Acknowledgment. We acknowledge numerous discussions with our colleagues Professor Tom O'Haver, Professor Rinaldo Poli, and Thomas Clayton (of the Ohio State University). The generous financial support of the National Institutes of Health (P.D., AI 23688 and GM 37014) and the Swiss National Science Foundation (W.v.P., 2.033.086) is gratefully acknowledged.

Registry No. **1**, 13601-24-6; **2a**, 768-60-5; **2b**, 766-97-2; **2c**, 536-74-3; **2d**, 873-73-4; **2e**, 937-31-5; **3a**, 122967-38-8; **3b**, 122967-39-9; **3c**, 25281-92-9; **3d**, 122967-40-2; **3e**, 122967-41-3; **4a**, 3815-30-3; **4b**, 4023-84-1; **4c**, 1896-62-4; **4d**, 30626-03-0; **4e**, 30625-98-0; **5a**, 122948-29-2; **5b**, 122948-30-5; **5c**, 55091-68-4; **5d**, 122948-31-6; **5e**, 122948-32-7; **6**, 122967-42-4; **7**, 25281-94-1; 1-hexyne, 693-02-7; methyl propiolate, 922-67-8.

Supplementary Material Available: Plots of exponential decay/growth of ultraviolet absorbances for manganacycles **3a–e** (4 pages). Ordering information is available on any current masthead.

Silica-Bound Sulfonic Acid Catalysts

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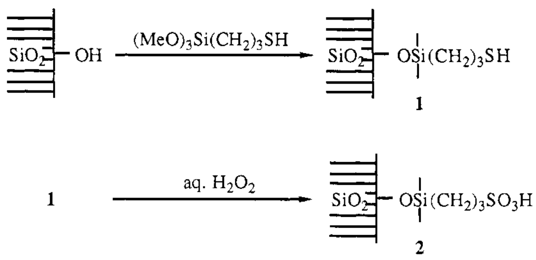
The catalytic activity of colloidal silica sulfonic acid for the hydrolyses of diazinon [diethyl 2-isopropyl-6-methyl-4-pyrimidinyl phosphorothioate] and triphenylmethyl fluoride was compared with that of silica gel sulfonic acids, gel and macroporous poly(styrenesulfonic acids), powdered and soluble Nafion, *p*-toluenesulfonic acid, and hydrochloric acid. For diazinon hydrolysis, the colloidal catalyst was only slightly less active than the soluble strong acid catalysts and 2.8 times more active than any of the other heterogeneous catalysts. The silica gel and polymeric sulfonic acid catalysts had similar activities. For triphenylmethyl fluoride hydrolysis all of the catalysts were only weakly active.

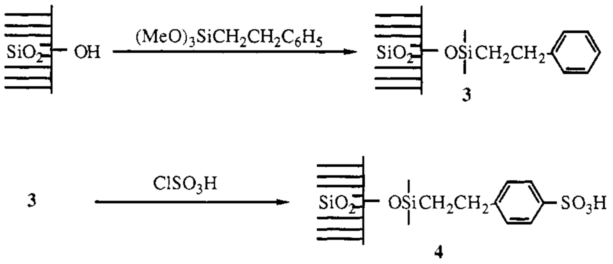
Introduction

Heterogeneous strong acid catalysts such as poly(styrenesulfonic acid) ion-exchange beads[1-3] and Nafion[4-7] can be separated easily from reaction mixtures and used under flow conditions, and they often give purer products and fewer side reactions than homogeneous acids. Aliphatic[8] and aromatic[9-12] sulfonic acids bound to silica gel have also been used as ion exchangers, but little is known about their use as acid catalysts.

Scheme I



Scheme II



Many heterogeneous catalysts are less active for fast reactions than the corresponding homogeneous catalysts because the reaction rates are limited by the transport of reactant to the active sites on the particle surface. The rate of a reaction that is limited only by mass transfer is directly proportional to the particle surface area.[13] One approach to high surface area heterogeneous catalysts is to use porous supports such as silica and macroporous polymers. Another approach is to use colloidal sized particles as the catalyst support. Since surface area is inversely proportional to particle size, by decreasing the particle size, the mass transfer limitations can be reduced and the catalyst should become more active. High activity of colloidal catalysts has been found with phase-transfer catalysts,[14] polystyrene latexes containing only surface sulfonic acid groups,[15] colloidal palladium,[16] colloids modeled after enzymes,[17-19] and transition-metal oxidation

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Table I. Particle Diameters Determined by TEM

sample	d_n, nm	d_w, nm	d_w/d_n
5	51.8	53.9	1.04
6	50.2	52.7	1.05
7	52.7	55.4	1.05
8	53.1	55.0	1.04

catalysts[20-23] bound to colloidal polymer particles.

Up to this time, the use of colloidal particles as catalyst supports has been limited mainly to organic polymer latexes. Silica is a rigid, stable support, and spherical, monodisperse colloidal silica particles can be easily prepared by the method of Stöber.[24] In this paper we describe the preparation of propanesulfonic acid modified colloidal silica and its catalytic activity for the hydrolyses of triphenylmethyl fluoride and diazinon [diethyl 2-isopropyl-6-methyl-4-pyrimidinyl phosphorothioate].

Results

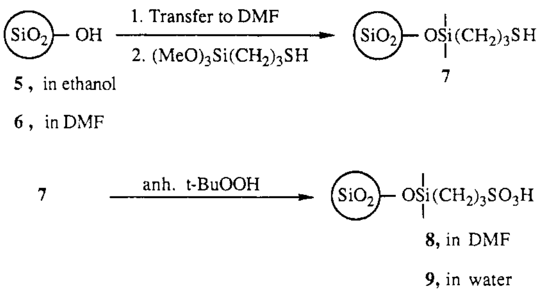
Silica Sulfonic Acids. Silica sulfonic acids were prepared both from high surface area chromatographic silica gel and from colloidal silica particles to compare the catalytic activity of sulfonic acid groups on the internal pore surfaces of large particles with the activity of sulfonic acid groups on the external surface of nonporous 55-nm particles.

Silica-bound propanesulfonic acid has been prepared previously by oxidation of surface-bound bis[3-(trimethoxysilyl)propyl disulfide to the sulfonic acid with aqueous H_2O_2.[8] Prior to disclosure of these results, we used the method shown in Scheme I. Silica gel (Davisil, surface area = 480 m^2/g, av pore diameter = 6 nm) was treated with (3-mercaptopropyl)trimethoxysilane, and the surface-modified mercaptan 1 was oxidized by using aqueous H_2O_2 to give 0.34 mequiv/g of silica gel bound sulfonic acid 2 (25% of total sulfur atoms in sulfonic acid form). An alternative oxidation with dimethyl sulfoxide, HBr, and water[25] resulted in an ion-exchange capacity of only 0.084 mequiv/g.

(2-Phenylethyl)trimethoxysilane was used to modify the silica gel surface to give 2-phenylethyl silica 3, which was sulfonated with chlorosulfonic acid to give the sulfonic acid 4 (Scheme II),[9,26] with an ion-exchange capacity of 0.56 mequiv/g. When the same synthesis was attempted with phenyltrimethoxysilane, an ion exchange capacity of only 0.04 mequiv/g was achieved. The cleavage of the aromatic C–Si bond by acid[27] is likely the cause of the low capacity obtained from the reaction with chlorosulfonic acid. The sulfonation reaction was also attempted with a 1:1 mixture of acetic acid and concentrated sulfuric acid according to Asmus, Low, and Novotny,[10] but this resulted in an ion-exchange capacity of only 0.094 mequiv/g. Thus the ethylene spacer of 3 is important for the synthesis of high-capacity silica arenesulfonic acids.

An ethanolic dispersion of colloidal silica (5) was prepared by hydrolysis of tetraethyl orthosilicate in water, ammonia, and ethanol.[24] The sizes of silica particles formed in this reaction were measured on transmission electron micrographs (TEM). Some particle clusters appeared in the micrographs, but since it is not known if the clusters were formed in the original dispersion or as the samples were dried on the TEM grid, only single primary particles were measured. The number average and weight average particle diameters (d_n and d_w) and uniformity ratio (d_w/d_n) were determined according to eq 1 and 2 and are

Scheme III



$$d_n = \sum n_i d_i / \sum n_i \qquad (1)$$

$$d_w = [\sum n_i d_i^6 / \sum n_i d_i^3]^{1/3} \qquad (2)$$

reported in Table I. The colloidal silica is nonporous, with a density of 2.06 g/cm^3, and contains 2.5% carbon as residual ethoxy groups. More details of the structure and properties of colloidal silica are given in a separate paper.[28]

When the colloidal silica (5) was treated with (mercaptopropyl)trimethoxysilane in an attempt to prepare (mercaptopropyl)silica 7 in the original ethanol, water, and ammonia mixture, a gel was obtained that could not be redispersed (Scheme III). Therefore, the ethanol and water were replaced by DMF to give a stable colloidal dispersion of silica in DMF (6) before functionalization.[29] Stable dispersions 6 were obtained only when the total volume of the dispersion was kept constant throughout the process by addition of DMF simultaneously with distillation of ethanol and water, and the water was completely removed. Otherwise, the silica precipitated after 1 to 2 weeks. Our most stable DMF dispersions 6 showed no signs of precipitation for 6 months, after which slow precipitation began.

After the silica was transferred to DMF, mercaptopropyl groups were attached by reaction with (mercaptopropyl)trimethoxysilane to give (mercaptopropyl)silica 7. The CP-MAS ^{13}C NMR spectrum of 7[30] showed peaks for mercaptopropyl, ethoxy from incomplete hydrolysis of tetraethyl orthosilicate, and methoxy from attachment of the trimethoxysilane. Surface coverage was determined by sulfur analysis to be 0.35 mg-atom/g, but only 0.22 mequiv/g of sulfur in the precipitated sample was thiol that reacted with Ellman's reagent.

Oxidation of the mercaptan groups of 7 with *tert*-butyl hydroperoxide in toluene gave the sulfonic acid dispersion 8 with 2.59 mg-atom S/g and an ion-exchange capacity of 0.17 mequiv/g. Reaction of 8 with Ellman's reagent showed 0.076 mequiv/g of unreacted thiol. The remaining sulfur atoms were present in various intermediate oxidation states. The CP-MAS ^{13}C NMR spectrum of 8[30] showed the presence of methoxy, ethoxy, and propane-

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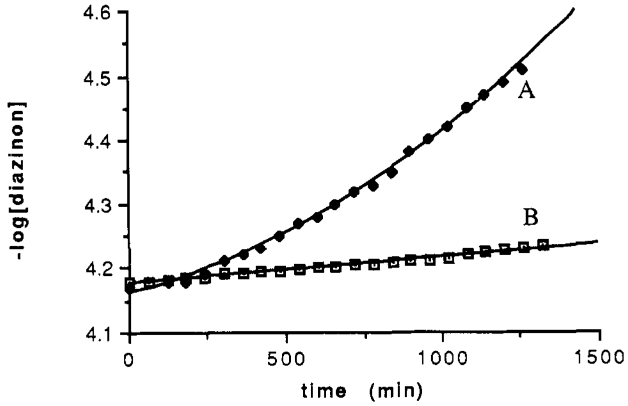
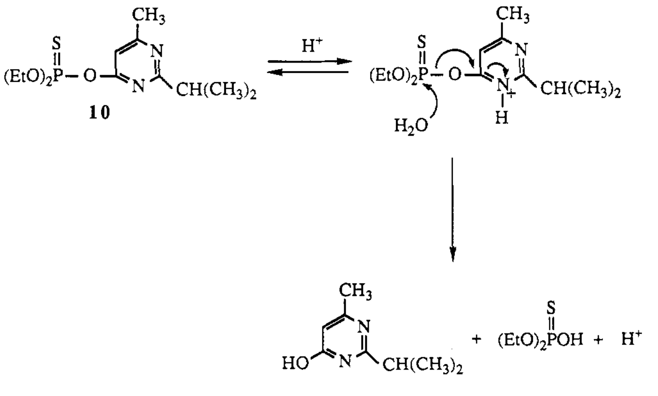


Figure 1. First-order plot for disappearance of diazinon from 6.688 × 10^{-5} M unbuffered (A) and pH 7 buffered (B) aqueous solutions at 62.0 ± 0.2 °C.

Scheme IV



sulfonic acid. Disulfide and at least two other groups with sulfur in intermediate oxidation states were also present.[31,32] The elemental analysis of **8** showed a much higher sulfur content than that of its precursor, **7**. Apparently, precipitation of the samples for elemental analysis by washing with water, acetone, and ether removed unbound silanes from **7**. However, after the mercaptans were partially oxidized to sulfonic acid **8**, the previously unbound silanes were either more tightly adsorbed or covalently bound to the silica and were not removed by washing. This hypothesis was confirmed by isolating the nonvolatile residues from the filtrates of **7** and **8** after the washing procedure. The filtrates and wash solutions from 20 mL each of **7** and **8** contained 234 mg and 36 mg of residue, respectively. In a separate control experiment, reaction of monomeric (mercaptopropyl)trimethoxysilane with *tert*-butyl hydroperoxide, under the same conditions used to oxidize the (mercaptopropyl)silica to sulfonic acid, gave a siloxane polymer. Thus polymerization of silanes adsorbed to **7** during the oxidation procedure could give nonextractable siloxane polymer adsorbed to **8**. However, in this control reaction, acid produced during the reaction may catalyze the polymerization. With (mercaptopropyl)silica present, the basic silica surface could neutralize the acid and prevent it from acting as a catalyst.

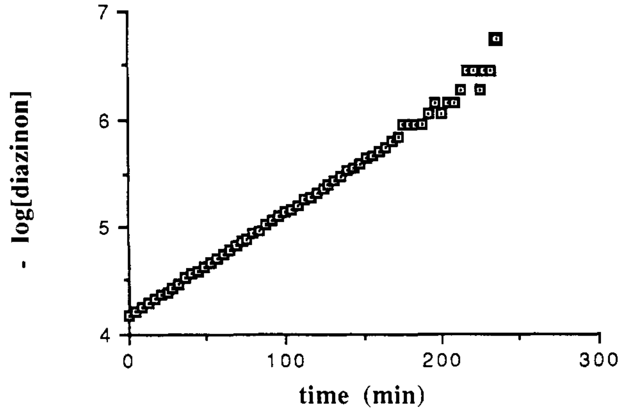


Figure 2. First-order plot for disappearance of diazinon from 6.688 × 10^{-5} M diazinon and 1.00 × 10^{-3} M HCl at 62.0 ± 0.2 °C.

Table II. Hydrolysis of 6.688 × 10^{-5} M Diazinon Catalyzed by 1.00 × 10^{-3} M Acid at 62.0 ± 0.2 °C

catalyst	mg catalyst[a]	$10^4 k_{obsd}$,[b] s^{-1}	% convrsn obsd[c]
HCl		230	99
9	7.4	209[d]	99
9	7.6	179[d]	99
Dowex 50W-X4[e]	1.5	76.3[f]	94
Nafion solution	3.3	75.5	99
4	5.3	28.0	55
		39.4[g]	75
Amberlyst 15[h]	0.64	27.8[f]	85
Nafion powder	3.3	12.3	55
		13.3[f,g]	55
2	11.4	9.72	51
		61.9[g]	80
uncatalyzed[i]		0.937	15
7	7.4	0.940[j]	20
5	7.4	5.35	37

[a] Amount of catalyst in 3.0-mL reaction volume. [b] All measured rate constants except for Amberlyst 15 are averages from two runs that differed by ≤6%. [c] % conversion of diazinon on which the calculation of k_{obsd} is based. [d] Two batches of **9**, prepared by the same method, were used as catalysts. [e] Sulfonated polystyrene gel. [f] Adsorption of diazinon and reaction products occurred. k_{obsd} was determined from concentrations remaining in solution after adsorption was complete. [g] Catalyst was placed in UV cell and wetted with 0.1 mL of ethanol for 15 min before adding the remaining 2.9 mL of the reaction mixture. [h] Macroporous sulfonated polystyrene. [i] Buffered at pH 7 with 0.01 M phosphate buffer. k_{obsd} was 2.73 × 10^{-4} s^{-1} until 7.3% of the diazinon was hydrolyzed, at which time k_{obsd} decreased to 0.940 × 10^{-4} s^{-1}.

Diazinon Hydrolysis. The hydrolysis reactions of diazinon and triphenylmethyl fluoride were chosen to serve as simulants for hydrolysis of the highly toxic phosphonyl fluoride nerve agents in order to test the catalytic activity of these silica-bound sulfonic acids. The hydrolysis of diazinon (**10**) is strongly acid catalyzed,[33] occurring via the protonated pyrimidine, as shown in Scheme IV. The pK_a of 4-hydroxy-2,6-dimethylpyrimidine is 3.06.[34] Therefore, at initial pH 3, as our reactions were carried out, a substantial fraction of the diazinon was protonated. Gomaa, Suffet, and Faust[33] reported that the acid-catalyzed hydrolysis of diazinon follows second-order kinetics:

$$-d[\text{diazinon}]/dt = k[\text{diazinon}][\text{acid}] \qquad (3)$$

As shown in Scheme IV, diethyl phosphorothioate (pK_a = 1.83)[35] is produced in this reaction, causing [acid] to increase as the reaction proceeds. This autocatalytic effect is shown in Figure 1. When the reaction mixture is buffered at pH 7, the reaction gives a linear first-order plot. But when the reaction is unbuffered, the reaction rate

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increases with time. If [acid] $\gg$ [diazinon], the rate equation becomes pseudo-first-order, eq 4, and k_{obsd} =

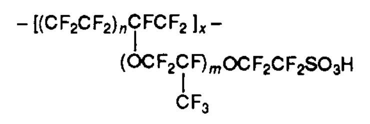
$$-d[\text{diazinon}]/dt = k_{obsd}[\text{diazinon}] \qquad (4)$$

k[catalyst]. The reaction now follows first-order kinetics as shown in Figure 2 for 1.00×10^{-3} M HCl and 6.688×10^{-5} M diazinon.

The first-order rate constants, k_{obsd}, for diazinon hydrolysis are reported in Table II for a variety of heterogeneous sulfonic acid catalysts. Two different batches of the colloidal silica-bound catalyst **9** gave rate constants nearly equal to that with HCl, and 2.4 to 2.8 times greater than with soluble Nafion. The most active batch of **9** was 2.8 times more active than the next most active heterogeneous catalyst, Dowex 50W-X4, a sulfonated polystyrene gel. Colloidal silica catalyst **9** was 21.5 and 7.5 times more active than silica gel catalysts **2** and **4**, respectively, when these silica gel based catalysts were added as a dry powder. When catalysts **2** and **4** were first treated with 0.1 mL of ethanol for 15 min, they were only 3.4 and 5.3 times less active than the colloidal catalyst **9**. Apparently, water alone failed to wet the surface of the silica gel catalysts **2** and **4**, and prewetting the surface with ethanol is necessary for utilization of their full activity. The surface of (mercaptopropyl)silica gel **1** was hydrophobic because of complete coverage of the surface with 1.47 mequiv/g of mercaptopropyl groups. The surface of **2** was also relatively hydrophobic because only 34% of the sulfur atoms were in sulfonic acid form. In the sulfonated (2-phenylethyl)silica **4**, 63% of the aromatic rings were sulfonated, which should make the surface more hydrophilic, and prewetting the surface does not have as large an effect on the catalytic activity.

Unfunctionalized colloidal silica **5** increased the rate of diazinon hydrolysis when buffered at pH 7. This is most likely due to nucleophilic catalysis by a small fraction of deprotonated surface silanols. At pH 7, silica gel contains approximately 0.41 SiO^-/nm^2, which would give 1.1×10^{-4} M SiO^- in the reaction mixture.[36]

Most of these reactions showed pseudo-first-order kinetics when the acid catalyst concentration was 1500 times the diazinon concentration. Exceptions were the sulfonated polystyrenes and the Nafion powder (**11**) when it was prewetted with ethanol. Using 1.5 mg of Dowex 50W-X4, 0.64 mg of Amberlyst 15, and 3.3 mg of Nafion powder, these catalysts adsorbed 8.76×10^{-8} mol (44%), 9.06×10^{-8} mol (45%), and 1.42×10^{-7} mol (71%) of diazinon and reaction products during the first 1.0 h reaction time from 3.0 mL of a solution that initially contained 6.688×10^{-5} M diazinon. The concentrations of diazinon, product, and (diazinon + product) are shown in Figure 3 for Dowex 50W-X4. If a first-order plot is made for the disappearance of diazinon remaining in solution after adsorption has reached equilibrium and the concentration of (diazinon + product) becomes constant, a linear plot is found (Figure 4). Since in any practical use, the amount of catalyst will be much less than the amount of substrate, the catalyst will become saturated, and the hydrolysis rate of diazinon remaining in solution under adsorption equilibrium conditions will be the important factor. Therefore, this is the value reported in Table II for Dowex 50W-X4, Amberlyst 15, and prewetted Nafion powder.



$$-[(CF_2CF_2)_n\underset{\displaystyle (OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}F})_mOCF_2CF_2SO_3H}{\underset{|}{C}FCF_2}]_x-$$

11

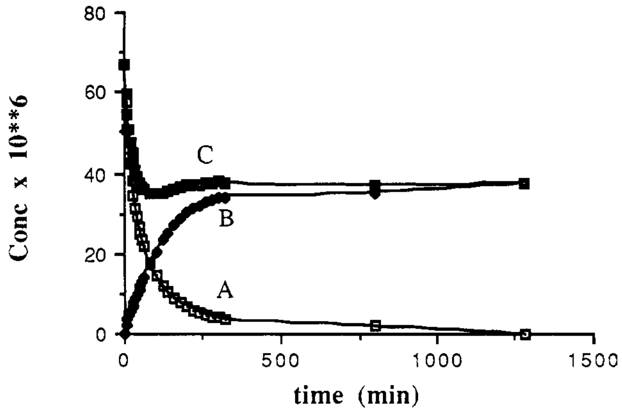


Figure 3. Concentrations of diazinon (A), product (B), and diazinon + product (C) in solution during Dowex 50W-X4 catalyzed hydrolysis.

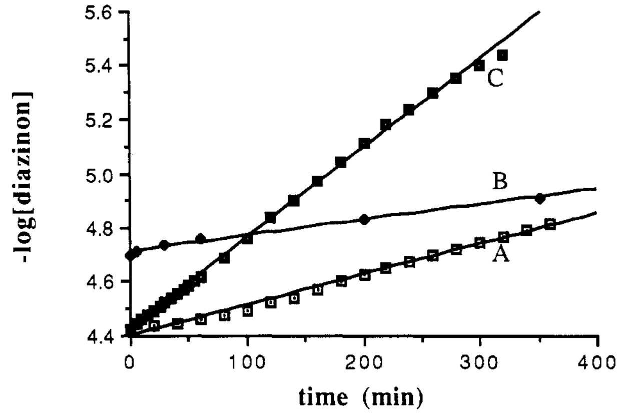


Figure 4. First-order plots for hydrolysis of diazinon remaining in solution after adsorption by Amberlyst 15 (A), Nafion powder (B), and Dowex 50W-X4 (C) is complete; time = 0 in this plot corresponds to 1.0 h actual reaction time, at adsorption equilibrium.

Triphenylmethyl Fluoride Hydrolysis. The hydrolysis of triphenylmethyl fluoride is only weakly catalyzed by acid, but we were interested in seeing if HF produced during the reaction would react with the silica support, thereby giving a catalyst that could both carry out the hydrolysis and at the same time remove the HF from the solution. Aqueous 0.1 M HF at room temperature dissolves vitreous silica.[37] The dissolution is driven thermodynamically by the Si–F single-bond energy of 128 kcal per g-bond, which greatly exceeds the Si–O single-bond energy of 89 kcal per g-bond.[38]

According to Coverdale and Kohnstam,[39] the rate equation for hydrolysis of triphenylmethyl fluoride (**12**) is

$$-d[Ph_3CF]/dt = [Ph_3CF](k_0 + k_{HF}[HF] + k_{H^+}[H^+]) \qquad (5)$$

where k_0 is the uncatalyzed rate constant, $[H^+]$ is the concentration of added catalyst, k_{H^+} is the rate constant

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Table III. Initial Rate Constants, k_{obsd}, for Hydrolysis of Triphenylmethyl Fluoride with Various Catalysts at 45.0 ± 0.5 °C[a]

catalyst	mg catalyst[b]	mol %	$10^{-2}k_{obsd}$, h^{-1}
Nafion solution	220.0	2.0	12.1
$CH_3C_6H_4SO_3H$	38.0[c]	2.0	10.5
9	1176	2.0	10.2
Nafion powder	220.0	2.0	10.1
$CH_3C_6H_4SO_3H$	190.2[c]	10.0	16.2
Amberlyst 15	212.8	10.0	9.6
4	178.6	10.0	8.9
2	294.1	10.0	8.9
5	284.6		8.6
uncatalyzed			8.6

[a] Reactions were run with 0.1 M triphenylmethyl fluoride, 0.01 M or 0.002 M acid catalyst in 70:30 (v/v) tetrahydrofuran/water. [b] In 100 mL of reaction mixture. [c] Added as *p*-toluenesulfonic acid monohydrate.

due to added catalyst, and $k_{HF}[HF]$ is an autocatalytic term due to HF produced during the hydrolysis (eq 6).

$$\underset{\mathbf{12}}{(C_6H_5)_3CF} + H_2O \xrightarrow{H^+} (C_6H_5)_3COH + HF \qquad (6)$$

In order to simplify the calculations, we determined the initial rate constant, k_{obsd}, from the first 20% of the reaction, where our data fit a pseudo-first-order rate law with $k_{obsd} = k_0 + k_{H^+}[H^+]$ as in eq 7.

$$-d[Ph_3CF]/dt = [Ph_3CF]k_{obsd} \qquad (7)$$

Initial rate constants of triphenylmethyl fluoride hydrolysis, measured by the increase in fluoride ion concentration, are given in Table III. The reaction is not strongly acid catalyzed, and only slight increases in rate are observed after the first 20% conversion. The only acid catalyst that increased the observed rate constant by a factor of more than 1.4 compared with that of the uncatalyzed reaction was 10 mol % *p*-toluenesulfonic acid. The relative activities of the heterogeneous catalysts are similar to those found in diazinon hydrolysis, except Nafion has a higher relative activity.

HF produced in the reaction did not react with the silica supports in any of the catalysts reported here, for we could detect all of the liberated HF with a fluoride ion selective electrode. Even with unmodified colloidal silica, [HF] detected at the end of the reaction was equal to the initial triphenylmethyl fluoride concentration. Therefore reaction between silica and HF at pH 3 is much slower than the rate of hydrolysis of triphenylmethyl fluoride.

Discussion

Silica Sulfonic Acids. The surface modification methods in Schemes I and II to give the propanesulfonic acid **2** and the arenesulfonic acid **4** both effectively bind sulfonic acids to silica gel. A major drawback to silica-bound propanesulfonic acid **2** is that only 34% of the sulfur is in the sulfonic acid form. The sulfur present in other oxidation states could become a problem in some applications. Silica-bound aromatic sulfonic acids such as **4** require an alkyl spacer chain between the aromatic ring and silane to avoid acid-catalyzed aromatic desilanation.[27]

The colloidal silica sulfonic acid catalyst in water (**9**) has a high ion-exchange capacity per surface area when compared with **2** and **4**, but its preparation (Scheme III) is more difficult because colloidal stability must be maintained. Care must be taken not to add salts or solvents that can precipitate the silica, because often a precipitated silica cannot be redispersed. Instability of colloidal (mercaptopropyl)silica **7** in the presence of water necessitated the use of anhydrous *tert*-butyl hydroperoxide for mercaptan oxidation, which gave a lower conversion to sulfonic acid than the aqueous H_2O_2 used with silica gel. Dispersions of **9** in water precipitated after 1–2 weeks, so that the catalyst could not be stored for long periods of time before use. The problem of colloidal stability is addressed in detail in another paper.[28]

Mechanism of Catalysis. In aqueous solution, low molecular weight soluble sulfonic acids are completely dissociated, and hydrolyses of diazinon and triphenylmethyl fluoride should be specific acid catalyzed. However, the heterogeneous sulfonic acid catalysts are less active than *p*-toluenesulfonic acid and HCl. We considered four possible reasons for lower activity of the heterogeneous catalysts: (1) incomplete dissociation of the sulfonic acid in the partly aqueous environment of the catalyst; (2) a medium effect that retards the hydrolysis in the heterogeneous catalst relative to water; (3) a lower concentration of substrate on the heterogeneous catalyst surface than in external aqueous solution; that is, an unfavorable substrate distribution between the solution and the catalyst; (4) mass transport limitation of the catalytic activity. Analysis of these possibilities follows.

(1) The pK_a of sulfonic acid resins is <1.[40] Therefore, all of the catalysts in Table II are completely dissociated under the conditions used, and the acid strength should not be a factor in the activity differences.

(2) Medium effects on catalytic activity cannot be ruled out because of the differences in structure of the various catalysts.

(3) Distribution of substrate appears to have only a small effect on diazinon hydrolysis. Nafion (**11**) powder is surprisingly much less active than the other heterogeneous catalysts in diazinon hydrolysis. We thought that the fluorocarbon network might not be wetted well when Nafion was added to water as a dry powder. However, when the surface was prewetted with ethanol, the rate constant increased by only 7.5%, even though a large amount of substrate adsorption occurred. Dowex 50W-X4 and Amberlyst 15 also adsorbed diazinon, but their catalytic activities were about the same as those of the silica gel catalysts **2** and **4**, which did not adsorb diazinon.

(4) The major cause of the lower activities of the large particle catalysts is probably limitation of the reaction rate by mass transport of substrate. With the macroscopic resin beads and powders, the substrate must diffuse inside pores or through the gel phase to the active sites. With the colloidal silica catalyst **9**, most or all of the active sites are on the outer surface of the particle, and the substrate must only diffuse from the bulk liquid to the particle surface. This diffusion apparently occurs faster than diazinon hydrolysis, allowing the colloidal silica-bound catalyst to have an activity equal to that of HCl. Much slower reactant diffusion in pores and in the gel phase of the silica gel and polymer bead catalysts makes their activities lower than that of the colloidal catalyst. Pore diffusional limitations are well known in other types of heterogeneous catalysis.[13]

Future Uses of Colloidal Silica Catalysts. Colloidal silica should be investigated more as a catalyst support. It gives activity similar to soluble catalysts and should still provide some of the benefits of other heterogeneous catalysts such as ease of separation. It can be removed from a reaction mixture by ultrafiltration or by precipitation with a salt or organic solvent followed by filtration. Another possibility is to use larger 400–500-nm colloidal silica particles that can be centrifuged out of a reaction mixture

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(40) Helfferich, F. *Ion Exchange*; McGraw Hill: New York, 1962; p 86.

in a few minutes. These results point the way to the use of colloidal silica as a support for a wide range of catalysts.

Experimental Section

Materials. Davisil silica gel, grade 634 (100–200 mesh, surface area = 480 m^2/g; pore volume = 0.75 mL/g; av pore diameter = 6 nm) was obtained from Aldrich. (2-Phenylethyl)trimethoxysilane and (3-mercaptopropyl)trimethoxysilane were obtained from Petrarch and used as received. Solutions of ammonia in ethanol (3–5 M) were prepared by passing ammonia gas through a column of NaOH pellets into absolute ethanol (U.S. Industrial Chemicals Co.) at 0 °C for 20–30 min. Ammonia concentration was determined by titration to the methyl red endpoint with 0.9953 M HCl. Water was treated with active carbon, deionized, and distilled in glass (1.0 μmho). Tetraethyl orthosilicate (Petrarch or Fisher) was distilled immediately before use. When used as solvents for trityl fluoride, acetonitrile and tetrahydrofuran (THF) were dried by refluxing over calcium hydride or sodium metal, respectively, and then distilling. The acetone used as a solvent for diazinon was dried by standing over Drierite (calcium sulfate) for 4 days and distilling. Fluoride standard solutions were prepared by diluting a 1.00 M fluoride solution obtained from Orion. Chlorosulfonic acid (Aldrich), hydrogen peroxide (Aldrich), anhydrous 3 M *tert*-butyl hydroperoxide in toluene (Fluka), 5,5′-dithiobis-(2-nitrobenzoic acid) (Aldrich), anhydrous potassium fluoride (Aldrich), triphenylmethyl chloride (Aldrich), and diazinon (Crescent Chemical Co., purity = 98%) were used as received. Nafion (1100 equiv wt) was obtained as a powder (passes through 100-mesh sieve) or as a 5% solution in 39% (w/w) 2-propanol, 35% *n*-propanol, and 26% water (determined by ^{1}H NMR) from C. G. Processing, Inc. (Box 133, Rockland, DE 19732). Dowex 50W-X4 was obtained as wet beads (50–100 mesh) from Baker. Ion-exchange capacities of commercial resins were determined by washing the resin with 0.1 M HCl, and with water until the washings were neutral, suspending the beads in 2.0 M NaCl for 30 min, filtering, and titrating the filtrate to the phenolphthalein endpoint with 0.02 M NaOH. Ion-exchange capacities of 1.99 and 4.70 mequiv/g were found for wet Dowex 50W-X4 and dry Amberlyst 15 (Aldrich, 20–50 mesh), respectively. All other solvents were reagent grade and were used as received.

Analytical Methods. CP/MAS ^{13}C NMR spectra were obtained by Dr. Frank McEnroe at Conoco, Inc., with an IBM WP-100 spectrometer at 25 MHz. The conditions used are given in a separate paper.[28] Fluoride ion determinations were done on an Altex Zeromatic IV pH meter using an Orion combination fluoride electrode, Model 960900. UV spectrophotometry was done on a Varian DMS-200 UV/vis spectrophotometer fitted with a magnetic stirrer and thermostated sample cell holders. A Hewlett-Packard 5840A gas chromatograph with a thermal conductivity detector was used. Elemental analyses were done at Galbraith Laboratories (Knoxville, TN). Transmission electron microscopy was done on a JEOL JEM-100 CX II microscope at 75 kV. Formvar and carbon grids were used for samples in ethanol and DMF, respectively. Particle sizes were determined by measurement of at least 35 particles on photographic negatives.

Colloidal samples were prepared for analysis by adding the dispersion to water and acidifying to pH 2 with 1.0 M HCl to precipitate the colloids. The precipitated particles were recovered by vacuum filtration, washed thoroughly with water, acetone, and ethyl ether, and dried at 60 °C under vacuum for 15 h.

Ion-exchange capacities of the silica-bound sulfonic acids were determined by adding 0.5 g of the silica gel sulfonic acid or 20 mL of the dispersion of colloidal silica-bound sulfonic acid to 75 mL of 2.0 M NaCl (this caused the colloidal samples to precipitate). This suspension was titrated potentiometrically with 0.0185 M NaOH, or the silica was removed by gravity filtration, washed with 75 mL of 2.0 M NaCl, and the combined filtrate was titrated to the phenolphthalein endpoint with 0.0185 M NaOH. Both methods gave the same ion-exchange capacity.

Thiol contents were determined by reaction with Ellman's reagent.[41,42] Standard solutions, 100 mL each, were prepared containing 1.0 × 10^{-4} M Ellman's reagent [5,5′-dithiobis(2-nitrobenzoic acid)], 1.5 × 10^{-5} M to 5.3 × 10^{-5} M (mercaptopropyl)trimethoxysilane, and 0.01 M EDTA in a pH 8.0 phosphate buffer (10^{-2} M KH_2PO_4). After 30 min, the absorbance of each solution was measured on a Spectronic 21 spectrophotometer at 412 nm (ϵ = 11 400 M^{-1} cm^{-1}). With use of precipitated samples prepared for analysis as described above, thiol contents were determined by preparing 100-mL solutions containing 0.014 g of substrate, 1.5 × 10^{-4} M Ellman's reagent, and 0.01 M EDTA at pH 8.0. The absorbance of these solutions was measured after 16 h, when the absorbance at 412 nm became constant.

Silica Gel Pretreatment. Silica gel (45.00 g) was suspended in 150 mL of 2 M HCl and refluxed for 4 h. The silica gel was removed by vacuum filtration and washed repeatedly with water and acetone until the filtrate contained no acid. It was allowed to air dry before further use.

(Mercaptopropyl)silica Gel (1). Pretreated silica gel (26.25 g) and 150 mL of toluene were mixed in a 250-mL flask fitted with a Dean–Stark trap. After being refluxed for 5 h under nitrogen, 10.0 mL of water was collected, leaving 16.25 g of dry silica gel. The Dean–Stark trap was then removed, 16.3 g (83.04 mmol) of (3-mercaptopropyl)trimethoxysilane was added, and the mixture was refluxed for 26 h. The functionalized silica was separated by vacuum filtration and washed repeatedly with toluene and acetone. It was then dried under vacuum at 60 °C for 15 h to give 20.0 g of (mercaptopropyl)silica 1.

Anal. Found: C, 7.39 (6.15 mg-atom/g); S, 4.72 (1.47 mg-atom/g); H, 1.71 (16.93 mg-atom/g). Calculating from the carbon and sulfur analyses, the hydrogen is due to mercaptopropyl (10.29 mg-atom H/g), ethoxy and methoxy (4.35 mg-atom H/g), and surface OH (2.29 mg-atom H/g).

Silica Gel Bound Propanesulfonic Acid (2). (Mercaptopropyl)silica gel 1 (7.91 g) was stirred under nitrogen in 40 mL of water and 96 mL of 30% hydrogen peroxide (959 mmol, 6.95 M) for 7 h at room temperature. The modified silica was removed by vacuum filtration, washed once with dilute hydrochloric acid, and washed repeatedly with water, acetone, and toluene with acetone as the final washing solvent. It was dried under vacuum for 16 h at 60 °C to give 5.83 g of **2**.

Anal. Found: C, 4.99 (4.15 mg-atom/g); S, 3.25 (1.01 mg-atom/g); H, 1.36 (13.47 mg-atom/g) due to $(CH_2)_3S$ (7.07 mg-atom H/g), ethoxy and methoxy (2.80 mg-atom H/g), and surface OH (3.60 mg-atom H/g). Ion-exchange capacity = 0.34 mequiv/g.

(2-Phenylethyl)silica Gel (3). Pretreated silica gel (26.0 g) and 150 mL of toluene were mixed in a 250-mL flask fitted with a Dean–Stark trap and a condenser. Upon refluxing under nitrogen for 5 h, 10.9 mL of water was collected, leaving 15.1 g of dry silica gel. The Dean–Stark trap was removed, 13.0 g (57.0 mmol) of (2-phenylethyl)trimethoxysilane was added, and the mixture was refluxed for 24 h. The functionalized silica gel was separated by vacuum filtration and washed repeatedly with toluene and acetone. It was dried under vacuum for 15 h at 60 °C to give 17.1 g of **3**.

Anal. Found: C, 7.74 (6.44 mg-atom/g); H, 1.02 (10.10 mg-atom/g) due to 2-phenylethyl (7.24 mg-atom H/g) and surface OH (2.86 mg-atom H/g).

[2-(4-Sulfophenyl)ethyl]silica (4). (2-Phenylethyl)silica gel 3 (16.11 g) was suspended in 112 mL of chloroform under a nitrogen atmosphere. Then 38 mL (557 mmol) of chlorosulfonic acid was added dropwise over a period of 45 min. The mixture was refluxed for 3.5 h, giving a dark brown suspension. The modified silica gel was recovered by vacuum filtration and washed repeatedly with chloroform, acetone, and water until the filtrate was colorless. It was dried under vacuum for 16 h at 60 °C to give 15.8 g of light brown 4.

Anal. Found: C, 6.45 (5.37 mg-atom/g); S, 1.65 (0.52 mg-atom/g); H, 1.06 (10.5 mg-atom/g) due to phenylethyl (2.61 mg-atom H/g), 2-(4-sulfophenyl)ethyl (4.68 mg-atom H/g), and surface OH (3.21 mg-atom H/g). Ion-exchange capacity = 0.56 mequiv/g.

Colloidal Silica (5). All glassware was cleaned with 2% HF and rinsed with purified water. Water (7.2 mL, 400 mmol, 0.999 M), 309 mL of 2.46 M ammonia in ethanol (760 mmol, 1.90 M ammonia), and 66 mL of absolute ethanol were mixed in a 500-mL Erlenmeyer flask fitted with a Teflon stopper. The flask was placed in water in an ultrasonic cleaning bath (Branson Model 5200), and 18 mL (80.7 mmol, 0.202 M) of tetraethyl orthosilicate

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[41] Ellman, G. L. *Arch. Biochem. Biophys.* **1959**, *82*, 70–77.

[42] Benedict, R. C.; Stedman, R. L. *Analyst* **1970**, *95*, 296–301.

was added rapidly during sonication. After 25 min, the reaction mixture began to turn cloudy as silica particles were formed. The temperature of the sonicator rose slowly from 20 °C to 45 °C over the first 5–6-h reaction time, and the mixture was sonicated a total of 18 h.

Anal. Found: C, 2.47 (2.06 mg-atom/g); H, 1.49 (14.8 mg-atom/g) due to ethoxy (5.15 mg-atom H/g) and surface OH (9.65 mg-atom H/g).

DMF Dispersion of Colloidal Silica (6). The ethanol and water were slowly distilled from 400 mL of **5** while about 500 mL of dimethylformamide (DMF) was added dropwise from an addition funnel in order to keep a constant volume of dispersion. The distillation was continued until 10–15 mL of distillate was collected at a constant bp of 152 °C.

Mercaptopropyl-Functionalized Colloidal Silica (7). (Mercaptopropyl)trimethoxysilane (5.0 mL, 26.5 mmol) and 400 mL of **6** (containing 4.9 g silica as SiO_2) were heated to 100 °C for 24 h under nitrogen to give **7**.

Anal. Found: C, 5.34 (4.45 mg-atom/g); S, 1.11 (0.35 mg-atom/g); H, 2.19 (21.7 mg-atom/g) due to mercaptopropyl (2.45 mg-atom H/g), ethoxy and methoxy (8.5 mg-atom H/g), and surface OH (10.8 mg-atom H/g). ^{13}C NMR: 17.7 and 61.1 ppm (ethoxy); 50.7 ppm (methoxy); 10.9 (C(1)) and 27.5 ppm (C(2) and C(3) of mercaptopropyl). Mercaptan content determined by Ellman's reagent = 0.22 mequiv/g.

Colloidal Silica-Bound Propanesulfonic Acid (8). To 300 mL of **7** was added 88 mL of 3.0 M *tert*-butyl hydroperoxide (264 mmol) in toluene under nitrogen. The mixture was stirred at 25 °C for 24 h and at 60 °C for 24 h to give a pale yellow dispersion of **8** that contained 0.022 g of solid/mL.

Anal. Found: C, 14.12 (11.8 mg-atom/g); S, 8.32 (2.59 mg-atom/g); H, 3.60 (35.6 mg-atom/g) due to $(CH_2)_3S$ (18.1 mg-atom H/g), ethoxy and methoxy (10.1 mg-atom H/g), and surface OH (7.4 mg-atom H/g). ^{13}C NMR: 17.1 and 60.6 ppm (ethoxy); 51.0 ppm (methoxy and C(3) of sulfonic acid); 23.0 (C(2)) and 42.0 ppm (C(3) of disulfide); 32 and 39 ppm (unassigned). Ion-exchange capacity = 3.82×10^{-3} mequiv/mL = 0.17 mequiv/g. Mercaptan content determined by Ellman's reagent = 0.076 mequiv/g.

Colloidal Silica-Bound Propanesulfonic Acid in Water (9). All but 50 mL of solvent was removed from 200 mL of **8** on a rotary evaporator. Then 50 mL of water was added to precipitate the solids. The functionalized silica was separated by vacuum filtration and washed with 300 mL of 2 M HCl, with water until the filtrate was neutral, and with acetone, ethyl ether, acetone, and water. The silica was redispersed in 75 mL of water by sonicating for 6 h to give **9**.

Ion-exchange capacity = 7.63×10^{-3} equiv/mL.

Preparation of Triphenylmethyl Fluoride. Potassium fluoride (24.74 g, 426 mmol) was placed in a flame-dried 250-mL three-necked flask fitted with a Dean–Stark trap and condenser. Toluene (100 mL) was added and refluxed for 4 h under nitrogen to remove 0.25 mL of water, and 16.36 g (58.7 mmol) of triphenylmethyl chloride in 100 mL of dry acetonitrile was added and refluxed. After 5.0 h, the progress of the reaction was checked by GC (20% SE-30; injection temperature 250 °C; TCD temperature 300 °C; column temperature 150 °C for 3.0 min, then rising to 250 °C at 25 °C/min). It showed 96.5% triphenylmethyl fluoride (t_R = 8.37 min) and 3.5% triphenylcarbinol (t_R = 9.42 min). No unreacted triphenylmethyl chloride remained. The triphenylmethyl fluoride was extracted from the acetonitrile with 12 × 75 mL portions of hexane. The hexane was removed under vacuum giving 12.61 g (82%) of a pale yellow solid, which was >99% triphenylmethyl fluoride by GC analysis: mp = 103–104.5 °C. IR: 3000, 1450, 1376, 1038, 917, 746 cm^{-1}.

Anal. Calcd: C, 86.98; H, 5.77; F, 7.24. Found: C, 86.77; H, 5.81; F 7.11.

Triphenylmethyl Fluoride Hydrolysis. Hydrolysis reactions were run in a Teflon bottle using a wrist-action shaker for mixing. Triphenylmethyl fluoride (2.62 g, 0.01 mol, 0.1 M) and either 1.0 or 0.20 mmol of acid catalyst were placed in enough THF to give 70 mL of solution. This solution was placed in a 45.0 °C water bath for 30 min and then 30 mL of water (45 °C) was added to start the reaction. At timed intervals, two 1.00-mL samples were taken and worked up in the following way.

Sample A. The sample (1.00 mL) was added to 20.0 mL of pH 5.0 buffer (0.10 M acetic acid/0.17 M sodium acetate). The fluoride concentration was determined by using a fluoride ion selective electrode, from a standard plot of mV vs log $[F^-]$. Sample A gave a measurement of [HF] in the reaction mixture: $[HF] = 21[F^-]_A$, where $[F^-]_A$ = measured $[F^-]$ for sample A, and the dilution factor = 21.

Sample B. The sample (1.00 mL) was added to 2.00 mL of 2.0 M NaCl. In the case of the colloidal catalyst, this caused precipitation, and the silica was removed by filtration. Then 1.00 mL of 0.05 M NaOH and 60 mL of 70% THF/30% water (v/v) were added, and the mixture was boiled for 2 h in a Teflon beaker covered with a watchglass to hydrolyze unreacted triphenylmethyl fluoride. After 2 h, the watchglass was removed and the solvent was distilled off. Then 20.0 mL of pH 5.0 buffer was added, and $[F^-]$ was determined by a fluoride ion selective electrode. Since all unreacted triphenylmethyl fluoride was hydrolyzed before analysis, sample B gave a measurement of the total fluorine concentration where $[F]_{total} = 20[F^-]_B = [HF] + [(C_6H_5)_3CF]$. Since [HF] was determined from sample A, $[(C_6H_5)_3CF]$ can be calculated.

The initial rate constant was determined for disappearance of triphenylmethyl fluoride during the first 20% of the reaction where pseudo-first-order kinetics were followed, by plotting log $[(C_6H_5)_3CF]$ vs time and determining the slope by linear least-squares analysis.

Diazinon Hydrolysis. A stock solution of 2.508×10^{-2} M diazinon in acetone was prepared. From this stock solution, 1.00 mL was placed in a 250-mL volumetric flask, and the acetone was removed by passing a stream of nitrogen over it. The volumetric flask was filled with water and the diazinon was dissolved by placing it on the wrist-action shaker for 1 h, giving a 1.003×10^{-4} M solution.

A 1.00-mL portion of this solution was placed in a UV cell equilibrated to 62.00 ± 0.2 °C, and 1.00 mL of a 62 °C solution of 3.00×10^{-3} M acid in water (for the soluble catalyst), or 1.00 mL of water and 3.00×10^{-6} equiv of insoluble catalyst were added to start the reaction. This gives 6.69×10^{-5} M diazinon and 1.00×10^{-3} M acid in the reaction mixture.

The reaction was carried out in a UV spectrophotometer at 62.0 ± 0.2 °C with magnetic stirring. The progress of the reaction was followed by measuring the absorbance every 4 min at 229 and 274 nm, where ϵ is 6130 and 1500 for the diazinon and 22 000 and 9400 for the 2-isopropyl-4-hydroxy-6-methylpyrimidine. The Beer's law plots for both diazinon and product were linear over 6.0×10^{-6} to 1.0×10^{-4} M range of concentration.

The concentrations of diazinon and product were calculated by using $A = A_1 + A_2 = e_1bc_1 + \epsilon_2bc_2$ and solving simultaneous equations for the absorbances at 229 and 274 nm. Using at least 25 data points, –log [diazinon] vs time was plotted, and the slope was determined by linear least-squares analysis. In cases where absorption of diazinon and product occurred, the concentration of diazinon free in solution was determined from [total] – [product], where [total] is the constant total concentration of (diazinon + product) at the end of the reaction and [product] is the measured concentration of the product. This excludes the adsorbed compounds from the calculation and gives the rate of hydrolysis of unadsorbed diazinon.

All reactions followed pseudo-first-order kinetics when using this data analysis. Standard deviations of data points within one run were <2.5%. Duplicate reactions gave results within 3% of the average value reported in Table II.

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