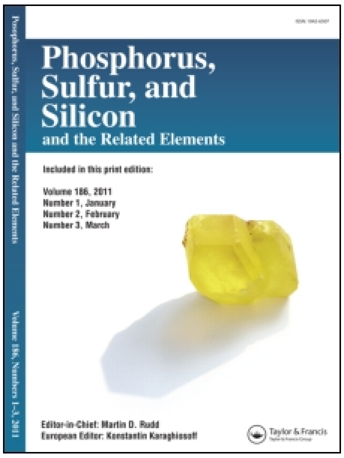


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# THE DESULFONATION OF PHENOLSULFONIC ACIDS IN AQUEOUS SODIUM HYDROGEN SULFATE MIXTURES

Mark E. Jason[a]
[a] Monsanto Company, The Chemical Group, Louis, Missouri

**To cite this Article** Jason, Mark E.(1993) 'THE DESULFONATION OF PHENOLSULFONIC ACIDS IN AQUEOUS SODIUM HYDROGEN SULFATE MIXTURES', Phosphorus, Sulfur, and Silicon and the Related Elements, 79: 1, 55 — 64
**To link to this Article: DOI:** 10.1080/10426509308034397
**URL:** http://dx.doi.org/10.1080/10426509308034397

*Phosphorus, Sulfur, and Silicon*, 1993, Vol. 79, pp. 55–64
Reprints available directly from the publisher
Photocopying permitted by license only

# THE DESULFONATION OF PHENOLSULFONIC ACIDS IN AQUEOUS SODIUM HYDROGEN SULFATE MIXTURES

MARK E. JASON
*Monsanto Company, The Chemical Group, 800 N. Lindbergh Blvd. T3W,*
*St. Louis, Missouri 63167*

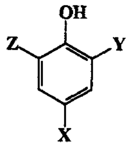
*(Received October 15, 1992; in final form February 1, 1993)*

Phenol and phenolsulfonic acids are rapidly sulfonated and desulfonated in aqueous sodium hydrogen sulfate, with or without added sulfuric acid. At temperatures above 130°C, desulfonation competes with sulfonaton sufficiently to allow steam stripping of phenol from the reaction mixtures, even under conditions of low water content. Above 170°C removal of phenol is less efficient because the water content is very low and the predominant species in the reaction mixture is 2,4,6-phenoltrisulonate.

*Key words:* Phenol; phenolsulfonic acid sulfonation; desulfonation; sodium hydrogen sulfate; kinetics; HPLC.

## INTRODUCTION

The sulfonation and desulfonation of aromatic compounds is chemistry that was well characterized by the end of the nineteenth century.[1] This pair of reactions was popular as a method for directing the electrophilic substitution of aromatic rings during multistep syntheses, and is one of the earliest examples of protection/deprotection strategy. Phenol, **1**, a structure activated toward electrophilic aromatic substitution, gives rise to the mono- and polysulfonated compounds **2–5** under the usual sulfonation conditions. These acids and their salts have been important raw materials for synthetic chemists and the chemical industry for over a century.



| **cmpd** | **X** | **Y** | **Z** |
|---|---|---|---|
| **1** | **H** | **H** | **H** |
| **2** | **SO3H** | **H** | **H** |
| **3** | **H** | **SO3H** | **H** |
| **4** | **SO3H** | **SO3H** | **H** |
| **5** | **SO3H** | **SO3H** | **SO3H** |

The extent of sulfonation of phenol depends primarily on the phenol/$SO_3$ ratio and the temperature. The *meta*-isomer is observed only under high temperature equilibration conditions in strong sulfuric acid.

Desulfonation of aromatic sulfonic acids is possible because the additions of both proton and "$SO_3$" are reversible. The normal conditions for the desulfonation reaction are dilute, aqueous solutions of the sulfonated phenol catalyzed by strong acid at high temperature. The range of acids employed is extensive, though the most common are sulfuric and phosphoric acid and the hydrogen halides.[2] We have studied the equilibrium and kinetic behavior of phenolsulfonates in sodium hydrogen sulfate-sulfuric acid mixtures as a means of reclaiming phenol from mixtures of **2**–**5**. To reduce the number of waste products and to simplify the recovery of sulfuric acid, we viewed it important to use only acidic sulfate solutions as the media for the desulfonation reactions.

The reactions described in this study were performed using both purified **2** or **4** and the mother liquors from the crystallization of crude **2**. These mother liquors contained **2** and **3** as well as small amounts of **4** and the 2,4'- and 4,4'-bisphenolsulfones. The reaction media were mixtures prepared from sulfuric acid and anhydrous sodium sulfate. The water content of the reactions was controlled only by the reaction temperature and the sulfate composition; reactions were conducted at atmospheric pressure with water being removed by distillation.

The use of high pressure liquid chromatography distinguishes this from previous studies, allowing the simultaneous analysis of all of the organic species in solution, and providing a complete picture of the fate of phenol and the phenolsulfonic acids. Previous studies have been limited by the analytical disadvantage of following only one component, or worse, a single extensive variable related to the composition. As will be shown, HPLC provides new insight into these and previous experiments.

## DISCUSSION

Before studying the removal of phenol, the equilibrium composition of mixtures of phenol, phenolsulfonates, sulfuric acid, sodium hydrogen sulfate and water was briefly studied. Their compositions near equilibrium at 140 and 170°C, and normalized to the amount of **2**, are given in Table I. At 140°C, 4-phenolsulfonate is the principal component and the trisulfonate is undetectable by HPLC. 2,4,6-Phenoltrisulfonate, **5**, becomes a major constituent at 170°C but the predominant species is 2,4-phenoldisulfonic acid (**4**). 3-Phenolsulfonate, prepared separately, was not detected in any of the described experiments. Interestingly, the trisulfonate **5** becomes the major component of the equilibration mixture when sodium hydrogen sulfate is the only sulfate species in solution. In a 1:2 mixture of sulfuric acid

TABLE I

Phenolsulfonic acid equilibrium compositions (a)

| Temp(°C) | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| 140 | 0.146 | 1.000 | 0.151 | 0.141 | (b) |
| 170 | (b) | 1.000 | 0.080 | 5.221 | 1.209 |

Notes: a. Compositions are normalized to the concentration of 2.
b. Not observed in the HPLC analysis.

and sodium hydrogen sulfate, equilibrium is achieved much more rapidly, as expected, and **4** comprises 70% of the total phenolics. The difference between these last two reactions is not easily explained by common mechanisms for the polysulfonation of phenol.

The desulfonation rate of **3**, or equivalently, the ratio of the rates of desulfonation for **2/3**, have never been specifically measured. Previous studies on the desulfonation of phenolsulfonates alluded to a faster rate of desulfonation for **3** than for **2**.[2] It has been known for a long time that the ratio of the initial rates of formation of **2** and **3** is approximately 2, but that the position of the equilibrium between **2** and **3** highly favors **2**.[1] The simplest explanation is the *de*sulfonation rate for **3** is significantly faster than **2**. However, as will be shown, the initial composition of a mixture of **1–5** does not greatly influence the apparent desulfonation rate. Plots of the ratio of **2/3** for equilibrations at 140 and 170°C are shown in Figure 1. Both reactions began with pure **2** and a 1:1 mixture of sulfuric acid and sodium hydrogen sulfate as the desulfonation medium. The time = 0 points are arbitrarily set to a value for the **2/3** ratio of 2000 for plotting purposes. Equilibration between **2** and **3** is complete within the first sampling interval at 170°C, 4 minutes, and within about 30 minutes at 140°C. Therefore, any information about the rate of sulfonation or desulfonation after these times is relevant only to the equilibrium mixture of isomers. Though not plotted, the ratio of **2/4** for these experiments requires the same length of time to achieve a stable value. At 170°C, the equilibrium value of **2/4** is 0.19, and at 140°C the value is 8. Plots of all of the phenolic species for these two reactions are shown in Figures 2 and 3.

It is, however, the phenol concentration at equilibrium that is of greatest interest because it will directly affect the rate and efficiency of phenol removal. Phenol was not detected in any of the equilibration studies at or above 170°C.[6] At 140°C

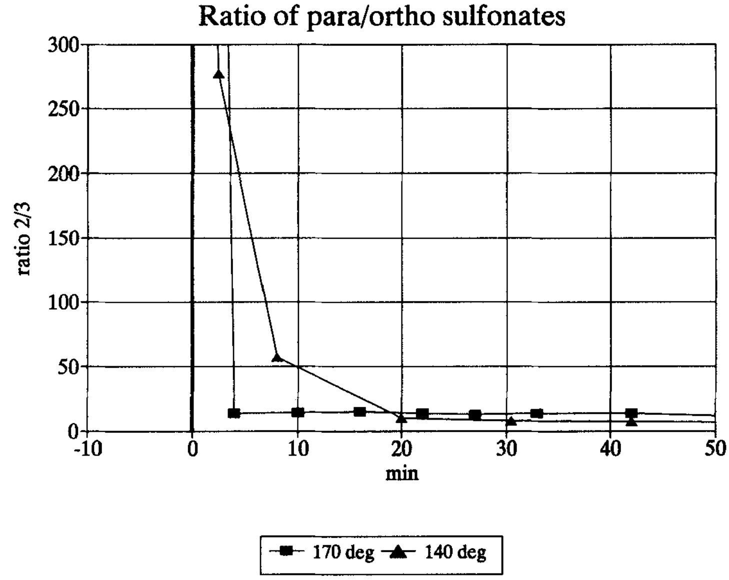


FIGURE 1. Plot of the ratio of **2/3** at 170 and 140°C. The *t*0 values are set arbitrarily high.

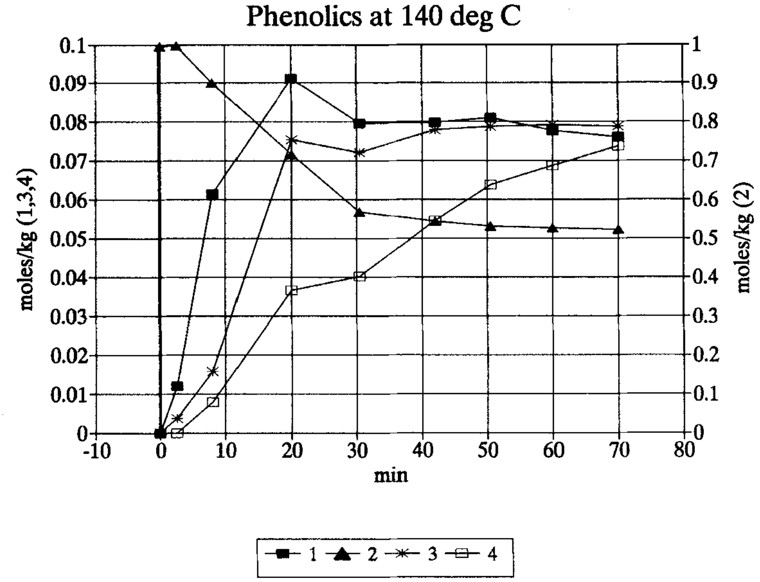


FIGURE 2. Plot of the phenolic materials during an equilibration experiment at 140°C using a $H_2SO_4$/$NaHSO_4$ ratio of 1.0. The trisulfonate, **5**, was not observed.

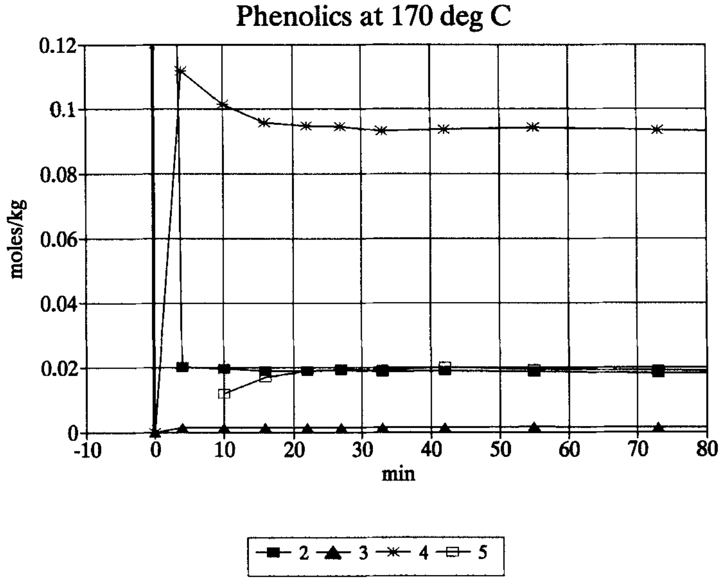


FIGURE 3. Plot of the phenolic materials during an equilibrium experiment at 170°C using a $H_2SO_4$/$NaHSO_4$ ratio of 1.0. Phenol, **1**, was not observed.

the equilibrium concentration of phenol was equal to the concentrations of **3** and **4**, approximately 10–12 mole%. The difference in phenol concentrations at these two temperatures is the result of a large change in the water content of the reaction mixture.

The water concentration is established by the equilibrium between the aqueous mixture and steam at the same temperature. It could not be reliably measured in the equilibration studies; however, the water concentration could be calculated from consideration of the material balances in the stripping experiments discussed in the Experimental section. Typical values for 140 and 170°C are 22–25 wt% and 3–5 wt%, respectively. At both temperatures the reaction mixtures are more adequately described as molten salt mixtures than aqueous solutions. It should be noted that all reaction mixtures remained fluid throughout the course of the desulfonations.

The object of this study was to determine conditions useful for recovering phenol from mixtures of phenolsulfonates by desulfonation. Removal of phenol from these desulfonation mixtures made use of the fact that phenol and water form a low-boiling azeotrope.[7] Water was continuously added and distilled from the batch reactions, and the heat input adjusted to allow for the distillation of the water while maintaining constant reaction temperature.

The reaction conditions for the batch desulfonations shown in Table II require some explanation, particularly the column headed "Excess Sulfuric Acid." Sulfuric acid was added to the reaction mixtures to acidify all of the weaker acid salts: sodium sulfate and the phenolsulfonates. A positive value is the number of moles of sulfuric acid greater than that needed to acidify the salts relative to the total number of moles of weaker acid. A negative value indicates that insufficient sulfuric acid was added to acidify all of the sodium salts. Runs 1 through 7 were performed on the mother liquor from the recrystallization of **2**, and runs 8 through 10 on the pure, recrystallized components. The fifth column contains the rates of addition of water, in grams per minute, and normalized to one mole of phenolic material in the reaction mixture. The last column is the observed first order rate constant, in min$^{-1}$, calculated from the disappearance of the total quantity of phenolic material. This rate constant, $k_0$, is described below and found in Table II.

The course of a typical batch desulfonation at 140°C, Run No. 4, is shown in Figure 4. The original mixture of sulfonates contained compounds **2–4**. Phenol removal is rapid early in the reaction and slows with the depletion of phenolics in the reaction mixture. Figure 5 shows a first-order analysis of the removal of phenol.

TABLE II

Typical batch desulfonations

| Run No. | Cmpds. | Temp(°C) | Excess H2SO4 | $\frac{d(H20)}{dt}$ | $k_0$ |
|---|---|---|---|---|---|
| 1 | 2,3,4 | 166 | -0.12 | 0.254 | 0.0168 |
| 2 | 2,3,4 | 163 | 0.09 | 0.082 | 0.0094 |
| 3 | 2,3,4 | 140 | 0.09 | 0.141 | 0.0161 |
| 4 | 2,3,4 | 140 | 0.09 | 0.264 | 0.0174 |
| 5 | 2,3,4 | 140 | 0.09 | 0.079 | 0.0103 |
| 6 | 2,3,4 | 140 | -0.29 | 0.141 | 0.0098 |
| 7 | 2,3,4 | 130 | 0.09 | 0.141 | 0.0051 |
| 8 | 2 | 140 | 0.36 | 0.317 | 0.0163 |
| 9 | 2 | 130 | 0.36 | 0.317 | 0.0063 |
| 10 | 4 | 140 | 0.36 | 0.615 | 0.0153 |

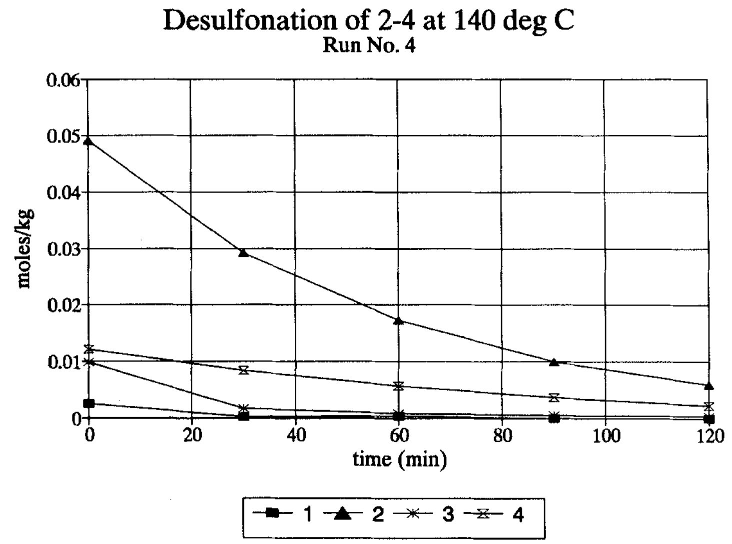


FIGURE 4. Plot of the phenolic components during Run No. 4.

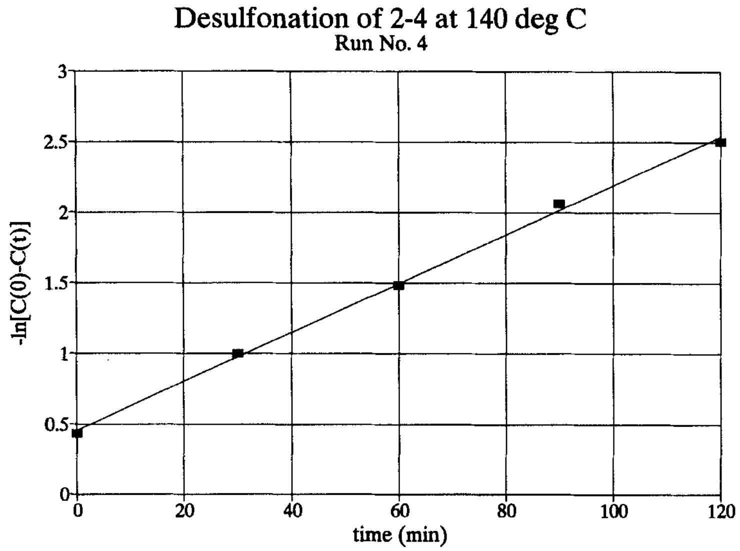


FIGURE 5. First-order kinetics analysis of Run No. 4, based on the sum of the phenolic components in the reaction mixture. See text for discussion.

The symbols $C(0)$ and $C(t)$ refer to the total molal concentration of phenolics at time = 0 and time = $t$, respectively. This reaction, like all of the batch desulfonation reactions, demonstrated a good fit of both the distilled phenol and the residual phenolic content to first order kinetic analysis through two to three half-lives. Though the actual process is anything but first-order, these effective rates, which are called $k_0$, are useful for the calculation of the half-life of the reactions under different conditions and for the evaluation of the economics of the desulfonation process. They are inappropriate for calculation of phenol concentrations after extensive desulfonation has taken place.

The ability to simultaneously analyze all of the phenolic species in these solutions, rather than a bulk desulfonation rate based on phenol or sulfate evolution, provides the opportunity to compare the behavior of a pure component with a mixture of sulfonates. The desulfonation of pure **2** at 140°C, Run No. 8, is shown in Figure 6, and plots of the appearance of phenol in the distillate for Run Nos. 4, 8, and 10 shown in Figure 7. Though performed under slightly different conditions, these reactions show the similarities between the desulfonation of pure **2**, pure **4**, and mixtures of **2**–**4**. A faster rate of desulfonation for **3** best explains the observed slower rates of evolution for the pure materials (Run Nos. 8, 10) at the beginning of the respective experiments. It is clear the similarity of these reactions after approximately 30 min is the result of the rapid equilibration of the sulfonated species under the reaction conditions.

The rate of introduction of water (in g/mole of phenolics/min), d($H_2O$)/dt, will determine the relationship between the rates of desulfonation of **2** and **3**, $k_D$,[8] and the observed appearance of phenol in the distillate, $k_0$. At low values of d($H_2O$)/dt, the rate at which phenol is removed from the reaction/reactor system (called the stripping rate) will be slow relative to the sulfonation and desulfonation rates. Consequently, the concentrations of phenol and the phenolsulfonates will be close to their equilibrium values and the observed rate, $k_0$, will be a direct function of d($H_2O$)/dt. As d($H_2O$)/dt rises, the stripping efficiency will increase and $k_D$ will not, the equlibrium concentration of phenol will fall, and $k_0$ will approach a maximum value dependent on $k_D$. Figure 8 shows the expected asymptotic behavior of observed rate, $k_0$, as a function of d($H_2O$)/dt. The point at (0, 0) is placed on the graph to demonstrate the sharp turnover above a critical d($H_2O$)/dt value. The value of interpreting of $k_0$ is somewhat clouded because the stripping efficiency

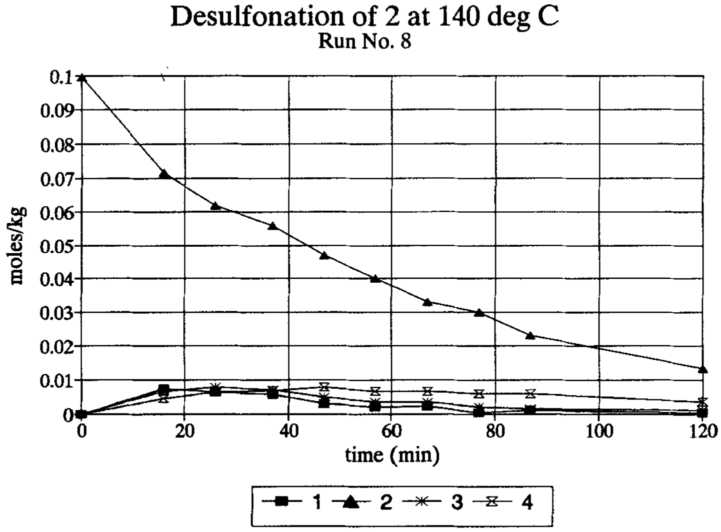


FIGURE 6. Plot of the phenolic components during Run No. 8.

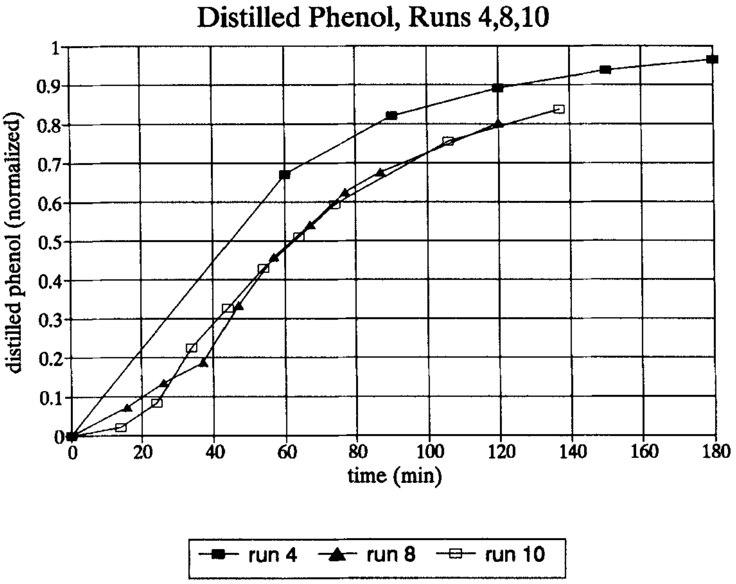


FIGURE 7. Plot of the cumulative amount of phenol distilled from desulfonation Run No. 4, 8, and 10.

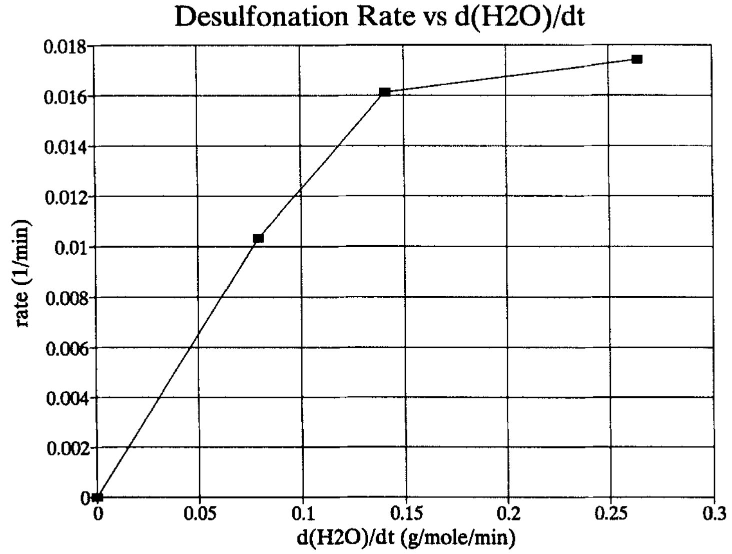


FIGURE 8. Plot of the observed first-order rate of desulfonation as a function of the rate of water addition. See text for discussion.

depends on the volume of the liquid and vapor phases and the effective reflux ratio as well as $d(H_2O)/dt$ and $k_D$.

Sulfuric acid will be the strongest acid in mixtures where it is present (ignoring such complex forms as $H_2S_2O_7$). Sulfuric acid and the phenolsulfonic acids, having $pK_a$'s of $-4$ to $-8$,[9] are indistinguishably strong acids in an aqueous solution. The bisulfate ion, $pK_a = 1.99$, is only a relatively weak acid by comparison. Regardless of whether the mixture contained excess acid, i.e. the "Excess Sulfuric Acid" is either positive or negative, strong Brönsted acids are present in the reaction mixtures. As the sulfonic acids are desulfonated, they leave behind sulfuric acid. Thus, to a crude approximation, the concentration of the strong acid catalyst should be independent of the extent of desulfonation, and roughly first-order kinetics might be expected for all reactions in this study. Such behavior was observed and confirms that sulfuric acid and phenolsulfonic acids are equivalent in the catalysis of the desulfonation of phenolsulfonic acids.

The phenol recovered from these desulfonation-stripping experiments was superior in quality to the commercial phenol used to prepare the sulfonic acids. The phenol was analyzed by gas chromatography as well as by the preparation of 4-phenolsulfonic acid from the recovered material. Many of the impurities in commercial phenol (α-methylstyrene, 2-phenyl-2-propanol, acetophenone, and 2-methylbenzofuran) are sulfonated and oxidized to materials that do not survive the sulfonation/desulfonation process and become part of the desulfonation residue. All desulfonations produced a small amount of dark, tarry material insoluble in the sodium hydrogen sulfate.

The process outlined in the previous discussion represents an efficient and inexpensive method for the desulfonation of complex mixtures of phenolsulfonic acids and the recovery of the liberated phenol. Aqueous sodium hydrogen sulfate, even of very low water content, is a convenient medium for performing these desulfonations, allowing the use of sulfuric acid as acidulant and catalyst.

## EXPERIMENTAL

*Materials and Methods.* All the compounds in this study are known and were prepared by adaptations of literature procedures. 4-Phenolsulfonic acid sodium salt, **2**, was prepared under normal sulfonating conditions followed by neutralization and crystallization. The salt was recrystallized from water and isolated as the dihydrate. 2-Phenolsulfonic acid sodium salt, **3**, was prepared by low temperature (40°C) sulfonation of phenol.[3] The mixture of sodium salts (approximately 2/1 *para/ortho*) was recrystallized from water to remove most of the 4-phenolsulfonate, **3** being more soluble in water than **2**. The 2-phenolsulfonate was then precipitated with methanol and recrystallized as the anhydrous sodium salt from methanol. In methanol, **2** is more soluble than **3**. 2,4-Phenoldisulfonic acid, **4**,[4] and 2,4,6-phenoltrisulfonic acid, **5**,[5] were prepared as their potassium salts by literature procedures.

$^1H$ and $^{13}C$ nmr spectroscopy were performed in a Varian VXR-300 instrument. All quantitative analyses were performed by HPLC using a Varian 5500 instrument equipped with a variable wavelength UV detector. HPLC conditions: column: 150 × 4.3 mm, 3 μm, C18 column from Varian (P/N 03-912041-42); mobile phase: 78% 0.005 M tetrabutylammonium phosphate, 0.01 M potassium hydrogen phosphate, pH 5.5 and 22% acetonitrile; flow: 1.0 mL/min; wavelength: 250 nm. Multiple level, non-linear calibration was employed to reduce the effects of detector saturation at high concentrations.

*Desulfonation Experiments.* Batch desulfonations were performed by heating a mixture of water, sulfuric acid and sodium sulfate to approximately 100°C in a three neck, round bottomed flask fitted for distillation. A hot (90–100°C) aqueous mixture of **2**, **4**, or **2–4** was added all at once, and the temperature raised as quickly as possible to the desired operating temperature. After this temperature had been reached, water was continuously added with an HPLC pump through a narrow cannula. The distillation receiver was replaced at intervals and the organic composition of the distillate and the reaction mixture analyzed at these times. Material balance closure at the end of the reaction was better than 95% for all reactions, well within the sum of errors over the eight to eleven cumulative analyses. The amount of the bisphenolsulfones did not change during the course of the reactions. Because these materials represented far less than 1% of the organic composition, they are not included in any of the material balances or discussion.

## REFERENCES AND NOTES

1. E. E. Gilbert, *Sulfonation and Related Reactions*, Interscience Publishers, New York, 1965.
2. J. Obermiller, *Chem. Ber.*, **40,** 3623–3647 (1907).
3. B. H. Chase and E. McKeown, *J. Chem. Soc.*, 50–52 (1963).
4. E. M. Chamot and D. S. Pratt, *J. Amer. Chem. Soc.*, **32,** 630–637 (1910).
5. C. Senhofer, *Ann. der Chim.*, **170,** 110–116 (1873).
6. The detection limit was approximately 0.005 wt%, based on the minimum detectable peak size during a routine HPLC analysis of a desulfonation mixture.
7. *Handbook of Chemistry and Physics*, 70th Ed., R. C. Weast, Ed., Chemical Rubber Co., 1989, p. D-12.
8. There is no simple expression for the desulfonation of **2** and **3** to give phenol. $k_D$ is meant to represent the sum over these two complex functions.
9. H. Cerfontain, *Mechanistic Aspects in Aromatic Sulfonation and Desulfonation*, Interscience Publishers, New York, 1968, p. 187.