

## Dehydration of Alcohols Catalysed by Metallic Sulphates Supported on Silica Gel

Takeshi Nishiguchi\* and Chizuko Kamio

Department of Chemistry, Faculty of Liberal Arts, Yamaguchi University, Yamaguchi 753, Japan

Many metallic sulphates and hydrogen sulphates supported on silica gel efficiently catalyse dehydration of secondary and tertiary alcohols under mild conditions. The sulphates of  $\text{Ce}^{\text{IV}}$ ,  $\text{Ti}^{\text{IV}}$ , and  $\text{Fe}^{\text{III}}$  were most active. Silica gel was essential for the efficient dehydration in each case. The dehydration catalysed by  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{CuSO}_4$ , and  $\text{NaHSO}_4$  on silica gel was studied in detail. The order of the reactivity of alcohols was tertiary > secondary > primary. The dehydration activity of methanesulphonic acid was also enhanced (*ca.* 14 times at 90 °C) by the presence of silica gel. Some mechanistic investigations were carried out.

The use of reagents or reactants on insoluble inorganic supports for the dehydration of alcohols is increasingly popular.<sup>1</sup> Such heterogeneous reactions compared with their homogeneous counterparts, often have the advantage of ease of set-up and work-up, mild reaction conditions, increased yields, and greater selectivity.<sup>2</sup> We have already reported in preliminary form results for the dehydration of alcohols catalysed by  $\text{CuSO}_4$  supported on silica gel (abbreviation;  $\text{CuSO}_4\text{-SiO}_2$ ).<sup>3</sup> Here we describe the corresponding results for other metallic sulphates and hydrogen sulphates.

### Results and Discussion

Since  $\text{FeCl}_3$  supported on silica gel is reported to catalyse the transformation of cholesterol to a chlorinated compound and an ether with evolution of hydrogen chloride on heating,<sup>4</sup> we chose to work with metallic sulphates because of their thermal stability<sup>5</sup> and the low nucleophilicity of the sulphate ion.

The catalysts were prepared by mixing sulphate solutions with chromatographic silica gel and evaporating the water under reduced pressure with heating. There seems to be an optimal temperature for drying the catalysts,  $\text{CuSO}_4\text{-SiO}_2$  dried at 240 °C for 1 h, or at 200 °C for 3 h, being the most active and that dried at 300 °C the least: most were dried at 240 °C for 1 h. Catalysts containing less thermally stable sulphates and hydrogen sulphates, were dried under milder conditions. (See Experimental section). The importance of the amount of water in supported reagents has been mentioned in several reports.<sup>6</sup>

The dehydrations were straightforward and after completion, the olefins, isolated from the catalyst by filtration, were generally obtained pure. Increased yields of product were obtained by washing the catalysts with a polar solvent (acetone): small quantities of alcohols were also recovered.

**Catalytic Activity.**—The catalytic activity of sulphates and hydrogen sulphates (assumed to be thermally stable at the reaction temperatures) was examined in the case of cyclododecanol. The results are summarized in Table 1. The catalytic activity of the supported sulphates, decreased in the following order:  $\text{Fe}^{\text{III}} = \text{Ce}^{\text{IV}} = \text{Ti}^{\text{IV}} > \text{Sn}^{\text{IV}} > \text{Al}^{\text{III}} > \text{Cu}^{\text{II}} > \text{Zn}^{\text{II}} > \text{Co}^{\text{III}} > \text{Ni}^{\text{II}} > \text{Fe}^{\text{II}} > \text{Mn}^{\text{II}} > \text{Cd}^{\text{II}}$ . Sulphates of  $\text{Mg}^{\text{II}}$ , Li, Na, and K were inactive in refluxing tetrachloroethylene. This suggests that the greater the Lewis acidity of a sulphate, the greater its catalytic activity on silica gel. Hydrogen sulphate salts of Na, K, and  $\text{NH}_4$  on silica gel were more active than  $\text{Al}_2(\text{SO}_4)_3\text{-SiO}_2$  but less than  $\text{Ti}(\text{SO}_4)_2\text{-SiO}_2$ . The proton liberated from the hydrogen sulphates presumably contributes

Table 1. Dehydration of cyclododecanol catalysed by sulphates and hydrogen sulphates<sup>a</sup>

Catalyst	Solvent	Time (min)	Yield and recovery (%)	
			Cyclo-dodecene	Cyclo-dodecanol
$\text{Fe}_2(\text{SO}_4)_3\text{-SiO}_2$	Hexane	60	99	0
	$\text{CH}_2\text{Cl}_2$	60	17	70
$\text{Fe}_2(\text{SO}_4)_3$	$\text{CCl}_4$	60	99	0
	Hexane	60	41	48
$\text{Ce}(\text{SO}_4)_2\text{-SiO}_2$	Hexane	60	98	0
	$\text{CH}_2\text{Cl}_2$	60	19	68
$\text{Ce}(\text{SO}_4)_2$	$\text{CCl}_4$	60	34	59
	$\text{Ti}(\text{SO}_4)_2\text{-SiO}_2$	$\text{CCl}_4$	60	99
$\text{Ti}(\text{SO}_4)_2$	Hexane	60	91	<1
	$\text{CH}_2\text{Cl}_2$	60	23	65
	$\text{CCl}_4$	60	15	70
$\text{NaHSO}_4\text{-SiO}_2$	$\text{CCl}_4$	60	99	0
	Hexane	60	47	44
$\text{NaHSO}_4$	$\text{C}_2\text{Cl}_4$	60	5	90
	$\text{SnSO}_4\text{-SiO}_2$	$\text{C}_2\text{Cl}_4$	15	99
$\text{CCl}_4$		60	58	29
$\text{SnSO}_4$	$\text{C}_2\text{Cl}_4$	60	3	88
	$\text{NH}_4\text{HSO}_4\text{-SiO}_2$	$\text{C}_2\text{Cl}_4$	15	99
$\text{CCl}_4$		60	44	51
$\text{NH}_4\text{HSO}_4$	$\text{C}_2\text{Cl}_4$	60	3	94
	$\text{KHSO}_4\text{-SiO}_2$	$\text{C}_2\text{Cl}_4$	15	99
$\text{CCl}_4$		60	43	38
$\text{KHSO}_4$	$\text{C}_2\text{Cl}_4$	60	<1	92
	$\text{Al}_2(\text{SO}_4)_3\text{-SiO}_2$	$\text{C}_2\text{Cl}_4$	15	99
$\text{CCl}_4$		60	31	56
$\text{Al}_2(\text{SO}_4)_3$	$\text{C}_2\text{Cl}_4$	60	<1	97
	$\text{CuSO}_4\text{-SiO}_2$	$\text{C}_2\text{Cl}_4$	60	98
$\text{CCl}_4$		60	4	86
$\text{CuSO}_4$	$\text{C}_2\text{Cl}_4$	60	8	91
	$\text{ZnSO}_4\text{-SiO}_2$	$\text{C}_2\text{Cl}_4$	60	91
$\text{CCl}_4$		60	1	78
$\text{CoSO}_4\text{-SiO}_2$	$\text{C}_2\text{Cl}_4$	60	86	13
	$\text{NiSO}_4\text{-SiO}_2$	$\text{C}_2\text{Cl}_4$	60	47
$\text{FeSO}_4\text{-SiO}_2$	$\text{C}_2\text{Cl}_4$	60	38	48
	$\text{MnSO}_4\text{-SiO}_2$	$\text{C}_2\text{Cl}_4$	60	11
$\text{CdSO}_4\text{-SiO}_2$		$\text{C}_2\text{Cl}_4$	60	6

<sup>a</sup> Cyclododecanol (1 mmol) and a salt (1 mmol), which was in some cases supported (3 mmol  $\text{g}^{-1}$   $\text{SiO}_2$ ), were heated in a refluxing solvent (10 ml).

to the high activity of the salts because  $\text{Na}_2\text{SO}_4\text{-SiO}_2$  and  $\text{K}_2\text{SO}_4\text{-SiO}_2$  were inactive. The activity of sulphates which had been dried and powdered but not supported on silica gel was also examined. The results showed that silica gel is essential for efficient dehydration of the alcohols (Table 1).

Various kinds of solid adsorbents were tested in the reaction of  $\text{CuSO}_4$  (Table 2). Silica gel BW-300 (Fuji-Davidson, 230–400 mesh) was the most effective, and silica gel 60 (Merck, 70–230 mesh), silica gel 60 (Merck, 230–400 mesh), and silica gel H (Merck, for t.l.c.) less so. Alumina, Celite-545, powdered molecular sieves 3A, and active carbon were ineffective. Unless

otherwise noted, silica gel BW-300 was used throughout this study.

Reagent activity was weakened by absorption of moisture from the air but was restored by drying. Such reagents could be stored for long periods without any appreciable loss of the activity when protected from moisture.

*Dehydration of Various Alcohols.*—Dehydration of several alcohols was studied using the following three reagents:  $\text{Fe}_2(\text{SO}_4)_3\text{-SiO}_2$ , one of the most active catalysts but causing vigorous side reactions in some cases (see later),  $\text{CuSO}_4\text{-SiO}_2$ , moderately active but less prone to cause side reactions than  $\text{Fe}_2(\text{SO}_4)_3\text{-SiO}_2$ , and  $\text{NaHSO}_4\text{-SiO}_2$ , thermally more stable than  $\text{KHSO}_4\text{-SiO}_2$  and  $\text{NH}_4\text{SO}_4\text{-SiO}_2$ <sup>5</sup> but is still subject to proton loss. The results are summarized in Table 3. Although most simple secondary and tertiary alcohols gave olefins in high yields with each catalyst, 1-phenylethanol was an exception probably because of the tendency for styrene to polymerize. Furthermore, although in the reaction catalysed by  $\text{Fe}_2(\text{SO}_4)_3\text{-SiO}_2$  cholestanol and cholesterol yielded exclusively rearranged products whose structures remain ill-characterized,<sup>4</sup> they gave the expected  $\Delta^2$ -ene and  $\Delta^{3,5}$ -diene respectively with  $\text{CuSO}_4\text{-SiO}_2$  and  $\text{NaHSO}_4\text{-SiO}_2$  (Table 3). Aromatic alcohols such as 1-

**Table 2.** Dependence of catalytic activity on solid support<sup>a</sup>

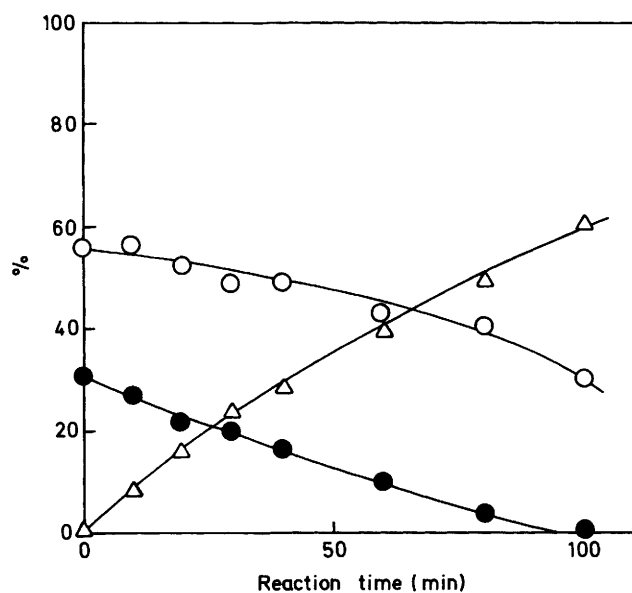
Supporting solid	Yield of cyclododecene (%)
Silica gel WB-300 (Fuji-Davidson, 230–400 mesh)	63
Silica gel 60 (Merck, 70–230 mesh)	48
Silica gel 60 (Merck, 230–400 mesh)	47
Silica gel H (Merck, for t.l.c.)	41
Alumina (ICN, N-Super 1)	1
Active carbon (powder)	<1
Celite-535	0
Molecular sieves 3A (powder)	0

<sup>a</sup> Cyclododecanol (1 mmol) and  $\text{CuSO}_4$  (1 mmol) supported on a solid (0.33 g) were heated in refluxing tetrachloroethylene (10 ml) for 15 min.

**Table 3.** Dehydration of alcohols catalysed by  $\text{CuSO}_4$ -,  $\text{Fe}_2(\text{SO}_4)_3$ -, and  $\text{NaHSO}_4\text{-SiO}_2$ <sup>a</sup>

Alcohol	Metal salt	Solvent	Time (min)	Product	Yield (%)
Cyclo-octanol	$\text{CuSO}_4$	$\text{CCl}_4$	60	Cyclo-octene	92
	$\text{Fe}_2(\text{SO}_4)_3$	$\text{CH}_2\text{Cl}_2$	30	Cyclo-octene	87
	$\text{NaHSO}_4$	Hexane	20	Cyclo-octene	98
Cyclododecanol	$\text{CuSO}_4$	$\text{C}_2\text{Cl}_4$	25	Cyclododecene	98
	$\text{CuSO}_4$	$\text{C}_2\text{Cl}_4$	60 <sup>b</sup>	Cyclododecene	20
	$\text{CuSO}_4$	Iso-octane	60 <sup>b</sup>	Cyclododecene	24
	$\text{CuSO}_4$	Toluene	60 <sup>b</sup>	Cyclododecene	14
	$\text{CuSO}_4$	PhCl	60 <sup>b</sup>	Cyclododecene	10
	$\text{CuSO}_4$	Anisole	60 <sup>b</sup>	Cyclododecene	5
	$\text{Fe}_2(\text{SO}_4)_3$	$\text{C}_2\text{Cl}_4$	10	Cyclododecene	96
	$\text{NaHSO}_4$	$\text{C}_2\text{Cl}_4$	50	Cyclododecene	95
	$\text{CuSO}_4$	$\text{C}_2\text{Cl}_4$	50	4-t-Butylcyclohexene	98
4-t-Butylcyclohexanol <sup>c</sup>	$\text{Fe}_2(\text{SO}_4)_3$	Hexane	15	4-t-Butylcyclohexene	94
	$\text{NaHSO}_4$	Hexane	200	4-t-Butylcyclohexene	97
	$\text{CuSO}_4$	$\text{C}_2\text{Cl}_4$	30	Non-4-ene	99
Nonan-5-ol	$\text{Fe}_2(\text{SO}_4)_3$	$\text{CCl}_4$	30 <sup>d</sup>	Non-4-ene	95
	$\text{NaHSO}_4$	$\text{CCl}_4$	60	Non-4-ene	96
	$\text{CuSO}_4$	Hexane	20	Styrene	49
1-Phenylethanol	$\text{Fe}_2(\text{SO}_4)_3$	$\text{CH}_2\text{Cl}_2$	5	Styrene	0 <sup>f</sup>
	$\text{NaHSO}_4$	Hexane	10	Styrene	64
	$\text{CuSO}_4$	Hexane	20	1-Phenylpropene	75 (93/7) <sup>e</sup>
1-Phenylpropan-1-ol	$\text{Fe}_2(\text{SO}_4)_3$	$\text{CH}_2\text{Cl}_2$	15	1-phenylpropene	18 <sup>f</sup> (94/6) <sup>e</sup>
	$\text{NaHSO}_4$	Hexane	5	1-Phenylpropene	86 (95/5) <sup>e</sup>
	$\text{CuSO}_4$	$\text{C}_2\text{Cl}_4$	240	1-Phenylpropene	71 (83/17) <sup>e</sup>
1-Phenylpropan-2-ol	$\text{CuSO}_4$	$\text{C}_2\text{Cl}_4$	240	3-Phenylpropene	15
	$\text{Fe}_2(\text{SO}_4)_3$	Hexane	40	1-Phenylpropene	37 (81/19) <sup>e</sup>
	$\text{Fe}_2(\text{SO}_4)_3$	Hexane	40	3-Phenylpropene	4
	$\text{NaHSO}_4$	$\text{C}_2\text{Cl}_4$	40	1-Phenylpropene	72 (86/14) <sup>e</sup>
	$\text{NaHSO}_4$	$\text{C}_2\text{Cl}_4$	40	3-Phenylpropene	15
	$\text{CuSO}_4$	$\text{C}_2\text{Cl}_4$	40	2,3-Didehydrocholestanol	88 <sup>g</sup>
Cholestanol	$\text{Fe}_2(\text{SO}_4)_3$	Hexane	30	2,3-Didehydrocholestanol	0 <sup>f</sup>
	$\text{NaHSO}_4$	$\text{C}_2\text{Cl}_4$	40	2,3-Didehydrocholestanol	50
	$\text{CuSO}_4$	$\text{C}_2\text{Cl}_4$	20	3,4-Didehydrocholesterol	95 <sup>g</sup>
Cholesterol	$\text{Fe}_2(\text{SO}_4)_3$	$\text{CH}_2\text{Cl}_2$	30	3,4-Didehydrocholesterol	20 <sup>f</sup>
	$\text{NaHSO}_4$	$\text{C}_2\text{Cl}_4$	10	3,4-Didehydrocholesterol	36
	$\text{CuSO}_4$	$\text{CH}_2\text{Cl}_2$	10	1-Methylcyclododecene	51
1-Methylcyclododecanol	$\text{CuSO}_4$	$\text{CH}_2\text{Cl}_2$	10	Methylenecyclododecane	47
	$\text{Fe}_2(\text{SO}_4)_3$	$\text{CH}_2\text{Cl}_2$	10	1-Methylcyclododecene	42
	$\text{Fe}_2(\text{SO}_4)_3$	$\text{CH}_2\text{Cl}_2$	10	Methylenecyclododecane	54
	$\text{NaHSO}_4$	$\text{CH}_2\text{Cl}_2$	10	1-Methylcyclododecene	40
	$\text{NaHSO}_4$	$\text{CH}_2\text{Cl}_2$	10	Methylenecyclododecane	58
	$\text{NaHSO}_4$	$\text{CH}_2\text{Cl}_2$	10	Methylenecyclododecane	58

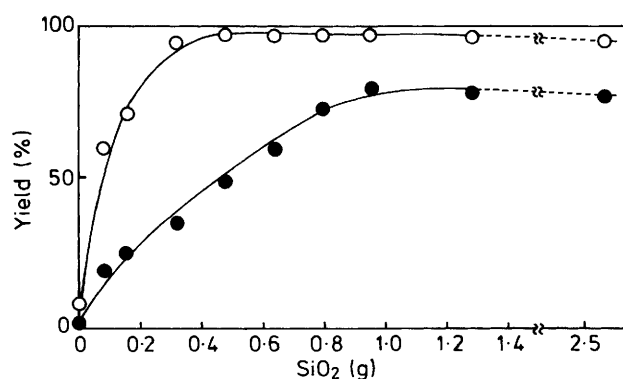
<sup>a</sup> An alcohol (1 mmol) and a catalyst (1 mmol; 1 mmol  $\text{g}^{-1}$   $\text{SiO}_2$ ) were heated in a refluxing solvent (10 ml). <sup>b</sup> This reaction was performed at 100 °C. <sup>c</sup> *cis* and *trans* Mixture (64:36). <sup>d</sup> This reaction was carried out at 70 °C. <sup>e</sup> *E/Z* Ratio. <sup>f</sup> Extensive side reactions occurred. <sup>g</sup> See ref. 3.



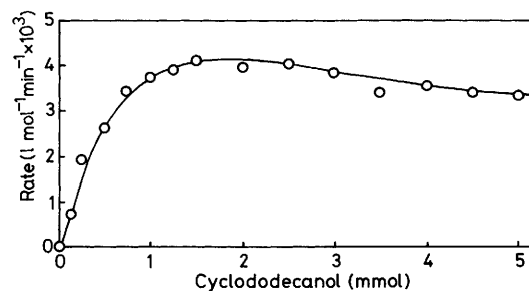
**Figure 1.** Dehydration of 4-t-butylcyclohexanol catalysed by  $\text{NaHSO}_4\text{-SiO}_2$ : 4-t-butylcyclohexene ( $\Delta$ ); the *cis* alcohol ( $\circ$ ); the *trans* alcohol ( $\bullet$ ). The alcohols (1 mmol) and the catalyst (1 mmol;  $3 \text{ mmol g}^{-1}\text{-SiO}_2$ ) were heated in refluxing hexane (10 ml)

phenylethanol, and 1-phenylpropan-1-ol, and tertiary alcohol 1-methylcyclododecanol reacted at lower temperatures in less time than aliphatic secondary alcohols. Primary alcohols such as dodecan-1-ol and hexan-1-ol failed to react in the presence of  $\text{CuSO}_4$  and  $\text{NaHSO}_4\text{-SiO}_2$ , while they gave complex mixtures containing little of the expected olefins with  $\text{Fe}_2(\text{SO}_4)_3\text{-SiO}_2$ . This order of reactivity suggests that the key step is formation of cationic intermediates.

It has been reported that in *cis*- and *trans*-4-t-butylcyclohexanol the hydroxy group is fixed exclusively at axial and equatorial positions, respectively and that *cis*-4-t-butylcyclohexyl toluene-*p*-sulphonate undergoes *E2* elimination more rapidly than the *trans* isomer by a factor of  $>100$ .<sup>7</sup> In our work, in the dehydration of a *cis/trans* mixture of 4-t-butylcyclohexanol (64:36), the ratio of the reaction rates for the *trans*:*cis* isomers was 1.7:1 with  $\text{CuSO}_4\text{-SiO}_2$  in tetrachloroethylene, 1.5 for  $\text{Fe}_2(\text{SO}_4)_3\text{-SiO}_2$  in dichloromethane, and 1.6 for  $\text{NaHSO}_4\text{-SiO}_2$  in hexane. The yield *vs.* reaction time curves of the last reaction are shown in Figure 1 as an example of the three reactions and indicate that half the *cis* isomer was recovered after 100 min with no *trans* isomer. The wide linear dependence of the yield of 4-t-butylcyclohexene on reaction time may be due to the zero order dependence of reaction rates on alcohol concentrations, as described later. This method may have value as a way of separating the *cis*-alcohol from a *cis*- and *trans*-mixture. The fact that the ratio of the rates was changed little by the various catalysts suggests that there is a common dehydration mechanism not of the *E2* type.<sup>7</sup> *cis*-4-t-Butylcyclohexanol has been reported to be dehydrated faster than the *trans* alcohol by a factor of 3.5 in hot sulphuric acid.<sup>8</sup> Such a ratio is closely similar to that reported for the solvolysis of the toluene-*p*-sulphonates of these isomeric alcohols.<sup>6</sup> This discrepancy between our results and the reported ones in the relative reaction rates of the isomers may be explained by the following assumptions (i) that steric hindrance around the hydroxy group of *trans*-4-t-butylcyclohexanol is less than that in the *cis* isomer (this is supported by the evidence of molecular models), (ii) the decreased steric hindrance ensures easier *trans* isomer on silica gel; and (iii) only the alcohols adsorbed on the catalysts react in our system.



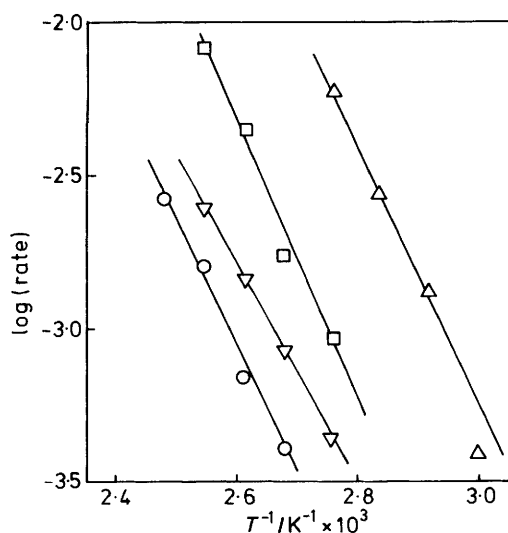
**Figure 2.** Yields of cyclododecene *vs.* the amount of silica gel. Cyclododecanol (1 mmol) and  $\text{CuSO}_4$  (1 mmol) on silica gel were heated under reflux in tetrachloroethylene (10 ml) for 15 min ( $\bullet$ ) and 1 h ( $\circ$ )



**Figure 3.** Initial rates *vs.* the amount of the alcohol. Cyclododecanol and  $\text{CuSO}_4\text{-SiO}_2$  (1 mmol;  $3 \text{ mmol g}^{-1}\text{ SiO}_2$ ) were heated in refluxing tetrachloroethylene (15 ml)

**Dependence of Yield of Olefin on Amount of Silica Gel.**—Equimolar amounts of cyclododecanol and  $\text{CuSO}_4\text{-SiO}_2$  in tetrachloroethylene for 1 h gave cyclododecene almost quantitatively when the amount of silica gel loading 1 mmol of  $\text{CuSO}_4$  was  $>0.3 \text{ g}$  (Figure 2). In the 15 min reaction the yield increased with each increment of  $\text{SiO}_2$  until the yield became constant (*ca.* 80%) when  $>0.8 \text{ g}$  of silica gel was used. This shows that, initially, the catalytic activity of  $\text{CuSO}_4$  increases with increasing amounts of silica gel and then becomes constant when the amount is  $>0.8 \text{ g}$ . This critical value,  $1.2 \text{ mmol CuSO}_4 \text{ g}^{-1}\text{-SiO}_2$ , appears to correspond to saturation of the silica gel surface by sulphate: the surface area, then effectively covered with  $\text{CuSO}_4$ , is assumed to be  $0.7 \text{ nm}^2$  on the basis that the surface area of silica gel WB-300 is *ca.*  $500 \text{ m}^2 \text{ g}^{-1}$ .<sup>9</sup> A monolayer of permanganate has been reported at a loading of  $0.51 \text{ mmol KMnO}_4 \text{ g}^{-1}\text{-SiO}_2$ <sup>10</sup> and dodecan-1-ol at  $0.15 \text{ nm}^2$  on silica gel,<sup>11</sup> values close to that found in our work. Although the role of silica gel might be explained in terms of increasing the surface area of the sulphates so as to provide greater contact with alcohols, it is obvious that other factors are at work since (i) other solid supports scarcely affected the catalyst activity, and (ii) methanesulphonic acid which is soluble in organic solvents showed greatly enhanced catalytic activity when adsorbed on silica gel (see Figure 4). Needless to say, one of the essential functions of silica gel may be to concentrate alcohols on the catalyst surface by adsorption.

**Dependence of Initial Rates on Various Factors.**—Reaction rates, readily observed since there was no induction period, were measured with  $\text{CuSO}_4\text{-SiO}_2$  constant, and the amount of cyclododecanol changing: the rate increased and then became nearly constant as the amount of the alcohol increased (Figure 3). This result suggests that the surface of the catalyst was



**Figure 4.** Plots of logarithm of initial rates ( $1 \text{ mol}^{-1} \text{ min}^{-1}$ ) vs.  $1/T$  (K) in the reactions catalysed by  $\text{CuSO}_4\text{-SiO}_2$  (○),  $\text{NaHSO}_4\text{-SiO}_2$  (□),  $\text{MeSO}_3\text{H-SiO}_2$  (△), and  $\text{MeSO}_3\text{H}$  (▽). Cyclododecanol (1 mmol) and the designated catalyst (1 mmol;  $3 \text{ mmol g}^{-1} \text{ SiO}_2$  for the solid catalysts) were heated in tetrachloroethylene (15 ml)

almost completely covered with the alcohol when the alcohol:catalyst molar ratio reached *ca.* 1:1.

The dehydration rate of cyclododecanol catalysed by  $\text{CuSO}_4\text{-SiO}_2$  was unaffected by a doubling or quadrupling of the amount of tetrachloroethylene present when other conditions were constant. This result also suggests either the nearly complete adsorption of the alcohol or the saturation of the catalyst surface with the alcohol.

When the amount of  $\text{CuSO}_4\text{-SiO}_2$  was varied and that of cyclododecanol was fixed, the initial rates were proportional to the amount of the catalyst.

The dehydration catalysed by  $\text{CuSO}_4\text{-SiO}_2$  proceeded well at  $100^\circ\text{C}$  in hydrocarbons and chlorinated hydrocarbons, but scarcely occurred in basic solvents such as dioxane, benzonitrile, and butanol (see Table 3).

**Mechanism.** As described before, the order of the reactivity of alcohols, tertiary > secondary > primary, suggests that formation of carbenium ion intermediates is the key step. In the dehydration catalysed by  $\text{CuSO}_4\text{-SiO}_2$ ,  $\text{NaHSO}_4\text{-SiO}_2$ ,  $\text{MeSO}_3\text{H-SiO}_2$ , and methanesulphonic acid, log initial rates vs.  $1/T$  showed a linear relation (Figure 4) with activation energy ( $H^*$ ) values of 75.5 (at  $115^\circ\text{C}$ ), 81.4 (at  $105^\circ\text{C}$ ), 77.5 (at  $75^\circ\text{C}$ ), and 63.6 (at  $105^\circ\text{C}$ )  $\text{kJ mol}^{-1}$ , respectively. These are both similar and in the range of the activation energy of solvolysis.<sup>7,12</sup> As described before, the ratios of reaction rates of *cis*- and *trans*-4-*t*-butylcyclohexanol were nearly the same in the reactions catalysed by  $\text{CuSO}_4\text{-SiO}_2$ ,  $\text{NaHSO}_4\text{-SiO}_2$ , and  $\text{Fe}_2(\text{SO}_4)_3\text{-SiO}_2$ . This suggests that a similar mechanism works in all these systems. It is noteworthy that the reaction catalysed by  $\text{MeSO}_3\text{H-SiO}_2$  proceeded *ca.* 14 times faster than that catalysed by a similar amount of methanesulphonic acid at  $90^\circ\text{C}$  (Figure 4).

## Experimental

Reagents and solid supports were purchased and used without purification. Solvents were distilled and stored with 3A molecular sieves. G.l.c. analyses were carried out using a 25 m  $\times$  0.25 mm i.d. fused silica capillary column OV-1 or OV-1701.  $^1\text{H}$  N.m.r. spectra were recorded on a Hitachi R-600 (60 MHz). I.r. spectra were measured with a Hitachi 285

spectrometer. Analytical t.l.c. was performed on precoated silica gel 60F<sub>254</sub> (E. Merck) glass supported plates.

**An Example of the Preparation of Catalysts.**—To a solution of  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  (0.75 g, 3 mmol) in water (20 ml) was added silica gel WB-300 (1.0 g). Removal of water in a rotary evaporator gave a blue powder which was dried at  $240^\circ\text{C}$  for 1 h under reduced pressure ( $2.5 \times 10^2 \text{ Pa}$ ) with stirring. This pale blue reagent contains *ca.*  $2.0 \text{ mmol g}^{-1}$  of  $\text{CuSO}_4$ .

$\text{Ce}(\text{SO}_4)_2$ ,  $\text{Ti}(\text{SO}_4)_2$ ,  $\text{FeSO}_4$ , and  $\text{NH}_4\text{SO}_4$ , and their supported reagents were dried at  $100^\circ\text{C}$  for 1 h and  $\text{KHSO}_4$  and its supported reagent were dried at  $160^\circ\text{C}$  for 1 h. These drying temperatures are *ca.*  $50^\circ\text{C}$  lower than the decomposition temperatures of the salts.<sup>5</sup>  $\text{MeSO}_3\text{-SiO}_2$  was dried at  $100^\circ\text{C}$  for 1 h.

The catalysts were stored in a vessel sealed with parafilm or over  $\text{P}_2\text{O}_5$  in a desiccator.

**An Example of the Dehydration Reaction.**—Cyclododecanol (185 mg, 1.0 mmol),  $\text{CuSO}_4\text{-SiO}_2$  (0.5 g, 1.0 mmol;  $3 \text{ mmol g}^{-1} \text{ SiO}_2$ ), and pentadecane (50  $\mu\text{l}$ ) (internal standard in g.l.c. analysis) in tetrachloroethylene (10 ml) were heated for 30 min under nitrogen with stirring in a bath kept at  $125^\circ\text{C}$ : rotation rate of the stirring bar was *ca.* 450 r.p.m. The reaction was monitored by t.l.c. (ethyl acetate-hexane, [1:3]) or g.l.c. The reaction mixture was transferred to a small glass column with a cotton plug and the solid was separated by filtration. The solid was eluted with acetone (10 ml). The filtrate and the eluant were combined and submitted to g.l.c. analysis.

In the reaction of cholestanol and cholesterol the reaction mixtures were analysed by n.m.r. using chlorobenzene as an internal standard. Purification and identification of the products were performed as described earlier.<sup>3</sup>

**Initial Rate Measurement.**—The alcohol (1.0 mmol) in solvent (1 ml) was added to a mixture of the catalyst (1.0 mmol), an internal standard, and a solvent (14 ml) heated in a bath kept at a regulated temperature ( $\pm 1^\circ\text{C}$ ) for 10 min. Reactions were repeated four or five times with varying reaction times, so that the conversions of the starting materials fell in the range of 5–40%. Initial rates were calculated from the linear parts of the conversion vs. time curves.

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