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A Reconsideration of the Kinetics of Aromatic Sulfonation by Sulfuric Acid

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ABSTRACT: The kinetics of sulfonation of aromatics by sulfuric acid is examined in terms of a negative effect of the product, a sulfonated aromatic ring. The systems evaluated in former reports include *atactic* polystyrene in concentrated sulfuric acid, poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) in a mixture of 96.4% sulfuric acid and 99% methanesulfonic acid, and *tert*-butylbenzene in 87.2% sulfuric acid. The sulfonation kinetics of PEEK in 96.3% sulfuric acid has also been studied. For all these examples, the sulfonation rate is found not to be strictly first order in aromatic ring content. Indeed, the rate is found to be inversely first order with respect to the sulfonated aromatic ring, in competition with a first order of unreacted aromatic ring. Literature results are thus more reliably explained by the negative effect of the sulfonated aromatic ring, rather than as a retardation caused by the water produced by the reaction.

Introduction

Aromatic sulfonation has widely been used in chemical synthesis and fuel refining. Various aromatic structures have been sulfonated with sulfuric acid to give the corresponding arylsulfonic acids.[1-5] The sulfonic acid group is strongly acidic and thus useful for modifying the properties of aromatic polymers. Indeed, some of poly(arylsulfonic acid)s have been commercialized; for example, poly(styrenesulfonic acid) is used as a flocculant and a rheology modifier of water.[6] Cross-linked poly(styrenesulfonic acid) is used as an ion exchange resin.[6]

Aromatic sulfonation kinetics are useful for commercial production and have been studied since 1908.[7] Most studies before 1967 have been summarized by Cerfontain,[8] and before 1970, they were reviewed by Taylor.[9]

The following equation has commonly been used to express the aromatic sulfonation rate in aqueous sulfuric acid:[8,9]

$$-\mathrm{d}[\mathrm{Ar}]/\mathrm{d}t = k[\mathrm{Ar}]A_{\mathrm{H_2SO_4}}{}^2/A_\mathrm{w} \qquad (1)$$

wherein [Ar] = concentration of aromatic ring to be sulfonated, $A_{\mathrm{H_2SO_4}}$ = activity of sulfuric acid, which is proportional to the concentration of H_2SO_4 in the system, A_w = activity of water, which is proportional to the concentration of water in the system, k = reaction rate constant, and t = reaction time.

In this expression, the rate is first order with respect to the substrate, the aromatic ring. The second order of the activity of the acid has been rationalized by a reaction of two H_2SO_4 molecules producing the sulfonation species. The effect of water on the reaction species has been considered to result in the reaction retardation and appear as the inverse term.[8,9] These terms may be treated as nearly constant over a narrow concentration range of sulfuric acid. Water as a byproduct is reported to slow aromatic sulfonation,[5] since it dilutes the sulfuric acid to affect the reactivity of the sulfonating species.[8,9] The relationship between the rate and the acid concentration has been studied and summarized.[5,8-12] Generally, the experimental conditions have been carefully chosen to be at a very low concentration of the substrate (aromatic ring to be sulfonated) and/or at low conversion to reduce the effect of water produced in the reaction.

Some reports show that the rate is clearly first order with respect to the substrate.[10-12] In spite of carefully chosen conditions, some data did not follow the simple first-order rate expression with respect to the substrate.[1-4] The rate is seen to gradually slow down from that of the expected first-order rate. It is not possible to attribute the retardation to water. Aromatic sulfonation by sulfuric acid has been known to be complicated by isomerization[13,14] and reversibility,[2,5] as well as by water produced by the reaction. Some arylsulfonic acids have been reported to affect the transition state of aromatic sulfonation in sulfuric acid.[8]

In this paper, a negative effect of the sulfonated aromatic ring on sulfonation and the contribution to the rate expression has been studied. The evaluation has been made from examples in former reports[1-3] for polymers including the authors' experimental results[3] and on a small aromatic.[4]

Results and Discussion

Kinetic Expression. 1. Negative Effect of Sulfonated Aromatic Ring on the Rate Expression. If the quantities of sulfuric acid consumed and the produced water are both very small compared with their initial amounts, the factor of $[H_2SO_4]^2/A_\mathrm{w}$ in eq 1 changes insignificantly. If the product, sulfonated aromatic ring has a negative effect on the sulfonation of the unsulfonated aromatic ring, the contribution may appear as an inverse term in the rate expression as:

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{k_1 C}{k_\mathrm{d}(C_0 - C)} \qquad (2)$$

wherein C = substrate concentration at a time t, C_0 = initial substrate concentration (at $t = 0$), k_1 = rate constant of sulfonation, k_d = constant for the negative effect of the product, sulfonated aromatic ring, and $C_0 - C$ = the product (sulfonated aromatic ring) concentration at a time t.

This equation can be integrated from C_0 to C to give eqs 3a and 3b.

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$$-\int_{C_0}^{C}\frac{C_0 - C}{C}\,\mathrm{d}C = \frac{k_1}{k_\mathrm{d}}\int_0^t \mathrm{d}t \tag{3a}$$

$$-\frac{C_0 - C}{C_0} - \ln\frac{C}{C_0} = \frac{k_1}{k_\mathrm{d}}\frac{1}{C_0}t \tag{3b}$$

Here, the concentration of the unreacted substrate is described as:

$$C = C_0(1 - X) \tag{4}$$

wherein X stands for sulfonation conversion. X is zero at the beginning of the reaction and goes to 1 at the end of the reaction. In the case of polymer, X may be regarded as the degree of sulfonation per repeat unit. As a consequence, C in eq 3b is substituted by $C_0(1 - X)$ to give eq 5.

$$C_0\{-X - \ln(1 - X)\} = (k_1/k_\mathrm{d})t \tag{5}$$

The data calculated via eq 5 have been plotted as a function of time in part a of Figures 1, 3, 5, and 6. If the data points fall on a straight line, it is confirmed that the reaction is distinctly affected by a negative effect of the product. The straight line in part a is the least-squares fit of the plots.

2. **First-Order Rate Expression.** Equation 1 may be simplified as eq 6 at nearly constant concentration of sulfuric acid and water.

$$-\mathrm{d}C/\mathrm{d}t = k_1C \tag{6}$$

where k_1 represents the first-order rate constant. This equation can be integrated from the beginning of the reaction ($C = C_0$ at $t = 0$) to a concentration ($C = C_0$ at $t = t$) to give eq 7.

$$-\ln\frac{C}{C_0} = k_1t \tag{7}$$

C in eq 7 may be substituted by eq 4 to give:

$$-\ln(1 - X) = k_1t \tag{8}$$

If the rate is first order with respect to the substrate, a plot of $-\ln(1 - X)$ vs time will fit a straight line.

The data calculated through eq 8 has been plotted as a function of time, which is given in part b of Figures 1, 3, 5, and 6.

Replot and Reinterpretation of Examples. Reports detailed reaction progress in the form of tables and/or plots, by the reaction conditions, and by the analysis method. The data calculated through eqs 5 and 8 give plots shown in parts a and b of Figures 1, 3, 5, and 6, respectively. Published data of acid density vs the acid concentration[15] were used for the calculation of water in sulfuric acid. The standard error (SE) and the zero intercept (ZI) of the linear least-squares fit of the plots are given in Table 1.

Example 1: *Atactic* Polystyrene (PS) Sulfonation. Sulfonation kinetics of polymers in sulfuric acid has also been studied. Akovali and Özkan reported the kinetics of *atactic* polystyrene (PS) with concentrated sulfuric acid from 85 to 125 °C.[1] The viscosity-average molecular weight of the polymer was 1.70×10^5. The substrate was the phenyl ring of each repeat unit of the polymer. Their proton NMR study showed that only the para-position of the phenyl ring in the repeat unit was sulfonated. The sulfonation level was measured by titration to sodium hydroxide solution with phenolphthalein as an indicator. The reaction progression was given in a table and a plot of sulfonation degree vs reaction time. The initial concentration of the PS was 2 g of PS/20 mL of sulfuric acid (0.96 mol of repeat unit/L of sulfuric acid). The concentration of the sulfuric acid used was not cited but was supposedly in the commercial range of 90–100%.

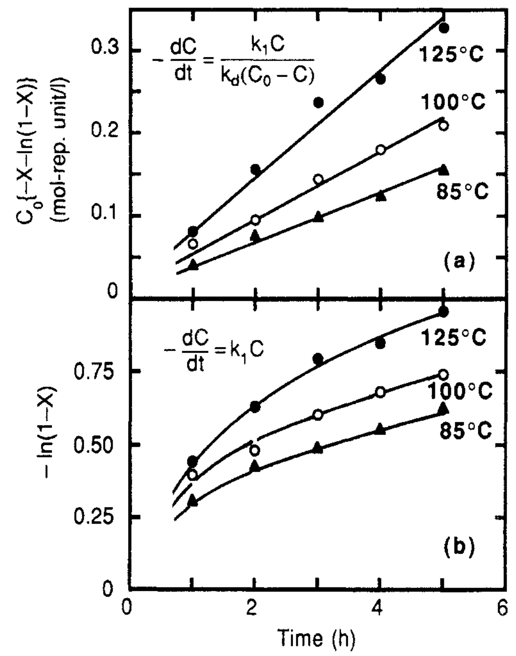

Figure 1. Sulfonation kinetics of *atactic* polystyrene in concentrated sulfuric acid. Replotted from reported data by Akovali et al.[2] X is the degree of sulfonation per repeat unit. a is of the result of the rate treatment according to eq 5, and b is that of the first-order rate treatment.

The plot of Figure 1a fits a straight line for all these experiments (85–125 °C). On the contrary, the data do not agree with a first-order rate expression (Figure 1b). In Figure 1a, each of the least-squares fits of the plots does not intersect (0,0). This may result from a very little contribution of the negative effect of the sulfonated repeat unit in the early stage of the reaction. A heterogeniety of the reaction mixture due to the poor solubility and relatively high viscosity of the polymer may also affect the sulfonation progress in the stage.

Here, assume the initial concentration of sulfuric acid to be 95.0%. For the experiment at 125 °C and for X from 0.357 to 0.616, the amount of water produced is calculated to be 4.9 g/L of sulfuric acid. This amount is 5 wt % of the water (91.4 g/L of sulfuric acid) in the sulfuric acid at X = 0.357. The concentration of sulfuric acid changes from 94.6% to 94.3%, which is within the conversion range (from 0.357 to 0.616), by this estimation. The data in example 1 are consistent with eq 2 but not with eq 1. This implies that the contributions of the water produced and H_2SO_4 consumed are insignificant in this range.

Example 2: PEEK Sulfonation in the Mixture of Sulfuric Acid and Methanesulfonic Acid. Poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) was found to be sulfonated in sulfuric acid by Bishop and co-workers.[16] Jin and his colleagues determined the chemical structure by elemental analysis, IR, and carbon-13 NMR spectroscopy,[17] as given in Figure 2. The substrate is a phenyl ring flanked by two ether groups in the repeat unit, with only one of the four protons being substituted by a sulfonic acid group. Introduction of the strong electron-withdrawing group deactivates the bonding phenyl ring to further sulfonation. Bailly and

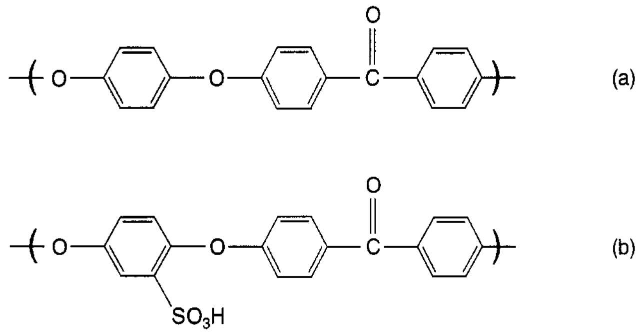

Figure 2. Chemical structure of the PEEK (a) and sulfonated PEEK (b) repeat units.

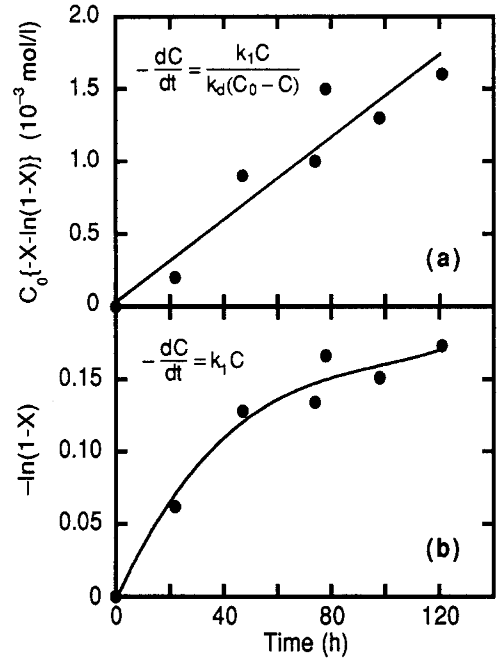

Figure 3. Sulfonation kinetics of PEEK in 2/1 (v/v) acid mixtures of sulfuric acid (96.4%) and methanesulfonic acid (99%) at room temperature. Replotted from the data of Bailly et al.[3] X is the fraction of sulfonation per repeat unit. a and b are the results of the rate treatment according to eqs 5 and 8, respectively.

collaborators found that PEEK was also sulfonated in the mixture of methanesulfonic acid (MSA) and sulfuric acid.[2] They also studied the kinetics of the reaction in this acid mixture with various formulations at room temperature. They found that the sulfonation degree was a function of the fourth power of the sulfuric acid concentration. The data of the reaction progress were given, but a rate equation was not described in the report. For the kinetic measurements, the initial concentration of the polymer was 33.3 g/L of the acid mixture (0.116 mol of PEEK repeat unit/L of the acid mixture). The formulation of the acid mixture was 2/1 (v/v) of sulfuric acid and MSA. The concentration of the sulfuric acid was 96.4% and that of MSA was 99%. The sulfonation degree per repeat unit was determined from the glass transition temperature of the sodium salt. The maximum molar sulfonation degree in these measurements was 0.16 per repeat unit.

The reaction progress was evaluated from the plot in the report.[3] Figure 3a shows a straight line with some deviation, as derived from the original data. This plot indicates that the sulfonated phenyl ring negatively affects the sulfonation of the unsulfonated phenyl ring. The least-squares fit of the plots does not intersect (0,0). This may be derived from a very little contribution of the negative effect of the sulfonated repeat unit in the early stage of the reaction. Also, this may be partly affected by the deviation in the original data. In Figure 3b, the plot of $-\ln(1-X)$ vs time exhibits curvature, showing that the rate is not simply first order with respect to the substrate.

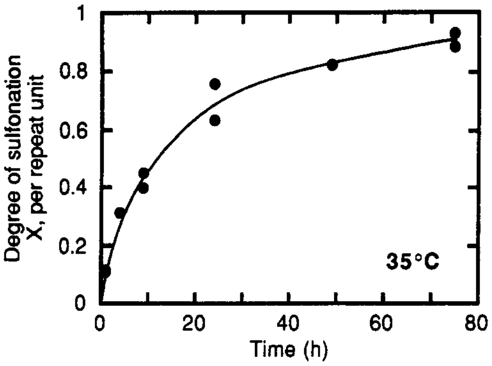

Figure 4. Sulfonation progress of PEEK in concentrated sulfuric acid (96.3%) at 35 °C. X represents the fraction of sulfonation per repeat unit. The origin of the time scale is from the onset of the complete dissolution.

The amount of water produced is calculated to be 0.5 g/L. This is very small (1.2%) compared with that used in the sulfuric acid at the beginning of the reaction (44.2 g/L). The sulfuric acid is calculated to be diluted from 96.4% to 96.3% over the reaction course.

Example 3: PEEK Sulfonation in Concentrated Sulfuric Acid. The sulfonation kinetics in sulfuric acid (96.3%) was measured at 35 °C by these authors.[4] Initial concentrations of PEEK were set at relatively low levels (20.0 g and 0.0217 g of PEEK/L of H_2SO_4) to examine the effect of water produced during reaction. The concentration of sulfuric acid was 96.3%. The chemical structure of sulfonated samples was confirmed by comparison of carbon-13 NMR and IR spectra with a prior report.[16] The reaction progress at 0.0217 g/L was measured by UV-visible spectroscopy. For the experiment at 20.0 g/L, the degree of sample sulfonation was calculated from the sulfur-to-carbon ratio from elemental analysis. The reaction progress at 20.0 g/L is given in Figure 4. The data calculated through eq 5 and through eq 8 were plotted in Figure 5, parts a and b, respectively. The plot of $C_0\{-X-\ln(1-X)\}$ vs time fits a straight line, but that of $-\ln(1-X)$ vs time does not, showing the rate is described as the expression of eq 2 but not eq 6. This indicates the existence of a negative effect derived from the sulfonated aromatic ring in the reaction system. The amounts of water produced by complete sulfonation ($X = 1.0$) are calculated to be 1.25 and 0.00136 g/L, for the experiments at 20.0 and at 0.0217 g/L, respectively, which are very small (1.85% and 0.002%, respectively) compared with that in the original sulfuric acid (67.7 g/L). The reaction progress at 20.0 g/L and at 0.0217 g/L is in agreement within a limit of experimental error. This agreement indicates that the reaction is not sensitive to the water produced in this range. The concentration change of sulfuric acid is calculated to be less than 0.1% at 20.0 g/L. This difference is too small to significantly affect the rate.

Example 4: *tert*-Butylbenzene (TBB) Sulfonation. There is an example to which eq 2 can be applied in the reports for the aromatic sulfonation of small aromatics. Cerfontain and his research group have studied the sulfonation of various aromatics with various concentrations of sulfuric acid and oleum.[4,8,11,13,18] They reported sulfonation and disproportionation kinetics of TBB in aqueous sulfuric acid (87.2%) at 25 °C.[4] The initial concentration of the substrate was 2.52×10^{-4} mol/L. The major product was *tert*-butylbenzenesulfonic acid. Partial

Table 1. Standard Error (SE), the Zero Intercept (ZI), and the Correlation Coefficient (CC) of the Least-Squares Fit of the Plots as the Result of Kinetic Treatments According to the First-Order Rate and the Same with the Negative Contribution of Sulfonated Phenyl Group on the Sulfonation

	SE		ZI		CC	
substrate	1st order with the negative effect	1st order	1st order with the negative effect	1st order	1st order with the negative effect	1st order
PS (85 °C)	0.00382	0.0195	0.0171	0.254	0.9971	0.9905
PS (100 °C)	0.00581	0.0190	0.0281	0.314	0.9963	0.9932
PS (125 °C)	0.0162	0.0471	0.0328	0.360	0.9894	0.9793
PEEK (in MSA + H_2SO_4, rt)	0.000217	0.00187	0.0000615	0.0304	0.9478	0.9472
PEEK (in H_2SO_4, 35 °C)	0.00943	0.224	0.00130	0.267	0.9768	0.9710
TBB (25 °C)	0.000017	0.199	−0.0157	0.127	0.9840	0.9667

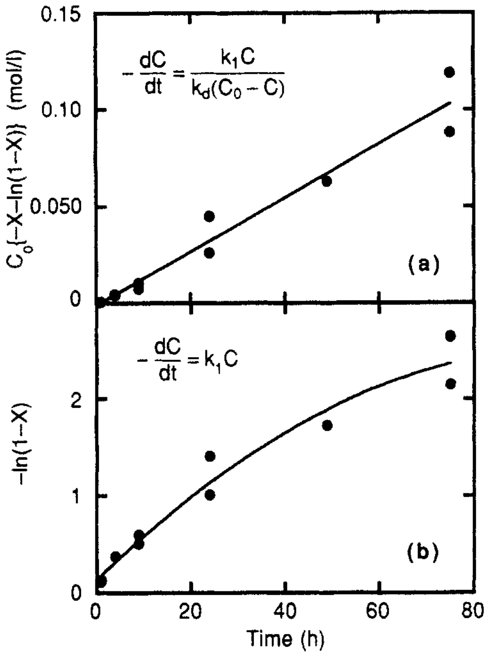

Figure 5. Kinetics of PEEK sulfonation in sulfuric acid (96.3%) at 35 °C. X stands for the fraction of sulfonation per repeat unit. a and b describe the results of the rate treatment conforming to eqs 5 and 8, respectively. The origin of the time scale corresponds to a time after the entire dissolution.

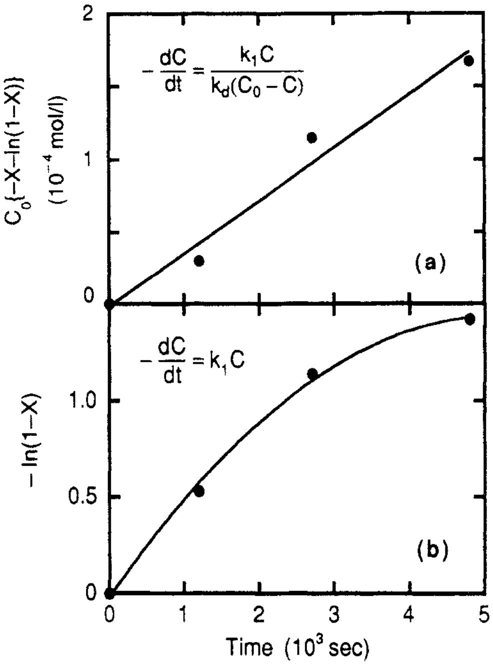

Figure 6. Kinetics of *tert*-butylbenzene sulfonation in aqueous sulfuric acid (87.2%) at 25 °C. Replotted from data reported by Cerfontain et al.[5] a and b indicate the results of the treatment according to eqs 5 and 8, respectively.

dealkylation took place to give benzene and di-*tert*-butylbenzene as minor products. The level of sulfonation was measured by UV–visible spectroscopy.

The results of calculation through eqs 5 and 8 were plotted in parts a and b of Figure 6. The plot of $C_0\{-X - \ln(1 - X)\}$ vs time follows a straight line, consistent with the coexistence of sulfonation and a negative effect to the sulfonation derived from the major product in the system. The plot of $-(1 - X)$ vs time exhibits curvature and is not a straight line. The water produced (2.52×10^{-4} mol/L) for the substrate TBB is calculated to be 4.54×10^{-3} g/L. This amount is negligibly small compared with that of the water (229 g/L) in the sulfuric acid (87.2%).

The statistical data, given in Table 1, were evaluated by a linear least-squares fit of plots according to eq 5 (slant a) and that conforming to eq 8 (slant b). The unit, which is not indicated in the table, is the same as the ordinate given in the plot for each example. The calculation was performed using computer software designated "Microsoft Excel, Version 4.0" published by Microsoft Corp. The statistical data indicate that eq 5 is more suitable for the kinetic treatment of sulfonation progress than eq 8, for all of the examples tested. The standard error (SE) calculated for slant a is far smaller than that for slant b, for each example. Also, the calculated zero intercept (ZI) of slant a is much closer to zero than that of slant b. As a future confirmation, the value for the correlation coefficient (CC) for slant a is also larger than that for slant b.

For all of the sulfonation examples evaluated, the concentration changes of water and H_2SO_4 are found not to contribute primarily to the slowing down of the reaction rate. It is more reasonable to explain the slowing down of the first-order reaction rate by a negative effect of the sulfonated aromatic ring than by the water produced and H_2SO_4 consumed by reaction. This negative effect can be associated with desulfonation or a type of retardation on a reaction intermediate.

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