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The K_{a_2} Values of Sulfoacetic and 3-Sulfopropionic Acids

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The K_{a_2} values for sulfoacetic and 3-sulfopropionic acids were determined potentiometrically. The values obtained were much lower than those predicted by the Branch and Calvin treatment. It is proposed that the assumption of single bond character for the sulfur-oxygen bond in the Branch and Calvin treatment yields high results for K_a values of acids with substituted sulfonate groups. It is suggested that the sulfonate group be classified as a resonating group for the Branch and Calvin treatment and that it be given an inductive constant as a unit. It is also suggested that intramolecular hydrogen bonding might account for some of the discrepancy between the calculated and experimental values of K_{a_2}.

INTRODUCTION

Sulfoacetic acid and 3-sulfopropionic acid were prepared and studied by the authors in an effort to obtain complexing agents that were not extractable into chloroform.

The thermodynamic K_{a_2} values of these acids were determined potentiometrically. The K_{a_2} value for sulfoacetic acid was found to be $(8.6 \pm 0.3) \times 10^{-5}$ and that for 3-sulfopropionic acid was found to be $(3.0 \pm 0.1) \times 10^{-5}$.

Backer[1] obtained a value of 8.9×10^{-5} for the K'_{a_2} of sulfoacetic acid by measuring the conductivity of solutions of the acid, its monosodium salt and its disodium salt. Backer[2] subsequently obtained K'_{a_2} values of 7.2×10^{-5} and 9.7×10^{-5} by measuring the *p*H of solutions of the monosodium salt and of equal mixtures of the monosodium and disodium salts. The three K'_{a_2} values were obtained by averaging results of each group of measurements, each taken over a wide range of concentration.

The K_{a_2} values of sulfoacetic acid and 3-sulfopropionic acid were calculated using the Branch and Calvin[3] equation for the calculation of pK_a values of derivatives of acetic acid. Values of 7.6×10^{-2} and 7.3×10^{-4} were obtained for sulfoacetic and 3-sulfopropionic acids, respectively. The ratios of the calculated K_{a_2} value to the experimental value for sulfoacetic and 3-sulfopropionic acids were 885/1 and 24/1, respectively.

However, in applying their treatment, Branch and Calvin assumed that in the sulfonate group the sulfur-oxygen bond was a single bond, that the sulfur atom had a formal positive charge of two, and that each oxygen atom had a formal negative charge of one. It has been stated[4-9] that sulfur-oxygen bonds in compounds such as SO_2, R_2SO_2 and SO_3 display much double bond character. The formal positive charge on the sulfur in such compounds should lie between 0 and 1. Moffitt[8] calculated charges of 0.48 and 0.90 for the sulfur atoms in SO_2 and SO_3, respectively. Pauling[9] calculated the same charges to be 0.46 and 0.71. The charge on sulfur in RSO_3, using the Pauling treatment, was calculated to be 0.71. As a generalization, the effective charge on sulfur in the sulfonate group probably lies between 0.5 and 1. It is therefore proposed that the sulfonate group be treated as a resonating group. Branch and Calvin stated that a resonating group should be considered as one inductive unit and that one inductive constant must be applied to the entire group. If a charge of from 0.5 to 1 for sulfur is assumed, the inductive constant for the entire group is between 7.3 and 11.2. On this basis the calculated values of K_{a_2} for sulfoacetic acid are between 1.10×10^{-3} and 5.75×10^{-3} and between 7.41×10^{-5} and 1.70×10^{-4} for 3-sulfopropionic acid. The ratios of the calculated to the experimental values of K_{a_2} are 12.8/1 to 67/1 for sulfoacetic acid and 2.5/1 to 5.7/1 for 3-sulfopropionic acid.

There is probably another factor which contributes to the discrepancy between the calculated and experimental values of K_{a_2}. Branch and Calvin[10] discussed the discrepancy between the calculated and experimental values of K_{a_2} for sulfoacetic acid. They based their discussion upon experimental values of 5.8×10^{-3} and 8.9×10^{-5} for the K'_{a_1} and K'_{a_2} of sulfoacetic acid. These K'_a values were probably obtained from Backer[1] but the value for K'_{a_1} was apparently transcribed incorrectly since it was actually reported as 0.58. The value of 5.8×10^{-3} could hardly be the correct value since Smith[11] found that the sulfonic acid hydrogen in sulfoacetic acid is more highly dissociated in glacial acetic acid than is the first

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[1] Backer, *Proc. Acad. Sci. Amsterdam*, **25**, 359 (1923).

[2] Backer, *Proc. Acad. Sci. Amsterdam*, **26**, 83 (1923).

[3] Branch and Calvin, *The Theory of Organic Chemistry*, Prentice-Hall, Inc., New York, 1941, p. 221.

[4] Phillips, Hunter, and Sutton, *J. Chem. Soc.*, 146 (1945).

[5] Barnard, Fabian, and Koch, *J. Chem. Soc.*, 2442 (1949).

[6] Koch, *J. Chem. Soc.*, 408 (1949).

[7] Koch and Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

[8] Moffitt, *Proc. Roy. Soc.*, **A 200**, 409 (1950).

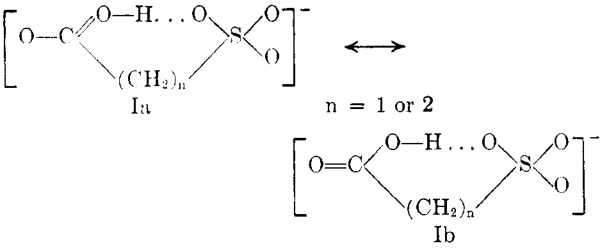
[9] Pauling, *J. Phys. Chem.*, **56**, 361 (1952).

[10] Reference (3) p. 230.

[11] Smith, *J. Am. Chem. Soc.*, **75**, 3566 (1953).

acid hydrogen of sulfuric acid. Furthermore, the authors of this publication found that the first hydrogen in sulfoacetic acid is completely titrated at a *p*H of 2 to 2.6. Branch and Calvin[10] suggested a tautomeric equilibrium to explain the abnormally low value of 5.8×10^{-3} for K'_{a_1} and the discrepancy between the calculated and experimental values of K_{a_2}. This equilibrium involves a competition between the sulfonic acid hydrogen and the carboxylic acid hydrogen to form an intramolecular hydrogen bond.

Since the reported value of 0.58 for K'_{a_1} for sulfoacetic acid does not seem to be abnormally low, intramolecular hydrogen bonding might be postulated to be present in both sulfoacetic acid and 3-sulfopropionic acid in the form Ia and Ib.



The presence of intramolecular hydrogen bonding has been used for the explanation of the lowered values of K_{a_2} in maleic acid, *cis*-caronic acid, and several others.[12]

Infrared spectra of carefully dried mixtures of the monosodium and disodium salts of sulfoacetic acid and 3-sulfopropionic acid and of deuterated samples of the above indicated the presence of intramolecular hydrogen bonding and intramolecular deuterium bonding, respectively, in the solids. Stronger intramolecular bonds were observed in the case of the sulfoacetate samples. This might lead one to suspect (but does not prove) that such bonds are present in aqueous solutions of these compounds. Therefore, intramolecular hydrogen bonding may well be the factor contributing both to the discrepancy between the calculated and experimental values of K_{a_2} for the acids and to the greater discrepancy found in the case of sulfoacetate.

EXPERIMENTAL WORK

Sulfoacetic acid. Technical-grade sulfoacetic acid was obtained from City Chemical Corporation, New York, New York. It was dissolved in water to give an approximately three *molar* solution. The *p*H was adjusted to 10 with sodium hydroxide solution and decolorizing charcoal was added. After filtration the solution was extracted with a 10 per cent solution of 8-quinolinol in chloroform and washed with chloroform. A solution of the acid then was obtained by cation exchange with Dowex 50-X12 resin.

3-Sulfopropionic acid. The inner anhydride of 3-sulfopropionic acid was prepared by the method of Kharasch.[13] The anhydride was recrystallized from thionyl chloride and then was refluxed under ligroin for 48 hours. A water solution of the anhydride was adjusted to *p*H 9 and the disodium salt of 3-sulfopropionic acid was precipitated by the addition of a 3:1 mixture of ethanol and methanol. The acid then was obtained by cation exchange.

pK_{a_2} Values. Solutions of the two acids were titrated with carbonate-free sodium hydroxide under nitrogen flow. The pK_{a_2} values were obtained for each acid by plotting the *p*H at the point midway between the first and second breaks (pK'_{a_2}) against the square root of the ionic strength, and extrapolating to zero ionic strength as shown in Figure 1.

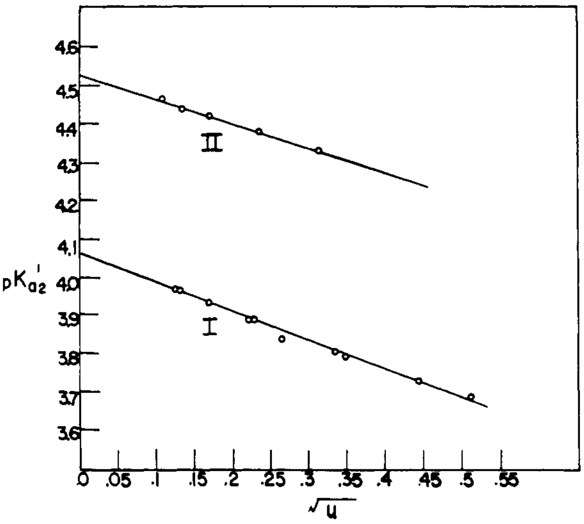


FIG. 1. VARIATION OF pK'_{a2} WITH THE SQUARE ROOT OF THE IONIC STRENGTH FOR I, Sulfoacetic Acid and II, 3-Sulfopropionic Acid.

Hydrogen bonding. A solution of an approximately equivalent mixture of the monosodium and disodium salts of sulfoacetic acid was prepared by adjusting a 3 *molar* solution of sulfoacetic acid to *p*H 2.30. A solution of an approximately equivalent mixture of the monosodium and disodium salts of 3-sulfopropionic acid was prepared by adjusting a 1.5 *molar* solution of 3-sulfopropionic acid to *p*H 3.37. Each solution was evaporated to dryness on a steam-bath. Each residue was ground to a powder and dried in an Abderhalden drying apparatus under a vacuum, over phosphorus pentoxide at the temperature of refluxing toluene. The powders were reground and dried in the same fashion with heat provided by refluxing glacial acetic acid. The infrared absorption spectra of the two powders were obtained with a Baird Model B recording infrared spectrophotometer, using Nujol mulls and sodium chloride cells.

A sample of each powder prepared above was dissolved in deuterium oxide. Each solution then was evaporated to dryness in an Abderhalden drying apparatus under a vacuum, over phosphorus pentoxide at the temperature of refluxing absolute ethyl alcohol. Each residue was ground to a powder and dried in the same fashion with heat provided by refluxing glacial acetic acid. The infrared absorption spectra of the two powders were obtained with a Perkin-Elmer Model 13 recording infrared spectrophotometer, using Nujol mulls and sodium chloride cells.

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[12] Braude and Nachod, *Determination of Organic Structures by Physical Means*, Academic Press, Inc., New York, 1955, pp. 631-634.

[13] Kharasch, Chao, and Brown, *J. Am. Chem. Soc.*, 62, 2393 (1940).