A Study of the Reactions in the Formation of Sulfoacetic Acid and of the Preparation of Pure Crystalline Sulfoacetic Acid

Barbara Jean Eichel

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A STUDY

of the

REACTIONS IN THE FORMATION OF SULFOACETIC ACID

and of the

PREPARATION OF PURE CRYSTALLINE SULFOACETIC ACID

Barbara Jean Michel
Ursinus College
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Introduction:

This past summer the Pennsylvania Salt Manufacturing Company sponsored a research program at Ursinus College in which this researcher participated. In the course of this program several sulfonic acids were considered. In the chemical literature these acids are described as colorless hygroscopic crystalline hydrates with relatively low melting points. The preparations, which were seemingly straightforward, yielded only dark syrups from which crystals could not be isolated. This investigator has chosen one of these acids, sulfoacetic acid, and has endeavored through this research project to find an explanation for the difficulty in obtaining crystalline solids.

Two alternate, equally practical preparations for sulfoacetic acid were selected. The proposed reactions depended on the reaction (I) between sulfuric acid and acetic anhydride through the formation of the intermediate acetylsulfuric acid (compound A) and on the reaction (II) between fuming sulfuric acid and acetic acid. The reactions as originally proposed were:

\[
\begin{align*}
(\text{I}) & \quad \text{H}_2\text{SO}_4 + \text{CH}_3\text{C}^\text{O\text{O}}\text{OCH}_3 \rightarrow \text{CH}_3\text{C}^\text{O}{\text{OSO}_3}\text{H} + \text{CH}_3\text{COOH} \\
& \quad \text{CH}_3\text{SO}^\text{O} \quad \text{CH}_3\text{COOH} \quad \text{eme. CH}_3\text{COOH} \\
(\text{II}) & \quad \text{SO}_3 + \text{HOOCCH}_3 \rightarrow \text{CH}_2\text{SO}_3\text{OH} \\
& \quad \text{CH}_3\text{COOH}
\end{align*}
\]
It is this researcher's contention that the difficulty in inducing crystallization lies in the side products of the reactions, including the acetic acid formed in reaction I; these extraneous substances tend to hinder crystal formation by their very nature and to cause certain secondary reactions to occur with the desired product.
Preliminary Investigation:

In the reactions as originally proposed no restrictions are imposed with regard to temperature, since sulfoacetic acid is reported to be thermally stable to a temperature of 245°C; above this temperature decarboxylation occurs.

In both cases the instantaneous mixing of the reactants at room temperature results in a vigorous exothermic reaction with the simultaneous evolution of gas; this gas proves to be carbon dioxide, even though the highest temperature observed is only 196°C. This peak temperature varies only slightly with the order in which the reactants are mixed. Crystallization cannot be induced in the resultant heavy black syrup.

By mixing the reactants over a period of time greater than fifteen minutes, slightly better results are obtained, in that the resulting solutions are lighter in color; however, no crystals can be isolated.

Effects of Temperature on the Reaction:

Carefully regulating the temperature of the reaction eliminates the decarboxylation side-reaction and produces colorless, viscous solutions; the desired product is not formed to any appreciable extent in this case. That the same resultant compound is obtained in both reaction I and reaction II is shown through the addition of barium chloride. From this evidence it is advisable to assume that there is an intermediate step in both reactions, leading to the formation of acetylsulfuric acid.
According to Stillich\(^1\) reaction I results in the formation of acetylsulfuric acid (A), which in the presence of excess acetic anhydride and the acetic acid formed in the reaction rearranges at 70°C to form sulfoacetic acid (B).

\[
\frac{\text{CH}_3\text{COO}\text{SO}_2\text{OH}}{\text{A.}} \quad \xrightarrow{\text{70°C}} \quad \frac{\text{CH}_3\text{SO}_2\text{COOH}}{\text{B.}}
\]

This thermal rearrangement proceeds as Stillich postulated, and a positive identification of the sulfoacetate may be obtained in the barium salt. The sulfoacetate appears in a very impure condition, and the acetic acid formed in the reaction, as well as the excess acetic anhydride necessary for the rearrangement of the acetylsulfate to sulfoacetate, impedes crystallization.

However, if in the thermal rearrangement the 70°C limit is exceeded by more than one degree, a spontaneous exothermic reaction is initiated, resulting in the evolution of carbon dioxide. This decarboxylation of sulfoacetic acid produces methane sulfonic acid (C).

\[
\frac{\text{CH}_3\text{SO}_2\text{COOH}}{\text{B.}} \quad \xrightarrow{\text{677°C}} \quad \frac{\text{CH}_3\text{SO}_2\text{OH}}{\text{C.}} + \text{CO}_2
\]

**The Effect of Excess Sulfuric Acid:**

Stillich\(^2\) also suggested that an excess of sulfuric acid at any time during the reaction is undesirable; it is his contention that
the sulfuric acid is responsible for the exothermic blackening reaction (III) leading to the formation of methane sulfonic acid. The exact mechanism whereby sulfuric acid initiates this decarboxylation is not known.

On the basis of Stillich's observation it is advisable to devise a balanced reaction and a procedure in which an excess of sulfuric acid is avoided at all times. A combination of reactions I and II leads to such a balanced situation, whereby the sulfuric acid in the oleum of reaction II reacts with acetic anhydride as in reaction I.

\[ \text{IV. } 3\text{SO}_3\cdot 4\text{H}_2\text{SO}_4 + 18\text{CH}_3\text{COOH} \xrightarrow{15\% \text{ oleum}} 3\text{SC}_2\text{H}_3\text{COOSO}_2\text{O}_2\text{H} \]

At this point the order of mixing the reactants becomes important. At the end of the reaction no sulfuric acid should remain to initiate the undesirable secondary reaction III. In practice it was found that 3.6-4.8% (by weight) of the resultant mixture was unreacted sulfuric acid, but within the temperature range required for the rearrangement of the acetylsulfate, this concentration of sulfuric acid is too low to cause reaction III.

The Disturbing Aspects of Excess Acetic Acid:

Unfortunately the sulfate-free solutions of sulfoacetic acid are not stable over a period of time. Within twelve hours the material darkens to a deep red, and the mixture is predominantly neither
sulfoacetate, acetylsulfate, nor sulfate.

The only remaining initiator for any chemical side-reaction is acetic acid, which is present in excess. An article by Peski points out that the thermal rearrangement of acetyl sulfuric acid into sulfoacetic acid also produces traces of acetylsulfoacetic acid (D). If sulfoacetic acid stands in the presence of excess acetic acid for several hours, this acetylation equilibrium is driven to the right.

\[ \text{V. } CH_3COO\text{SO}_3\text{OH} \xrightarrow{70^\circ C} CH_3\text{COO}^+ \text{SO}_3\text{OH} + CH_3\text{COOCH}^+\text{SO}_2\text{OH} \]

The acetylated sulfoacetic acid, furthermore, undergoes condensation with itself to form another sulfur compound, disulfodehydroacetoacetic acid (E).

\[ \text{VI. } 2 CH_3\text{COOCH}^+\text{SO}_2\text{OH} \rightarrow CH_3\text{COOCH}^+\text{SO}_2\text{OH} + CH_3\text{COOCH}_2\text{COOH} \]

The problem has seemingly reduced itself to the discovery of a practical way to remove the excess acetic acid without shifting the reaction in favor of the acetylation.
Experimental:

Thermal Control: When the reaction was placed in an ice-salt bath and the reactants were mixed at such a rate that the internal temperature did not exceed 50°C, the intermediate was formed. Heating on a steam-bath did not accomplish the rearrangement I'; careful heating over an open flame did. However, if the temperature reached 72°C, reaction III occurred, even if the external source of heat were then removed. When the maximum of 70°C was reached, the flask had to be placed immediately in ice.

Removal of excess sulfate: For the first time in the reaction series the order in which the reactants were mixed became important, so that an excess of sulfate was avoided during the entire reaction. In all experiments the sulfuric acid now had to be added to the acetic acid-anhydride mixture, not the acetate to sulfate.

The unreacted sulfuric acid at the end of the reaction was removed as insoluble barium sulfate. Barium chloride, the reagent normally used to precipitate sulfate, could not be used, as it added different extraneous ions, chloride ions, which might also produce new undesirable reactions.

By adding either barium acetate or hydroxide no new ions would be introduced. Of these two, the barium acetate was the more practical, since the barium hydroxide neutralized the acidic medium and caused the barium sulfoacetate to precipitate with the barium sulfate. The original product had a pH of 0.5 and the addition of barium hydroxide
caused the continual formation of a precipitate to a pH of 8.0, so that it could not be determined when the sulfate precipitation had ended and the sulfoacetate had begun.

Removal of excess acetic acid: Ordinary distillation to remove the acetic acid from the reaction was not feasible as long as any unreacted sulfuric acid remained in the solution, for the quantities of sulfuric acid present, although too small to cause reaction III at 70°C, did cause this decarboxylation at the boiling point of acetic acid (b.p. 118°C). Neither was there any convenient way to remove the acetate ion as a precipitate. The only recourse was to remove all unreacted sulfuric acid as explained in the preceding section and then to distil off the acetic acid. Vacuum distillation proved more successful than distillation at atmospheric pressure.

Confirmation of the product: Infra-red spectroscopy was the main tool for the final identification of the product; the disodium salt was used, since the free acid is quite corrosive and attacks the sodium chloride crystals. A quantity of practical grade sulfoacetic acid from the Eastman laboratories was available and its disodium salt was used for comparison curves. (See Figure I and Figure II). The Eastman sulfoacetic acid was in the form of hygroscopic dark-brown chunks without a well-defined crystal structure.

The disodium salt was prepared by dissolving the acid in methanol and adding the amount of 1 N sodium hydroxide calculated to neutralize the acid. The salt precipitated immediately. Recrystallization
Figure I. The Infra-red Spectrum of Disodium Sulfoacetate.

The disodium sulfoacetate was prepared from the Eastman sulfoacetic acid (practical grade) by neutralization with 1 N NaOH in a methanolic medium. The sulfoacetate was not recrystallized. A Nujol-mull was used.
Figure II. An Infra-red Spectrum of Disodium Sulfoacetate.

This disodium sulfoacetate was prepared from a methanolic solution of my own preparation of sulfoacetic acid; the disodium salt was prepared using 1 N NaOH. No recrystallization of the product was necessary. A Nujol-mull was used as the phase for the spectrum.
did not alter the infra-red spectrum appreciably.

The readily identifiable bands in the spectrum are:
for the Nujol-mull: 2900-3020/cm
1420-1500/cm

for the sulfonic acid group: 1020-1080/cm.

Insolubility of barium sulfoacetate: Barium sulfoacetate may be precipitated only in a neutral medium. For this reason it was useful in identification work in the earlier stages of the project, since the barium salt of sulfuric acid precipitates in an acid medium.

Crystallization of sulfoacetic acid: Crystallization of the acid was attempted from the following solvents: solvent ether, absolute ether, chloroform, carbon tetrachloride, benzene, and alcohol.

Freezing out procedures were unsuccessful; they were attempted on mixtures with excess water and mixtures with just the amount of water to form the monohydrate.

The workable solution to the problem was in the evaporation of a pure water solution to the calculated weight of the monohydrate, since the monohydrate is the most common form of sulfoacetic acid. Seeding and standing produced light brown crystals. White crystals could not be obtained in any manner; the use of activated charcoal was unwieldy and unsuccessful. Recrystallization could be effected by heating the crude yield in benzene until the sulfoacetate melted and then allowing the solution to cool slowly.
**Preparation of Sulfoacetic Acid:**

57.1 ml glacial acetic acid and 755.5 ml acetic anhydride are placed in a large multi-necked flask, equipped with an efficient mechanical stirrer. The flask is kept in an ice-salt mixture of -10°C. 250.6 ml 15% oleum is added from a separatory funnel at such a rate that the temperature of the reaction mixture never exceeds 5°C.

The mixture at this stage represents the intermediate acetyl sulfurous acid which is converted to the desired sulfoacetic acid upon heating to 70°C. This heating should be very gradual, first under the hot water tap and then over a small open flame. At 70°C the heating is discontinued and the mixture is immediately chilled in ice. The solution should be clear and colorless.

1 M barium acetate is added dropwise to the mixture to remove any sulfuric acid (3.6-4.8% by weight of the total mixture). The solution is then vacuum distilled to drive off the excess acetic acid and water (30-36% by weight of the total mixture).

The light brown viscous solution remaining in the distillation flask is pure sulfoacetic acid (yield: 637 grams; 91% of theoretical). Water is added and the mixture is evaporated over an open flame until the weight of the acid-water mixture just equals the calculated weight of the monohydrate (719.8 grams). The mixture is seeded with a small crystal of sulfoacetic acid and allowed to stand undisturbed for several hours. This procedure yields light brown crystals which may be recrystallized from anhydrous benzene.
Conclusion:

Hygroscopic, light brown crystals can be isolated with reasonable success from mixtures prepared from the balanced reaction IV, if the necessary temperature control is exercised and the proper purification procedure is followed. Positive identification is effected by Infrared spectroscopy. The acid is soluble in alcohol and water, but insoluble in anhydrous ether, chloroform, and nitrobenzene. No sharp melting point can be obtained because of the hygroscopic nature of the crystals.

The preparation proceeds according to the two original reactions (I and II), but it is not completely independent of temperature. In both cases I and II an intermediate, acetyl sulfonic acid, is formed which thermally rearranges at 70°C in the presence of excess acetate to form sulfoacetic acid.

However, excess sulfuric acid in the reaction triggers an exothermic decarboxylation (III), while excess acetic acid is responsible for an acetylation reaction (V) and a condensation of the products (VI). Hence, the reaction is not as straightforward as the original equations appear.
FOOTNOTES.

1 Otto Stillich, Berichte der Deutschen Chemischen Gesellschaft, 38, 1243 (1905).


B I B L I O G R A P H Y.


