alumina. Like pyridine, *n*-butylamine reacts with Lewis acid sites but in addition can be expected to react with still weaker Brøsted acid sites.[11] This produces a catalytic surface with greater numbers of active basic sites and therefore with increased activity.

As separately indicated by the changes in specific activity when alumina is heated, the experiments with the added pyridine and *n*-butylamine show that the active sites on standard alumina have Brønsted acid activity with little or no Lewis activity. The total number of acid sites (active or not) that react with *n*-butylamine may be determined from the amount of amine added and the amount left in solution. This site concentration is 1.4×10^{-4} mol/g, which for this alumina with 140 M^2/g, corresponds to 5.8×10^{13} sites/cm^2, close to the number of active sites previously independently determined by adsorption and initial rate data (i.e., 5.4×10^{13} sites/cm^2).[2]

Summary of the Characterization of the Active Sites. The catalytic activity and general kinetic features of a standard, widely available alumina have been determined by means of a prototype reaction that is subject to general acid and base catalyst (i.e., mutarotation of glucose). As previously shown,[2] glucose is adsorbed on alumina at three different sites; irreversible noncatalytic sites, reversible noncatalytic sites, and reversible catalytic sites. The catalytically active sites are found to be fairly specific for adsorption of polyhydroxy compounds (and also shown a slight bias toward compounds with an aldehyde group). These sites are catalytic active predominately (90%) because of weak Brønsted (rather than Lewis) acidity.

When alumina is heated there is a reduction in the Brønsted acid sites which shows itself as reduced catalytic activitiy. However, above 800 °C, and inspite of reduced surface area, production of more reactive sites occurs. the inhibitory effects of carbon dioxide show that these active sites are now predominately (90%) basic in character. such changes in acid/base characteristics of thermally treated alumina can be further investigated by means of isotope effects which, together with mechanistic suggestions, will be reported separately.

Experimental Section

The method for kinetic analysis of this heterogeneous mutarotation has been previously described;[2] the standard conditions used here for comparison of catalyst activity were 1.6 g of alumina in 60 mL of 0.05 M glucose (in dimethyl sulfoxide) at 25 °C. The glucose used was reagent-grade α-D-glucose, dried over P_2O_5 at 60 °C for 24 h. The alumina chosen as a "standard" was aluminum oxide neutral (for thin-layer chromatography, without binder) manufactured by Woelm Pharma as distributed by ICN Pharmaceuticals (and others). α-Alumina supplied by Alfa Products showed high activity, and alumina produced by hydrolysis of purified aluminum isopropoxide[12] also showed high activity. Puratronic aluminum oxide (Alfa Products, 99.999%) had very low activity. The reproducibilities of the activities of batches of alumina thermally dehydrated at temperatures up to 1100 °C were very good and the activity remained within 4% after storage for 1 year. Standard alumina heated to 1250 °C showed reproducible activity but the activity decreased on storage over several days; freshly prepared samples were used for comparisons. The high activity of neutral alumina when heated to 1250 °C can be produced by the heating of basic alumina (for thin-layer chromatography, Woelm Pharma) after it has been neutralized by treatment with dilute HCl.[13] Analysis, using inductively coupled argon plasma spectrography, of samples of commercial aluminas did not indicate any correlation of catalytic activity with trace presence of metals (largest trace impurity in standard alumina was calcium, 1050 ppm, with sodium next at 229 ppm). All samples of aluminas showed an increase in the pH of aqueous slurries in distilled water after heating at 1250 °C for 6 h, i.e., type of alumina, initial pH in 10% slurry (pH after heating):

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Woelm neutral, 7.5 (10.1); Woelm acidic, 4.5 (9.2); Woelm basic, 9.8 (10.3).

The crystalline structures of the aluminas (in standard alumina, this was predominately the γ form with a small amount of κ and χ aluminas) were determined by X-ray powder photographs using a Phillips camera and nickel-filtered Cu K_α radiation. After heating at 1250 °C, only lines for alumina were present.[4] Surface areas were determined by the multipoint BET method[14] using a Quanta-Sorb instrument with nitrogen as adsorbate. Standard alumina neutral (as well as 800 °C alumina) showed adsorption and desorption isotherms indicating capillary condensation and hysterisis (type IV);[15] this alumina is porous and most of the pore volume is in pores of radius about 23 Å, while most of the pores have radii between 18 and 27 Å. Alumina heated to 1250 °C showed type II behavior with no capillary condensation nor hysterisis; thus heating to 1250 °C has removed the porous texture of the catalyst. As shown by Electrozone Celloscope, the particle size distributions are little changed by heating; the mean particle diameters are 7.9 μm for standard alumina and 7.4 μm for 1250 °C alumina, with 99% of the diameters between 2.8 and 30 μm.

A sample was first evacuated at room temperature (for 48 h) to remove excess water adsorbed on the surface to test for the effect of CO_2 on standard alumina. Dry CO_2 was passed through a portion of the evacuated sample packed in a glass column for 24 h. The control sample was prepared by passing dry nitrogen through another portion of the evacuated sample for 24 h. The procedure was repeated with aluminas pyrolyzed at 800 °C and at 1250 °C. However, with these samples the controls were not treated with dry nitrogen since they were already free of adsorbed water. The activities were determined by stirring 1.6 g of each sample with 60 mL of 0.05 M glucose.

Tests of possible inhibition by pyridine were carried out by stirring 1.6 g of standard alumina with 10 mL of Me_2SO containing either 0.5 or 3.0 mmol of pyridine (or by direct addition of 3 mmol of pyridine to the alumina) before adding a solution of 0.54 g of glucose in 50 mL of Me_2SO. Tests of the effects of *n*-butylamine were carried out with 1.6 g of standard alumina in 10 mL of Me_2SO containing 0.03 mL (3×10^{-4} mol) of *n*-butylamine. After 150 min, 50 mL of Me_2SO containing 0.54 g of glucose was added and the kinetics followed. The overall (homo- and heterogeneous) rate constant at 25 min was 3.8×10^{-4} s^{-1}. Filtered samples from the reaction gave a rate constant for homogeneous catalysis by the *n*-butylamine remaining in solution of 0.28×10^{-4} s^{-1}; therefore, the rate constant for heterogenous catalysis is 3.5×10^{-4} s^{-1}. (Under similar conditions, but in the absence of any additive, 1.6 g of alumina showed a rate constant of 2.5×10^{-4} s^{-1}). From a separate measurement of the second-order rate constant for homogeneous catalysis by *n*-butylamine in Me_2SO, the amount of amine remaining in solution (0.8×10^{-4} mol) could be determined and the amount adsorbed on the alumina (2.2×10^{-4} mol) calculated. This corresponds to 1.4×10^{-4} mol of acid sites per gram of catalyst.

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Registry No. Me_2SO, 67-68-5; α-D-glucose, 26655-34-5; alumina, 1344-28-1.

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Bichromophoric Compounds. Photophysics and Photochemistry of (1-Naphthyl)alkyl Esters of Fumaric, Maleic, and Oxalic Acids

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Fumarate, maleate, and oxalate groups quench the excited singlet state of naphthalene. When the naphthalene chromophore is combined in the same molecule with one of these quenching groups, its fluorescence quantum yield is reduced to about 1% of that of the corresponding (1-naphthyl)alkyl acetate as a result of efficient electron transfer to the diester. No exciplex emission is observed from the bichromophoric compounds. Although the rate of quenching is only weakly dependent on the number of atoms linking the two groups, ground-state charge-transfer interactions between the two groups were observed only in the di-1-naphthyl esters and were absent when the groups were separated by longer chains. (1-Naphthyl)alkyl fumarates and maleates undergo photochemical cis-trans isomerization with quantum yields on the order of 0.04. This photoisomerization was shown to proceed via the electron-transfer pathway and not by direct triplet energy transfer from the naphthalene chromophore to the unsaturated diester. The 1-naphthylmethyl esters yield 1-naphthaldehyde with quantum yields of 0.001. Free-radical chain addition to the fumarate double bond occurs on prolonged irradiation in solvents containing abstractable H, particularly in the presence of acetophenone or radical sources such as *tert*-butyl hydroperoxide. Even in thoroughly degassed benzene oligomerization of the fumarate group leads to partial loss of the double bond at long irradiation times.

Bichromophoric compounds are currently the subject of considerable attention because excited-state interactions between the two functional groups frequently result in unexpected photophysics and photochemistry.[1] A number of processes can lead to perturbation of the excited-state behavior of a chromophore by a functional group separated by a considerable number of σ-bonds. These effects include singlet and triplet electronic energy transfer,[2] exciplex formation,[3] electron transfer,[4] and the formation of

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