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Littlejohn, D.
Wizansky, A.R.
Chang, S.G.

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The Dissociation Constant and Acid Hydrolysis Rate of Hydroxysulfamic Acid

David Littlejohn, Abigail Wizansky and S.G. Chang*

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Reactions between nitrite ions and bisulfite ions occur in aqueous solutions and may be involved in the acid rain formation from SO_2 and NO_x in aqueous aerosols. These reactions can also be important in solution-based flue gas scrubbing systems. Most of the chemistry associated with the nitrogen sulfonate products of these reactions is fairly well understood.¹ An exception is the decomposition of hydroxysulfamic acid (HSA) in acidic conditions.

Ackermann and Powell^{2,3} have investigated the alkaline hydrolysis and oxidation by oxygen of HSA. The only quantitative study of the acid hydrolysis of HSA was done by Candlin and Wilkins,⁴ who used perchloric acid solutions as concentrated as 6M, but did not consider that HSA might be in the acid form under these conditions. We have investigated the acid dissociation constant of HSA, and made a determination of the acid hydrolysis rate.

Experimental Section

HSA was prepared in aqueous solution by hydrolyzing dissolved potassium hydroxyimidodisulfate (HIDS). The synthesis of potassium HIDS is more straightforward than for HSA,^{5,6} and higher yields and purity can be obtained. HIDS hydrolyzes much more quickly than HSA, and did not interfere in the studies. The potassium HIDS was

stored in a refrigerated dessicator to retard decomposition. Reagent grade compounds were used in the HIDS synthesis and in the solutions used for this study.

The dissociation constant for HSA was determined by observing solutions of HSA with varying concentrations of perchloric acid using Raman spectroscopy. Raman spectra of the HSA-perchloric acid solutions were obtained immediately after preparation to avoid problems with the hydrolysis of HSA. The heights of the Raman peaks for the two forms of HSA were compared with each other and the ClO_4^- peak to determine the dissociation constant. Since the peaks of the two forms of HSA overlap, reference spectra of the two forms were scaled to yield a flat baseline on subtraction to determine the concentrations. The spectra were corrected for the presence of HSO_4^- , which slightly overlapped the HSA peaks. All measurements were made with deaerated solutions at 298K.

The hydrolysis of HSA was studied using ion chromatography to monitor the decay of HSA and the growth of the sulfate product.⁷ Solutions were prepared by adding the HIDS salt to a deaerated perchloric acid solution. When the HIDS had completely hydrolyzed, the solution was placed in a controlled-temperature bath, and aliquots were taken periodically and diluted for analysis by ion chromatography. Measurements were made over a temperature range of 298-358K. Perchloric acid concentrations ranged from 0.03-2.0M, and HSA concentrations ranged from 0.001-0.03M.

Results and Discussion

For the determination of the dissociation constant of HSA, Raman spectra were obtained of 0.1M solutions with perchloric acid concentrations ranging from 0.001-5.1M over a temperature range of 288-338K. The spectra obtained at the lowest acid concentrations had only the deprotonated form of HSA present, with a Raman peak at

1056 cm^{-1} . These spectra were used to determine the amount of deprotonated HSA in other solutions and correct their spectra, so that the peak due to protonated HSA at 1063 cm^{-1} could be measured. From these measurements, it was found that the HSA acid and HSA anion had Raman scattering efficiencies of 0.5 and 0.48, respectively, compared to sulfate ion at 298K. Raman spectra of the two peaks are shown in Fig. 1. There was a significant amount of HSA anion present in the 5.1M perchloric acid solution. From the measured concentrations of the two forms of HSA and the hydrogen ion concentration, the dissociation constant was calculated. The average value obtained was $K = 1.5 \pm 0.5\text{M}$ at 298K. The uncertainty is due largely to the noise in the Raman spectra. Within the uncertainty, no significant temperature dependence of the dissociation constant was observed over a temperature range of 288-338K.

To determine the hydrolysis rate of HSA, a series of runs were done with 0.1M and 1.0M HClO_4 . In 0.1M H^+ , almost all of the HSA will be in the form of the anion. In 1.0M H^+ , there will be a mix of approximately 60% anion and 40% acid. In runs with fixed HClO_4 concentrations in which the HSA concentrations were varied, the rate displayed first-order dependence on HSA. The H^+ dependence reported elsewhere^{1,4} was found to be due only to the increasing fraction of HSA in the acid form. The relative rates of hydrolysis obtained in a series of runs at 348K with 0.01M HSA in HClO_4 with concentrations ranging from 0.03-1.0M, matched the calculated concentrations of the acid form of HSA more closely than the H^+ concentration. Also, a plot of $\log k$ vs. $\mu^{1/2}/(1+\mu^{1/2})$ for runs in which the ionic strength, μ , varied from 0.1-2.1M, yielded a slope close to zero. From the relationship of the rate constant to ionic strength and the charges of the reacting species,⁸ one would expect a slope of -1 for the plot if the reactants were the HSA anion and H^+ .

When the results obtained at 0.01M HClO₄ and 1.0M HClO₄ were corrected for the concentration of the acid form of HSA, consistent results were obtained. The values of the rate constant, k, for the relation $\frac{d[\text{HSA}]}{dt} = k[\text{HSA}]$ were calculated for the runs done at each temperature. The temperature dependence can be expressed as $k = A\exp(-E_a/RT)$, where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature. A plot of ln k vs. 1/T for the data is shown in Fig. 2. A least-squares fit to our data gave values of $A = 2.4 \times 10^{12} \text{ L mol}^{-1} \text{ sec}^{-1}$ ($\ln A = 28.5 \pm 1.0$) and $E_a = 24.9 \pm 0.7 \text{ kcal mol}^{-1}$. It appears that the anion of HSA is stable in moderately acid solutions.

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Figure Captions

Fig. 1 Raman spectra of the anion (1056 cm^{-1}) and acid (1063 cm^{-1}) forms of HSA.

Fig. 2 Arrhenius plot of the rate constant for the hydrolysis of HSA.

Fig. 1

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XBL 873-10035

Fig. 2

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