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Ion Exchange Resin Catalyzed Addition of Alcohols to Olefins

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An experimental study was carried out on addition of alcohols to tertiary olefins catalyzed by a macroporous sulfonic acid resin. The ion exchange resin displays an activity higher than soluble anhydrous *p*-toluenesulfonic acid.

The reactivity of primary alcohols with isobutene follows the order:

n-butanol > *n*-propanol > ethanol > methanol,

while the reaction of isobutene with an equimolar mixture of *n*-butanol and methanol leads to a preferential formation of methyl ether.

Between methanol and isobutene, kinetic orders were determined with respect to the concentrations of the reactants and SO_3H groups.

2-Methyl-1-butene and 2-methyl-2-butene give at the same time alcohol addition and double bond isomerization, while 3-methyl-1-butene does not react at all.

These results suggest that a carbonium ion can be the common intermediate and that olefin protonation is a more important kinetic step than the interaction with the nucleophile. The observed high order on SO_3H groups can be related to a nonlinear dependence of protonating power of the resin on the concentration of sulfonic groups.

INTRODUCTION

It has been extensively shown that ion exchange resin catalysts can be successfully employed in almost all the reactions homogeneously catalyzed by acids or bases (*1*). Nevertheless, only recently has substantial progress been made in distinguishing the different conditions under which the resins can operate and in the rationalization of the corresponding reaction mechanisms. We considered it interesting to try to explain the reactivity of tertiary olefins with alcohols on acidic resins with this more recent knowledge.

The reaction which leads to alkyl-tert-alkyl ethers was discovered by Reychler in 1907 (*2*), but in the literature we find no specific scientific work later than that of Evans and Edlund in 1936 (*3*); specifically we have not found any kinetic study either in homogeneous or in heterogeneous phase, unlike the similar reaction of olefin hydration, for which the literature is quite rich. This is somewhat surprising, since the alcohol addition offers, unlike hydration, the experimental opportunity of searching over a wide range of reactant ratios without miscibility limits and of emphasizing the role of the protic reagent, owing to the possibility of changing the alcohol characteristics.

ION EXCHANGE RESIN CATALYSIS IN THE LIQUID PHASE

According to the Helfferich approach, catalysis performed in the liquid phase on acidic resins in the absence of diffusion limitation is conveniently described as a homogeneous catalysis confined within the catalyst mass, wherein reactants, products and solvent are in distribution equilibrium with external solution (*4*). In this picture the same reaction mechanism is displayed by resins and corresponding dissolved electrolytes; experimental differences in catalytic performance are generally attributed to the selective swelling of the polymer network (*4*).

Efforts have been made to substantiate the concept of internal homogeneity which is the basis of the Helfferich model. For gel-type resins this concept may be quite intuitive at least on a colloidal scale if not on a molecular level (*5*), while for macroporous resins, wherein the internal solvent is distributed between gel and pores (*6*, *7*), the homogeneity concept may not be so clear.

The presence of a single NMR peak for the hydroxylic proton of water or alcohols adsorbed on acidic gel or macroporous resin (*7–9*), suggested to Frankel (*7*) that the rate of exchange of the solvent molecules between the various internal physical-chemical situations, gel and pores included, is orders of magnitude faster than that between external and internal solvent. In this picture the term "quasi-homogeneous" for ion exchange resin catalysts can be well accepted. The Helfferich approach agrees with many experiments, particularly those performed in dilute aqueous solutions (*4*, *10*), but the application of such a model, wherein linear relationships are assumed between reactant concentrations in the external solution and those at reactive sites within the resin, failed sometimes to fit the data over the full range of conversion.

Improved interpretation is then often obtained using approaches traditional to heterogeneous catalysis and based on classical models such as Langmuir–Hinshelwood or Rideal (*11–15*). Such an approach, according to Bochner *et al.* (*11*), assumes that a specific competitive adsorption of one or more molecules of reactants or products with hydrogen counterions essentially fixed at sites near the resin skeleton, causes local concentrations of sorbed species to be different from their values in the pore liquid, even though a linear distribution law may correctly relate concentrations in the bulk liquid and in the pore liquid. For instance, the detrimental effect of water formed in alcohol dehydration (*2*, *12*) and esterification (*11*) is well understood as an adsorption competitiveness. Recently, Gates and coworkers (*16–17*) pointed out that an excess of water or alcohol can shift the catalytic species from the more active undissociated sulfonic acid (general acid catalysis) to the less active solvated proton (specific acid catalysis). This mechanism agrees with ir investigations which show a network of hydrogen bonded SO_3H groups in anhydrous resin or in the absence of hydrogen bond acceptors (*17–19*); polar substances break up this array, first inserting a few molecules in the hydrogen bond structure and ultimately, as their concentration increases enough, dissociating and solvating the protons (*17*, *18*, *20*).

In general acid catalysis, the rate determining step is the interaction between two adsorbed molecules, as in alcohol dehydration (*12*, *21*), or between adsorbed and nonadsorbed molecules as in isobutene dimerization (*15*); when the functional groups transfer the proton to the solvent (specific acid catalysis) the localization of reaction on sulfonic acid groups is no longer possible and the system appears to be similar to a homogeneous solution.

Another interesting behavior of ion exchange resin catalysis is the nonlinear dependence of the reaction rates on sulfonic group concentration as found by Uematsu in butene isomerization (*22*) and by Gates *et al.* in butanol and formic acid dehydration (*17*, *23*, *37*) and in benzene-propylene alkylation (*24*). In these works, resins with low content of acid groups have always been obtained by partial neutralization of commercial resins. The nonhomogeneity of the acid centers is the basis of the Uematsu interpretation, so that the neutralization, preferentially proceeding from stronger sites to weaker ones, deactivates the catalyst in a nonlinear way (*22*). Gates *et al.*, on the other hand, supposed that at high acid group concentration the butyl alcohol dehydrations involved a nonionic concerted mechanism with nearly four SO_3H groups (*17, 23*): the insertion of SO_3Na groups would break up the network, preventing the concerted mechanism and shifting it toward a less effective ionic one. Since the strong dependence of rate on acid group concentration has been shown for the ionic reactions too, Gates supposed in that case a carbonium ion solvated by an acid group network, wherein the proton deficiency has been shared among the interconnected groups (*29*). The neutralization, breaking the counterion array, strongly reduced the carbonium ion stability and therefore the catalytic activity.

EXPERIMENTAL METHODS

Catalyst Preparation

Macroporous Amberlyst 15 resin was used (*25, 26*); samples containing lower free acid group concentrations have been obtained from original samples by partial neutralization with aqueous sodium bicarbonate. The resins were washed with distilled water, dried in air and heated to constant weight under vacuum; the catalyst samples were stored in sealed vials. Anhydrous *p*-toluenesulfonic acid was obtained from reagent grade monohydrate by azeotropic distillation with toluene and vacuum treatment to constant weight; titrations with standard NaOH indicated that anhydrous acid was obtained.

Reagents

1. *Olefins.* The following materials were used: isobutene polymerization grade, purity $\geqslant 99\%$; 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene reagent grade; C_4 olefins cuts, at high and low isobutene content, the composition of which are reported in Table 1. Mixtures of various isobutene content were prepared by mixing the low isobutene cut with pure isobutene.

2. *Alcohols.* Reagent grade methanol, ethanol, *n*-propanol and *n*-butanol, dried and stored over 4 Å molecular sieves, were used.

3. *Ethers.* Alkyl-tert-alkyl ethers for chromatographic standards were obtained by the Williamson reaction and characterized by MS and NMR.

Analytical Methods

The titration of acid groups in the resins was performed according to Fisher and Kunin (*27*).

Reactant and product analyses were performed by glc using a C. Erba Fractovap chromatograph and the following columns:

For separation of hydrocarbons, alcohols and ethers: 2 m of metabis-phenoxy-

TABLE 1

C_4 Olefinic Cuts Composition

	Isobutene	
	High (wt%)	Low
Ethane	—	Tr
Ethylene	—	Tr
Propane	0.19	0.27
Propylene	3.04	0.73
n-Butane	4.35	19.86
Isobutane	0.82	2.96
Butene-1	20.52	59.23
Isobutene	50.26	2.81
cis-Butene-2	8.03	0.25
trans-Butene-2	11.41	13.89
Butadiene	1.36	Tr

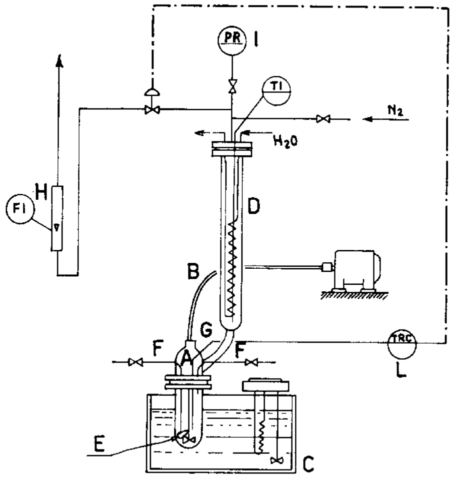

FIG. 1. Apparatus for Kinetic Tests. (A) Reaction vessel, capacity 600 ml; (B) mechanical stirrer; (C) thermostatic bath; (D) cooler; (E) catalyst containing vial; (F) top and bottom inlet; (G) thermocouple; (H) flowmeter; (I) pressure recorder; (L) temperature controller and recorder.

benzene 16% + Apiezon L 4% on Chromosorb W 60–80 mesh and 0.65 m of Diglycerol 70% on Chromosorb P 60–80 mesh; the carrier gas was helium.

For olefin mixture resolution (*28*): 5 m of squalane 10% on Spherosil XOB015 + 2 m of ethyl-hexyl sebacate 25% on Chromosorb P 60–80 mesh; the carrier gas was helium.

Apparatus

Experiments were performed in an autoclave provided with a mechanical stirrer. Reaction heat was removed by maintaining the reaction mixture boiling at the temperature of the experiment by a device controlling the system over-pressure (Fig. 1). Temperature was kept within ±0.5°C.

Procedure and Calculations

A sealed vial containing a weighed amount of catalyst and the corresponding reactants were brought to the temperature of the experiment in the autoclave immersed in a thermostatic bath. The reaction was begun by switching on the mechanical stirrer, causing vial rupture and contacting of the catalyst with the reactants. The overpressure drop provided an indication of the extent of reaction. During the experiment, samples were transferred to chilled capped serum vials, from which syringe samples were taken for glc injections. The kinetic analyses were performed on the initial rates expressed as: moles of ether per acid equivalent × second. The calculation of initial rates was made from the slopes of initial straight lines of experimental ether concentrations plotted versus the time.

RESULTS

Reactions on Amberlyst 15

Variation in stirring rate and in the ratio of the reactants to the resin catalyst mass did not affect reaction rates, indicating that, within the investigated range, liquid phase mass transfer resistance was negligible; induction periods were never observed. Initial rates of methyl-tert-butyl ether formation are plotted in Figs. 2–5 as functions of reactant and acid group concentrations and temperature. The results emphasize:

A zero order dependence of rate on methanol concentration for concentrations

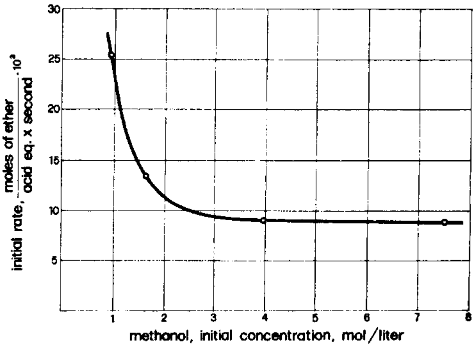

FIG. 2. Methyl-tert-butyl ether synthesis. Initial rate dependence on initial methanol concentrations at constant isobutene content (4 mol/liter). Temperature: 60°C; catalyst: Amberlyst 15.

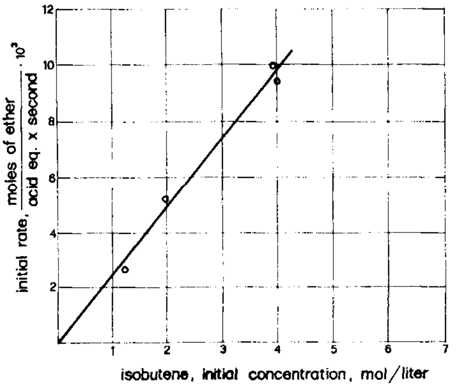

FIG. 3. Methyl-tert-butyl ether synthesis. Initial rate dependence on initial isobutene concentrations at constant methanol content (4 mol/liter). Temperature: 60°C; catalyst: Amberlyst 15.

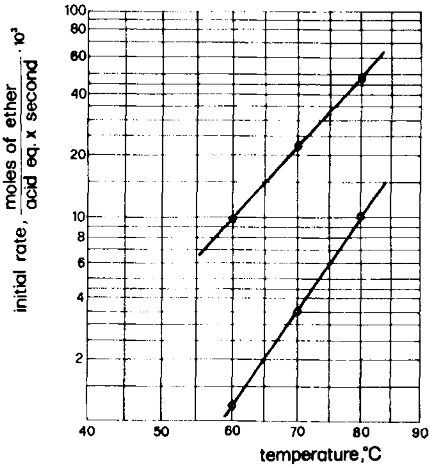

FIG. 5. Methyl-tert-butyl ether synthesis. Initial rate dependence on temperature. Catalysts: (●) Amberlyst 15; (○) anhydrous *p*-toluenesulfonic acid.

greater than 4 mol/liter, with negative orders at lower concentrations (Fig. 2);

A first order dependence of rate on isobutene concentration (Fig. 3);

A strong dependence of rate on acid group concentration, about third order (Fig. 4);

An activation energy of about 17 kcal/mol (Fig. 5).

In Fig. 6 the initial reaction rates of isobutene with various primary alcohols are reported; the reactivity order is:

n-butanol > *n*-propanol
> ethanol > methanol.

The data in Table 2 show that the overall reaction rate of the isobutene in equimolar methanol/*n*-butanol mixture lies between the etherification rates of isobutene with

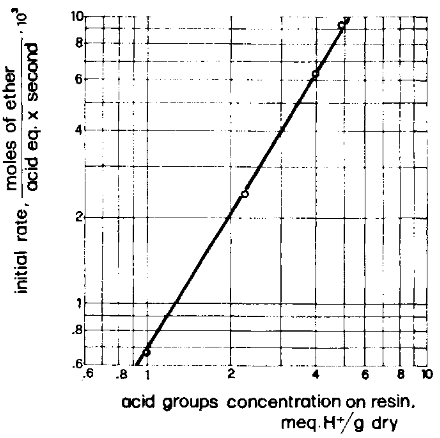

FIG. 4. Methyl-tert-butyl ether synthesis. Initial rate dependence on catalyst acid groups concentrations. Temperature: 60°C; catalyst: Amberlyst 15; reagents concentration: 4 mol/liter.

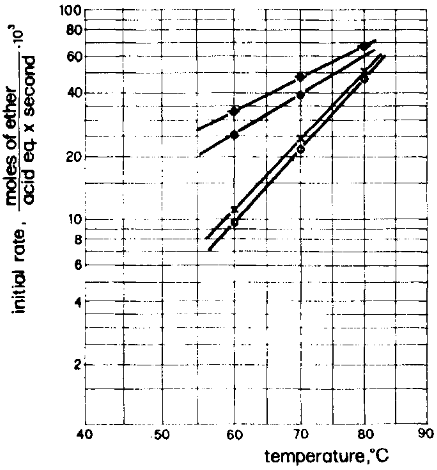

FIG. 6. Normal Alkyl-tert-alkyl ethers synthesis. Initial rate dependence on temperature. Catalyst: Amberlyst 15; (○) methyl-tert-butyl ether; (×) ethyl-tert-butyl ether; (●) *N*-propyl-tert-butyl ether; (⊖) *N*-butyl-tert-butyl ether.

TABLE 2

Initial Reaction Rates of Isobutene with Methanol, *n*-Butanol and Their Mixtures[a]

Protic reagent	Moles of ether/acid equivalent × second	
Methanol	22.4×10^{-3}	
n-Butanol	48×10^{-3}	
Methanol[b]	29.6×10^{-3}	42.3×10^{-3}
n-Butanol[b]	12.7×10^{-3}	

[a] 1:1 molar reagents ratio. Temperature: 70°C; Catalyst: Amberlyst 15.

[b] Methanol 0.5 moles and *n*-Butanol 0.5 moles/Isobutene moles.

methanol and *n*-butanol separately, with a prevalence of the methyl derivative in the reaction products.

Kinetic data for the methanol reaction with the three isomeric isoamylenes appear in Table 3. 2-Methyl-1-butene and 2-methyl-2-butene gave both bond isomerization and alcohol addition; 2-methyl-1-butene had a higher reactivity than 2-methyl-2-butene; 3-methyl-1-butene was unreactive.

Reactions with Anhydrous p-Toluenesulfonic Acid

Figure 5 shows the difference in catalytic activity between Amberlyst 15 and *p*-toluenesulfonic acid at the same ratio of reactant concentration to the number of acid equivalents. This difference, according to the Hammett definition, corresponds to an efficiency ranging between 5 and 8, depending on temperature.

TABLE 3

Initial Reaction Rates between Methanol and Isoamylenes[a]

Olefinic reagent	Moles of olefin/acid equivalent × second		
	Isomerization	Etherification	Overall
2-Methyl-1-butene	8.1×10^{-3}	17×10^{-3}	25.1×10^{-3}
2-Methyl-2-butene	0.7×10^{-3}	7.3×10^{-3}	8×10^{-3}
3-Methyl-1-butene	No reaction	No reaction	—

[a] 1:1 molar reagents ratio. Catalyst: Amberlyst 15; temperature: 70°C.

DISCUSSION

Owing to the swelling selectivity occurring with ion exchange resins (*29*), a correct interpretation of kinetic data cannot be made without an examination of the concentration inside the pores. Unfortunately no experimental data are available on swelling selectivity for alcohol, olefin and ether systems; however, we expect methanol to be preferably adsorbed within a wide range of concentrations. Such a hypothesis agrees with many data (*4*) and with chromatographic delay of the methanol when methanol/olefin mixtures are percolated through an anhydrous Amberlyst 15 bed. The excess of alcohol inside the resin causes the methanol to be the true solvent at the reaction sites; therefore it strongly conditions the resin activity and especially the achievement of a general or specific acid catalysis.

From the dependence of the rate of methyl-tert-butyl ether synthesis upon the methanol concentration, we see a transition from a more active catalyst at low methanol concentrations to a less active catalyst at higher ones. We can suppose, according to Gates and Rodriguez (*16*) and Thornton and Gates (*17*), that at low protic reactant concentration undissociated sulfonic acid groups operate, while, as the concentration increases, the methanol dissociates the acid groups and solvated protons become the catalytic agents; at concentrations greater than 4 mol/liter the methanol is no longer able to affect the rate either as reactant or as solvent, having completely leveled the catalyst activity.

At 4 mol/liter methanol concentration, the reaction shows a first order dependence on isobutene concentration, indicating that the olefin enters into a kinetically important step. According to the hypothesis on the nature of the catalysis, an ionic mechanism is the most probable and the olefin protonation can be seen as the rate determining step. This figure agrees with the behavior of the isoamylenes. In fact, the observed bond isomerization occurring in the isoamylenes during the etherification implies the existence of a carbonium ion as a common intermediate; moreover, the higher overall reactivity of 2-methyl-1-butene vs 2-methyl-2-butene shows that the carbon ion formation is kinetically more important than its interaction with the nucleophile.

Assuming the olefin protonation to be the most kinetically important step, the reaction rate is expected to depend on the following: (i) olefin basicity, (ii) acid strength of the catalytic species, and (iii) olefin distribution between resin and external solution.

The highly selective etherification for olefins having the double bond shared with a tertiary carbon and the inactivity of linear butenes and 3-methyl-1-butene confirms the weight of the olefin basicity, since it is possible to consider more basic the olefins which give, on protonation, the more stable tertiary carbon ion (*32*). The greater reactivity of 2-methyl-1-butene can be explained by an easier protonation due either to less steric hindrance (terminal double bond), or to energetic causes (proton addition on primary carbon).

Since less basic olefins like linear butenes (*22*) and 3-methyl-1-butene (*33*) give typical acid-catalyzed reactions on anhydrous resins and are unreactive in our system, it follows that less active proton donors are operating in the presence of polar solvents such as alcohols. Therefore, the acid strength of catalytic species seems to have a determining effect on the reaction rate. According to this acid–base interaction, the reactivity order experimentally found for primary alcohols should reflect the acidity order of the corresponding solvated protons and be inverse to the basicity order of the alcohols. Such an order agrees with the observed influence of the alcohols on a parameter strongly dependent upon an acid–base interaction, such as the distribution coefficient of *p*-nitroaniline between Amberlyst 15 and external alcoholic solutions (*34*). The Pietrzyk data (*34*), reported in Table 4, show that a shift from methanol to *n*-butanol causes a salting-in effect for the *p*-nitroaniline indicating an acidity increaes.

TABLE 4

Distribution Coefficients of *p*-Nitroaniline on Amberlyst 15, in Several Alcoholic Solvents (*34*)

Solvent	Dielectric constant	D^a
Methanol	32.6	318
Ethanol	24.3	398
n-Propanol	20.1	950
n-Butanol	17.1	1500

[a] D = distribution coefficient

$$= \frac{\text{quantity of amine on resin/g of dry resin}}{\text{quantity of amine in solution/ml of solution}}.$$

A further observation concerning the NMR chemical shift for hydroxylic protons of resin-adsorbed alcohols suggests an acidity increase from methanol to *n*-butanol. In fact the chemical shift follows the order (*9*):

n-butanol > *n*-propanol
> ethanol > methanol.

Since it is possible to associate a greater acidity with a greater chemical shift, it follows that the same order is to be expected in experimental reactivities.

It is interesting to consider the behavior of isobutene with an equimolar methanol/*n*-butanol mixture. The observed overall reactivity, which lies between that of the individual alcohols, can be explained by an intermediate resin acidity; the higher reactivity of methanol has to be attributed to its preferential absorption in the resin rather than to its greater nucleophilicity. We have experimentally determined the distribution coefficients (internal and external mole fraction ratios) for a methanol/*n*-butanol mixture on Amberlyst 15 resin, obtaining 1.14 for the methanol and 0.67 for the *n*-butanol; these values roughly agree with the ratio of the methyl and *n*-butyl derivatives in the reaction products.

The last factor, olefin distribution between resin and external solution, can be strongly dependent on the olefin basicity and on the acid strength of the catalytic species, as found for weak bases such as substituted acetanilides (*30*). In that case an acid–base interaction has been found to be the determining factor for their distribution coefficient.

All our experimental data, therefore, seem to confirm the acid–base nature of the interaction of the olefin with the resin; nevertheless, an interaction between ion and induced dipole could affect the distribution coefficient, according to the high olefin retention time found by Hirsch *et al.* (*31*) in gas–solid chromatography on neutralized macroreticular cation exchange resins. In this kind of interaction the reduction of the dielectric constant from methanol to *n*-butanol (see Table 4) would qualitatively account for the observed increase in reactivity.

C_4 olefin retention times measured on lithium exchanged Amberlyst 15 did not differ enough to account for their reactivity order, indicating that the ion dipole interaction is not a determining factor (*36*).

The nonlinear dependence of kinetics on acid group concentration cannot be attributed to a mechanism involving a hydrogen bonded network of acid groups, as in Gates model, on account of the high alcohol concentration inside the resin, at least at concentrations above 4 mol/liter. Moreover, the lack of homogeneity of acid centers, as supposed by Uematsu, is not in agreement with the "quasi-homogeneous" approach which justifies the other experimental data. It seems possible to advance another hypothesis which is consistent with the homogeneous model and also explains the observed greater efficiency of the resin with respect to the *p*-toluenesulfonic acid. The hydrogen ion concentration inside the resin, either calculated as a molar concentration in the whole volume of swollen resin, or as molal concentration in the volume of the absorbed liquid, reaches very high values (~ 3 equiv/liter). It is also known that in homogeneous catalysis at such levels the reaction rates are not proportional to the acid molar concentration, but follow better Hammett type acidity functions, which express the effective acid strength of the medium. An example of this type is the hydration of isobutene catalyzed by nitric acid (*35*). Since the acidity function increases with an exponent >1 with respect to the hydrogen ion concentration, the hypothesis explains both the nonlinear dependence of rate on the acid group concentration and the greater efficiency of the resin with respect to a homogeneous system which operates with the same acid equivalents, but using more dilute concentrations.

The above hypothesis could have been confirmed by comparing the rate in the resin with the rate in *p*-toluenesulfonic acid solution at a concentration equal to that expected inside the resin. Unfortunately the low solubility of the acid in our reaction medium prevented us from reaching such concentrations.

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