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Microenvironmental Effect in Polymer-Supported Reagents. 2. The Prins Reaction and the Influence of Neighboring Group Content on Catalytic Efficiency

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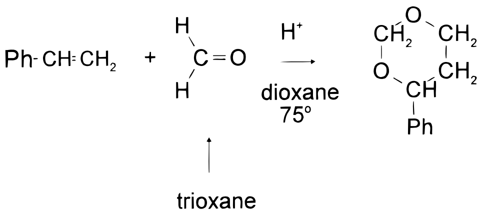
ABSTRACT: The microenvironmental effect on catalysis is quantified by the *neighboring group content*. Opposing variables in the reaction mechanism are then identified by the *critical neighboring group content*. The Prins reaction between formaldehyde and styrene is probed in the present study with immobilized sulfonic acid ligands as the catalyst. Cross-linked polystyrene beads were sulfonated to varying degrees of substitution. Styrene was also copolymerized with butyl methacrylate and methyl methacrylate followed by complete sulfonation of the phenyl rings. The reaction kinetics were correlated with the neighboring group content, defined as the mole percent of neighboring groups (i.e., phenyl, carbobutoxy, or carbomethoxy) relative to the total sites (neighboring and sulfonic acid) in the polymer. Increasing the phenyl group content from 0 to 25% (i.e., decreasing the degree of substitution from 100 to 75%) increases the rate constant from 23.1 to 56.2 M^{-1} s^{-1} while a further increase lowers the rate constant. The carbobutoxy and carbomethoxy groups show the same trend, but the neighboring group content at which the maximum rate constant is observed (i.e., the critical neighboring group content, CNGC) shifts to 15 and 10%, respectively. The rate constants are lower at the CNGC when phenyl groups are replaced by ester groups. When the neighboring group content increases from 20 to 55%, the rate constant decreases 3-fold with phenyl groups, 5.5-fold with carbobutoxy groups, and 12-fold with carbomethoxy groups. A less ionic microenvironment may allow for a higher concentration of styrene within the polymer and lead to an immediate reaction with protonated formaldehyde. When sulfonation drops below a given level, product formation decreases due to slower formation of protonated formaldehyde. The critical neighboring group content can thus be an important variable in tuning the performance of a catalyst for a given reaction through an optimum microenvironmental effect.

Introduction

Polymer-supported sulfonic acids have been used to catalyze numerous organic reactions.[1,2] Heterogeneous catalysts have many advantages, including ease of handling, eliminating corrosion, and adaptability to continuous processes. Successful applications include esterification of palmitic acid with isobutyl alcohol,[3] dimerization of α-methylstyrene,[4] transesterification of ethylene carbonate,[5] and monoacylation of 1,*n*-diols.[6] Sulfonic acid resins have also been used in preparative reactions such as the synthesis of aldylphenols,[7] bisphenol A,[8] and methyl *tert*-butyl ether.[9]

The Prins reaction is the acid-catalyzed condensation of aldehydes with olefins to give 1,3-diols, 1,3-dioxanes, and unsaturated alcohols.[10] Recent applications include its use in the synthesis of prostaglandins,[11] (±)-*β*-isocomene,[12] antibiotics,[13] and nucleosides.[14] Equilibrium studies using commercially available sulfonic acid resins have been published.[15−18] Significant improvement in the product yield has been observed: the condensation of paraformaldehyde with 4-methoxystyrene in the presence of H_2SO_4 gives a 61% yield after 6 h whereas there is a 97% yield with Lewatit SP 120 after 0.5 h.[16]

It has been found that the microenvironment surrounding an active site in a polymer-supported reagent can play an important role in determining the rate and yield of product formation.[19−21] Additionally, it has been proposed that the microenvironment within a polymer-supported reagent can be tailored to a given reaction in order to optimize performance.[21] This report further examines the mechanism by which the microenvironmental effect can be tuned to a given reaction for optimum kinetics and product yield. The Prins reaction between formaldehyde and styrene (eq 1) is used to probe the effect of differences in the groups neighboring the active site. The results will be compared to those for the small molecule analogue.



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Experimental Section

The suspension polymerization of styrene to form either microporous (i.e., gel) or macroporous (MR) beads has been detailed.[22] Copolymers of styrene with butyl methacrylate or methyl methacrylate at mole ratios noted in the text are prepared in an identical manner. Reactivity ratios of both methacrylates with styrene indicate that random copolymers are formed.[23,24] The degree of cross-linking is either 2% or 10% divinylbenzene (DVB), as noted.

Fully functionalized sulfonic acid resin was synthesized from 50 g of cross-linked polystyrene beads in a 500 mL round-bottom flask equipped with an overhead stirrer. The beads were swollen in 400 mL of ethylene dichloride (EDC) at room temperature for 1 h and then cooled to 0 °C. Chlorosulfonic acid (113.51 g) in 60 mL of EDC was added dropwise through

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an addition funnel. The mixture was stirred for 24 h during which time cooling was removed and the temperature increased to 25 °C. The beads were washed twice with EDC, dioxane, and a 4:1 (v/v) dioxane/water solution, each with 15 min stir times, and then with water until neutral. The resin was placed in a glass frit funnel and eluted with 1 L of H_2O, 1 N NaOH, H_2O, 1 N HCl, and H_2O, each for 1 h. Elution with 500 mL of ethanol, acetone, and isooctane and then drying at 70 °C in vacuo for 48 h gave the final polymer.

Partial sulfonation was achieved with stoichiometric amounts of chlorosulfonic acid. For example, a 2% DVB cross-linked resin with 45% functionalization can be prepared by reacting 100 g of copolymer beads (calculated to have 0.917 mol of phenyl groups) with 0.413 mol of chlorosulfonic acid. The synthesis procedure is the same as that for the fully functionalized resin. All resins were characterized by their acid capacities.

The Prins reaction was carried out by first dissolving 13.00 g of styrene and 15.00 g of 1,3,5-trioxane in 55.00 g of 1,4-dioxane. The solution was added to a 100 mL three-necked, round-bottom flask equipped with an overhead stirrer, thermometer, and condenser. The solution was stirred at 252 rpm and heated to 75 °C, and the zero-time sample was taken just prior to the addition of catalyst. Constant temperature was maintained with a regulator. Microliter samples were taken and analyzed gas chromatographically using 1,4-dioxane as the internal standard. Calibration curves were determined for styrene and 4-phenyl-1,3-dioxane. Percent conversion was calculated from the decrease in the styrene peak and percent yield from the increase in the product peak.

The gas chromatograph was a Hewlett-Packard model 5890 with an injection port, flame ionization detector, and a 15 mm × 0.53 mm × 1.5 μm dimethylpolysiloxane capillary column. It was connected to a Hewlett-Packard model 3353A recording integrator. The injection port and detector temperatures were 275 and 325 °C, respectively, the flow rate was set to a head pressure of 70 kPa, and the oven was set to increase 15 °C/min from 35 °C. A Hamilton 7000 series 1 μL positive displacement syringe was used for 0.1 μL injections of solution.

Results

A series of sulfonic acid resins was synthesized from the corresponding cross-linked copolymer beads prepared via suspension polymerization. To determine whether there was a microenvironmental effect at the site of catalysis, the sulfonate ligands were surrounded by varying ratios of three different neighboring groups (phenyl, carbobutoxy, and carbomethoxy). The ligands were immobilized on to polystyrene, poly(styrene-*co*-butyl methacrylate), or poly(styrene-*co*-methyl methacrylate) by reaction with chlorosulfonic acid after swelling the beads in ethylene dichloride. Studies with sulfuric acid have shown that in the absence of swelling solvent the beads are sulfonated from the shell in toward the core,[25,26] while in the presence of solvent the ligands are distributed throughout the particle to give uniform substitution.[26] After the reaction was complete, the beads were washed with ethylene dichloride, 1,4-dioxane, aqueous dioxane, and water. This mild hydrolysis resulted in beads that were free of cracks and thus appropriate for rate studies.

Partial sulfonation of polystyrene is achieved with stoichiometric amounts of chlorosulfonic acid, thus allowing for varying amounts of hydrophobic phenyl groups neighboring the catalytically active sulfonic acid sites. For example, a 2% DVB cross-linked resin with 45 mol % acid sites can be synthesized by reacting 100 g of polystyrene (0.917 mol of phenyl groups) with 0.413 mol of chlorosulfonic acid. The resin has a theoretical acid capacity of 3.10 mequiv/g and an experimental value of 3.07 mequiv/g. The resin beads are uniformly transparent when viewed under a microscope. The neighboring group content, defined as the mole percent of neighboring (i.e., inert) groups in the total number of sites, and the corresponding acid capacities are given in Table 1.

Table 1. Polymer-Supported Sulfonic Acid Catalysts Prepared for the Prins Reaction[a]

neighboring group	neighboring group content[b] (%)	acid capacity (mequiv/g) experimental	acid capacity (mequiv/g) theoretical
phenyl	0	5.18	5.29
	15	4.76	4.80
	20	4.56	4.62
	41	3.81	3.78
	55	3.07	3.10
	80	1.55	1.60
	92	0.65	0.69
carbobutoxy	8	4.83	4.95
	15	4.85	4.64
	20	4.21	4.42
	33	4.09	3.82
	58	2.84	2.64
	65	1.90	2.13
	75	1.39	1.60
carbomethoxy	10	4.83	4.97
	20	4.59	4.65
	41	3.88	3.85
	55	2.97	3.10
	75	2.21	1.94

[a] Copolymers cross-linked with 2% DVB. [b] (Neighboring group capacity)/(neighboring group + sulfonic acid capacities) × 100.

Resins with carbobutoxy and carbomethoxy neighboring groups were prepared by first copolymerizing styrene/DVB with either butyl methacrylate or methyl methacrylate. Subsequent chlorosulfonation of the poly(styrene-*co*-alkyl methacrylate) leads to reaction on the phenyl rings and no ester hydrolysis. FTIR spectra of the copolymer and the sulfonated resin show that the carbonyl peak remains unchanged at 1720 cm^{-1}. The agreement between the experimental and theoretical acid capacities, which are based solely on the number of phenyl rings, further confirms that sulfonation occurs on the phenyl rings without ester hydrolysis. The neighboring group content and acid capacities of the resins are given in Table 1.

The Prins reaction was carried out with 1,3,5-trioxane and styrene in 1,4-dioxane as the solvent at 75 °C. The performance of the polymer-supported catalysts was compared to that of the homogeneous analogue, benzenesulfonic acid. Under acidic conditions, the trioxane decomposes to formaldehyde, which then reacts with styrene to give 4-phenyl-1,3-dioxane. The structure of the final product was confirmed by ^1H NMR. Microliter samples of the reaction mixture were analyzed gas chromatographically with dioxane as the internal standard. Calibration curves were used to calculate the concentration of styrene and 4-phenyl-1,3-dioxane.[27]

Homogeneous Catalysis Kinetics. The reaction catalyzed by benzenesulfonic acid shows a linear correlation of styrene concentration vs time,[27] indicating that the reaction is zero order with respect to styrene. The slope of the line is the observed rate constant, k_{obs}. Plotting log k_{obs} vs log [$PhSO_3H$] from a series of experiments where only the acid concentration was varied showed that the reaction is 1.75 order with respect to the catalyst. The same method shows that the reaction is 1.75 order in trioxane. (Slopes and intercepts in all plots are determined by a linear least-squares analysis, with all correlation coefficients greater than 0.9920.) Equation 3 summarizes the rate expres-

Table 2. Reaction of Styrene and 1,3,5-Trioxane Catalyzed by Benzenesulfonic Acid[a]

mmol of $PhSO_3H$[b]	% conv[c]	% yield[d]	equil time (h)	k ($M^{-2.5}$ s^{-1})
7.373	100	49.8	120	0.406
9.112	95.0	46.0	65	0.396
12.14	96.8	50.5	50	0.441
15.46	99.4	56.1	30	0.383
19.62	98.9	54.8	24	0.411

[a] Styrene concentration at 1.563 M and trioxane concentration at 2.083 M in all reactions. [b] In 80 mL solution. [c] Calculated by GC from the decrease in the styrene peak. [d] Calculated by GC from the increase in the product peak.

Table 3. Reaction of Styrene and 1,3,5-Trioxane Catalyzed by Polymer-Supported Sulfonic Acid[a]

trioxane [M]	mmol of SO_3H[b]	% conv[c]	% yield[d]	equil time (h)	k (M^{-1} s^{-1})
1.042	3.401	100	67.7	5.0	20.3
2.778	3.577	100	77.3	2.5	20.5
1.390	3.572	100	71.1	3.5	20.2
2.083	3.593	100	82.1	3.0	18.8
2.083	2.533	100	72.0	4.6	20.4
2.083	5.310	100	75.1	1.6	20.6
2.083	7.127	100	80.5	1.4	18.6

[a] Styrene concentration at 1.563 M and resin particle size at 250−420 μm in all reactions. [b] In 80 mL solution. [c] Calculated by GC from the decrease in the styrene peak. [d] Calculated by GC from the increase in the product peak.

Table 4. Influence of Neighboring Group Content on the Prins Reaction[a]

neighboring group	neighboring group content (%)	% conv[b]	% yield[c]	equil time (h)	k (M^{-1} s^{-1})
phenyl	0	100	83.2	1.00	23.1
	15	100	81.9	0.55	44.4
	20	100	77.9	0.40	53.7
	41	100	75.2	0.85	36.0
	55	100	80.5	1.60	18.6
	80	99.7	82.9	2.50	6.40
	92	100	73.6	6.00	3.35
carbobutoxy	8	100	86.2	0.75	41.4
	15	100	84.8	0.75	42.0
	20	100	83.4	0.65	41.1
	33	100	74.1	0.90	34.6
	58	100	72.2	2.80	7.76
	65	100	60.3	36.0	0.72
	75	99.7	63.2	80.0	0.42
carbomethoxy	10	100	75.2	0.60	43.8
	20	100	79.8	0.80	37.5
	41	100	73.6	1.60	18.2
	55	99.9	67.4	7.00	3.17
	75	99.9	67.4	85.0	0.30

[a] 2% DVB gel resins, 7.20 mmol of sulfonic acid, 1.563 M styrene, 2.083 M trioxane. [b] Calculated by GC from the decrease in the styrene peak. [c] Calculated by GC from the increase in the product peak.

sion for the Prins reaction under homogeneous catalysis conditions. Rate constants calculated on the basis of eq 3 are given in Table 2; the average rate constant is 0.407 ± 0.022 $M^{-2.5}$ s^{-1}.

$$\text{rate} = -k[CH_2CHPh]^0[\text{trioxane}]^{1.75}[PhSO_3H]^{1.75} \quad (3)$$

Heterogeneous Catalysis Kinetics. Heterogeneous catalysis was evaluated with a sulfonic acid catalyst prepared from polystyrene beads with 45% substitution (chosen because it allowed for an accurate measure of the kinetics under a wide range of initial conditions; resins with greater levels of sulfonic acid ligands were too fast to accurately follow by GC under some conditions). The kinetics were found to be zero order with respect to styrene and first order with respect to both trioxane and the catalyst (eq 4). Rate constants calculated on the basis of eq 4 are given in Table 3; the average rate constant is 19.9 ± 0.8 M^{-1} s^{-1}.

$$\text{rate} = -k[CH_2CHPh]^0[\text{trioxane}][\text{mmol of } H^+/\text{mL}_{\text{soln}}] \quad (4)$$

The assumption that the kinetics determined with a given polymer-supported catalyst are valid for similar catalysts with the same functional group has been verified in reactions catalyzed by the sulfonic acid ligand.[28,29]

Effect of Particle Size, Matrix Rigidity, and Macroporosity. Comparable rates of reaction are found with 2% DVB gel resins having particle sizes of 250−420 and 420−600 μm (the smaller size was used in studies reported here). The results are sensitive to matrix rigidity: the fully functionalized 2% DVB gel resin catalyzes the reaction to completion in 1 h (100% conversion, 83.2% yield, 23.1 M^{-1} s^{-1}) while there is only 15% conversion with a 10% DVB gel resin in 25 h (4.0% yield). The rate increases significantly when the 10% DVB matrix is prepared with 50% pore volume. The 500−1000 Å macrochannels[30] allow rapid access to the ligands which leads to complete reaction within 0.1 h (100% conversion, 82.8% yield, 196 M^{-1} s^{-1}). The MR resin thus outperforms the lightly cross-linked gel resin since porosity compensates for a highly rigid matrix in a diffusion-controlled reaction.

Microenvironmental Effect. The effect of neighboring groups on catalysis by the sulfonic acid ligand was evaluated by surrounding that ligand with varying amounts of phenyl, carbobutoxy, and carbomethoxy groups. The neighboring group content was defined as the mole percent of inert (i.e., phenyl or ester) groups to total (inert and catalyst) groups present. Microporous supports cross-linked with 2% DVB were used; reaction with macroporous resins was too rapid to allow for an accurate determination of a microenvironmental effect on the reaction rate. The rate constants are reported in Table 4, and each entry is the average of two runs (each average is within 5% of the individual runs).

Starting with a fully functionalized sulfonic acid resin, the phenyl group content is increased from 0 to 92% (i.e., the degree of substitution is decreased from 100 to 8%). Figure 1, fitting the data from Table 4, shows that when the phenyl group content increases from 0 to 25%, the rate constant increases from 23.1 to 56.2 M^{-1} s^{-1}. Over this composition, the catalytic activity is inversely proportional to the acid capacity. When the phenyl group content increases above 25%, the catalytic activity decreases with decreasing acid ligand content. A maximum reaction rate is thus achieved when the neighboring group content reaches a critical value (25% when the neighboring group is phenyl). Changing the neighboring group to carbobutoxy and carbomethoxy does not change the correlation found with the rate constant (Figure 1) but does shift the critical neighboring group content (CNGC) at which the maximum rate constant is observed to 15 and 10%, respectively. Figure 1 also shows that the maximum reaction rate at the CNGC is lower when phenyl groups are replaced with esters (56.2 vs 42.0 and 43.1 M^{-1} s^{-1} for the phenyl, carbobutoxy, and carbomethoxy groups, respectively, compared to

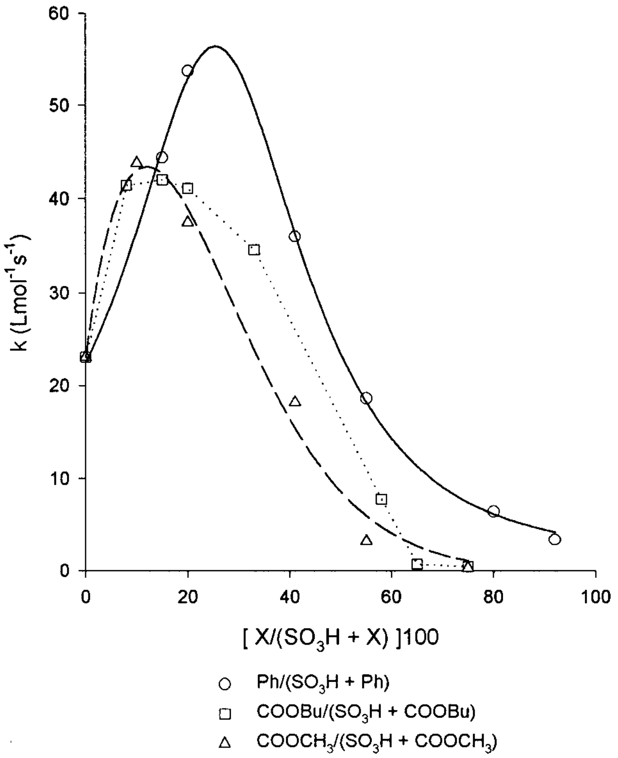


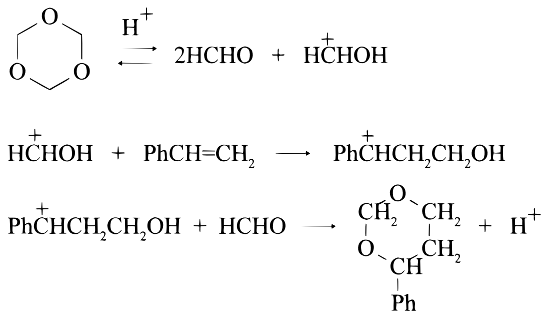
Figure 1. Microenvironmental effect on the reaction rate by varying the neighboring group content.

23.1 M^{-1} s^{-1} for the fully functionalized polymer). At the CNGC, all three resins have complete reactant conversion and comparable product yield, values which are similar to the fully functionalized resin. The four resins have an equilibration time of 1 h or less. When the neighboring group content increases from 20 to 55%, the rate constant decreases approximately 3-fold with phenyl groups, 5.5-fold with carbobutoxy groups, and 12-fold with carbomethoxy groups. The rate constants approach zero when the neighboring group content is 75% for both esters (0.42 and 0.30 M^{-1} s^{-1} for the carbobutoxy and carbomethoxy groups, respectively, at equilibration times of approximately 80 h) while a phenyl group content of 92% still gives a rate constant of 3.35 M^{-1} s^{-1} with a 6 h equilibration time.

Discussion

The homogeneous and heterogeneous Prins reactions follow different kinetics, and this does not allow direct comparison of the rate constants. However, product formation is much more rapid with the polymer-supported catalysts than with benzenesulfonic acid. In the homogeneous reaction, it is likely that the mixed order is due to comparable rates of trioxane decomposition and subsequent styrene–formaldehyde condensation. The latter reaction is subject to general acid catalysis,[31,32] and it proceeds through a protonated formaldehyde carbocation.[10,31] If this is the slow step, no trioxane should be found at the end of the reaction, yet it is present even after all of the styrene is consumed. On the other hand, trioxane decomposition has a first-order dependence on both trioxane and the homogeneous acid catalyst.[33] If this is the rate-determining step, the overall reaction should be second order, which is not the case. In the heterogeneous reaction, the overall reaction is second order, suggesting that the kinetics are determined by trioxane decomposition. The results are consistent with a mechanism wherein protonated formaldehyde formation is followed by a rapid reaction with styrene (Scheme 1).

Scheme 1



The dependency of the kinetics on the neighboring group content has been observed in the acid-catalyzed hydrolysis of benzophenone azine to hydrazine:[25] the reaction rate is maximized when there is one sulfonic acid group per five phenyl rings. Additionally, in the polymer-supported sulfoxide-catalyzed reaction of 1-bromooctane with sodium iodide,[34] the reaction rate increases almost 50-fold to a maximum when the mole ratio of phenyl to total sites increases from 0 to 50%. This suggests that both the catalyst ligand and the polarity of the microenvironment around the active sites affect the reaction rate. In the present case, a less ionic microenvironment may allow for a higher concentration of styrene within the polymer and thus lead to an immediate reaction with the protonated formaldehyde once it forms. However, when the acid content drops below a certain level, product formation decreases due to a lower level of trioxane decomposition and slower formation of protonated formaldehyde.

When the microenvironment is altered by replacing sulfonic acid sites with ester groups, the same general trend is found as with phenyl groups: the rate increases compared to the fully functionalized sulfonic acid resin but to a lower level and to a lower CNGC relative to what is found with phenyl groups (15 and 10% for the carbobutoxy and carbomethoxy groups, respectively) before the rate begins to decrease. Thus, the decrease in polarity caused by removing sulfonic acid sites may improve compatibility of the polymer for the styrene but to less of an extent than with phenyl groups due to the inherent polarity of the ester groups themselves. The earlier and more severe decrease in catalyst activity with further increases in ester group content may then be due to a decrease in the sulfonic acid content as well as a decrease in catalytic activity of the remaining acid sites through hydrogen bonding with the carbonyl moieties. That the effect is more pronounced with the more polar carbomethoxy group rather than the carbobutoxy group is consistent with this. The critical neighboring group content can thus be an important variable in tuning the performance of a catalyst for a given reaction through an optimum microenvironmental effect.

Conclusion

Polymer-supported sulfonic acid catalysts significantly outperform the small molecule analogue in the Prins reaction of styrene with 1,3,5-trioxane. Their catalytic activities are influenced by the microenvironment surrounding the acid ligands. The high acid ligand density within the polymer is probably most important in determining the catalytic activity and that activity is accentuated or attenuated by the neighboring group content. Opposing variables in the reaction mechanism are identified by correlating the rate constant with the neighboring group content and finding a nonlinear relationship. The catalyst ligands have their optimum microenvironment at the point where the neighboring group content corresponds to the maximum rate constant (i.e., at the critical neighboring group content).

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