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Kinetics of the Acid Hydrolysis of Nitridotrisulfate Ion

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Abstract

The kinetics of the acid-catalyzed hydrolysis of nitridotrisulfate ion in aqueous solution were studied over a pH range of 4.1 to 6.7 and a temperature range of 283 K to 333 K. The build-up of the reaction products was observed by ion chromatography. The reaction has first order dependence on both hydrogen ion and nitridotrisulfate ion. When the rate constant is expressed as $k = A \exp(-Ea/RT)$, values of $A = 1.5 \pm 0.7 \times 10^{13}$ l mol^{-1} sec^{-1} and $E_a = 16.5 \pm 0.3$ kcal mol^{-1} are obtained at an ionic strength of 0.05. The ionic strength dependence was also studied.

Introduction

A number of nitrogen-sulfonates are produced by reactions between bisulfite ions and nitrite ions in aqueous solution.[1] Thus, their chemistry is of interest in studies of aqueous aerosols in polluted air and in wet flue gas scrubbing systems. Some of the reactions involved with their formation and decomposition are shown in Figure 1. While the hydrolysis reactions of hydroxyimidodisulfate (HIDS) and imidodisulfate (IDS) have been studied,[2,3] those of nitridotrisulfate (NTS) and hydroxysulfamate (HSA) have not been thoroughly investigated. Sisler and Audrieth[4] observed the hydrolysis reaction of NTS at several temperatures:

$$N(SO_3^-)_3 + H_2O \rightarrow HN(SO_3^-)_2 + H^+ + SO_4^{2-} \qquad (1)$$

They found that the NTS hydrolysis reaction occurred much more quickly than the IDS hydrolysis reaction. However, they did not obtain any quantitative results. We have studied the hydrolysis of NTS over a temperature range of 283 K to 333 K at solution pHs ranging from 4.1 to 6.7. The influence of ionic strength was determined over a range of $\mu = 0.03$ to $\mu = 0.5$.

Experimental

The potassium salt of NTS was prepared by a modification of the method of Sisler and Audrieth.[4] 12.5 g of potassium nitrite and 107 g of potassium sulfite were added to 100 ml of hot water and sufficient concentrated HCl was added to adjust the solution to pH 7. The rest of the preparation was carried out in the manner outlined by Sisler and Audrieth. The potassium salt of IDS was prepared for use as a reference by the hydrolysis of NTS, again using the method of Sisler and Audrieth. The purities of the prepared compounds were determined by Raman spectroscopy and ion chromatography. No significant quantities of impurities were found. The compounds were stored in an evacuated desiccator at 0 °C. No noticeable deterioration of the compounds was observed over a period of several months.

Ion chromatography was used to monitor the hydrolysis reaction. A Dionex 2010i ion chromatograph with a conductivity detector was used in the measurements. Both hydrolysis reaction products, IDS and SO_4^{2-}, could be determined with this system. A Dionex AS3 anion column was used in SO_4^{2-} measurements and a Dionex AG4 anion column was used in IDS measurements. The procedure is described elsewhere in more detail.[5] NTS could not be observed because it was too highly retained by the columns used. With the system used, the response to SO_4^{2-} was linear up to about 4×10^{-4} M and the response to IDS was linear up to about 1×10^{-4} M. In the experiments done, SO_4^{2-} was usually the only reaction product monitored because of its greater range of linearity. When IDS measurements were made, they agreed well with the SO_4^{2-} measurements.

Solutions for the hydrolysis runs were prepared by dissolving the NTS salt in doubly deionized water made alkaline with a small amount of NaOH. These were then mixed with buffer solutions, also prepared from doubly deionized water, to initiate the hydrolysis reaction. The potassium salt of NTS has limited solubility at room temperature (< .02 M). The concentrations of NTS in the reacting solutions ranged from 1×10^{-3} M to 10×10^{-3} M. Most runs were done with a NTS concentration of 2.5×10^{-3} M to allow the ionic strength to be kept at a fairly low value. Buffers used included acetate, oxalate, phosphate, phthalate, malonate and succinate salts, which permitted buffering over the pH range of 4 to 7. The choice of buffer did not appear to influence the hydrolysis rate of NTS. Most runs were done with a buffer concentration of .025 M. The ionic strengths of the solutions were adjusted by varying the buffer concentration or adding sodium chloride. Reagent grade chemicals were used in all cases.

The pH values of the reaction mixtures at 25 °C were measured with a pH meter which was calibrated daily with standard buffer solutions. For pH measurements at other temperatures correction factors for the pH meter calibrated at 25 °C were obtained. This was done by measuring acetate and oxalate buffer solutions and adjusting for changes in the ionization constants with temperature.[6]

After mixing the NTS and buffer solutions to initiate the hydrolysis process, samples were withdrawn periodically for analysis. The samples were diluted 10:1 with water or 5×10^{-3} M sodium carbonate solution and injected into the ion chromatograph. The samples were diluted to ensure that the concentration of the reaction product to be measured was within the range of linearity of the instrument. The sodium carbonate solution was used as a diluting agent when there was concern that a significant amount of hydrolysis would occur if the sample was diluted with water. Injections of 1×10^{-4} M solutions of SO_4^{2-} or IDS were interspersed with injections of the diluted hydrolysis run samples to allow quantitative measurement of the reaction products. Samples were taken from the reacting solution at intervals of 10 to 30 minutes. The initial concentration of the NTS was checked by allowing the hydrolysis reaction to go to completion and measuring the final concentrations of the products.

Results and Discussion

Generally, the first few measurements of the reacting solutions were used in calculating the hydrolysis reaction rate. The pH decrease in the solutions was sufficient to cause a slightly larger hydrolysis rate at the end of the run than at the beginning of the run. The hydrolysis rate dependence on the concentrations of NTS and H^+ were investigated to determine if the assumed first order dependence was correct.[1] Using buffers to maintain the solutions at pH 5, runs were made in which the NTS concentration was varied from 1 x 10^{-3} M to 10 x 10^{-3} M. A plot of log (rate) vs. log [NTS] is shown in Figure 2. The points shown are averages of the runs done at each concentration. A weighted least-squares fit to the data gives a value of 1.12 ± 0.10 for the slope, indicating that the rate has first order dependence on NTS concentration. In addition, plots of ln $([NTS]_t/[NTS]_o)$ vs. time were linear, supporting this conclusion.

The hydrolysis rate dependence on H^+ concentration was studied at both 298 K and 313 K. The runs were done with 2.5 x 10^{-3} M NTS and the solution pH ranged from 4.1 to 6.7. The log (rate) is plotted against log $[H^+]$ in Figure 3 for the 298 K measurements. A least-squares fit to the points gives a slope of 0.99 ± 0.05. The measurements at 313 K gave similar results. The first order dependence on hydrogen ion concentration indicates that the observed reaction is acid catalyzed.

The temperature dependence of the hydrolysis reaction was studied by making measurements at 283, 298, 313 and 333 K. The alkaline NTS solution and the buffer solution were brought to the desired temperature before mixing. The mixed solutions were kept in controlled-temperature water baths. The rate constant was calculated from the expression

$$-\frac{d[NTS]}{dt} = k[H^+][NTS]$$

Since the H^+ concentration was maintained at a nearly constant level by the buffer solution, the equation can be integrated to the following form:

$$\ln([NTS]_o/[NTS]_t) = k[H^+]t$$

At an ionic strength of $\mu = 0.05$, the following values of the rate constant were obtained:

T = 283 K	k = 3.03 ± .17	$l\ mol^{-1}\ sec^{-1}$
298 K	12.7 ± 2.0	
313 K	70 ± 18	

333 K	227 ± 12

An Arrhenius plot of these values is shown in Figure 4. If the rate constant is expressed as $k = A \exp(-E_a/RT)$, then a weighted least-squares fit to the data gives $A = 1.5 \pm 0.7 \times 10^{13}$ l mol^{-1} sec^{-1} and E_a = 16.5 ± 0.3 kcal/mol.

The effect of ionic strength on the rate of the hydrolysis reaction was studied over the range of μ = 0.028 to 0.52. All measurements were done with an NTS concentration of 2.5×10^{-3} M at 298 K and pH 4.8 to 5.2.

Bronsted's equation for the influence of ionic strength on a reaction rate constant can be written as[3,7]

$$\log k = \log k_o + 2Az_1z_2\frac{\mu^{1/2}}{1+\mu^{1/2}}$$

where k_o is the limiting rate constant as the ionic strength approaches zero, A is the Debye-Huckel coefficient (.5065), z_1 and z_2 are the charges on the reacting ions and μ is the ionic strength. With this equation, the influence of the ionic strength on the rate of reaction can be used to determine the charge states of the reacting species. A plot of log k vs. $\mu^{1/2}/1+\mu^{1/2}$ is shown in Figure 5. The best fit to the points is a line with a slope of -2.88 ± 0.25 and an intercept of 1.651 ± 0.063. The slope indicates that the charge on NTS is -3 and it is reacting with H^+. This agrees with titrations we have done on slightly acidic NTS solutions with dilute NaOH solutions, which indicate that the third ionization constant is greater than 10^{-5}. The intercept gives a value of $k_o = 44.8$ l mol^{-1} sec^{-1} at 298 K.

The decomposition of NTS under alkaline conditions was also checked. Solutions of NTS in the range of pH 8 to 10 exhibit little or no deterioration over a period of many days. This indicates that the uncatalyzed hydrolysis reaction is insignificant compared to the acid-catalyzed hydrolysis.

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Figure Captions

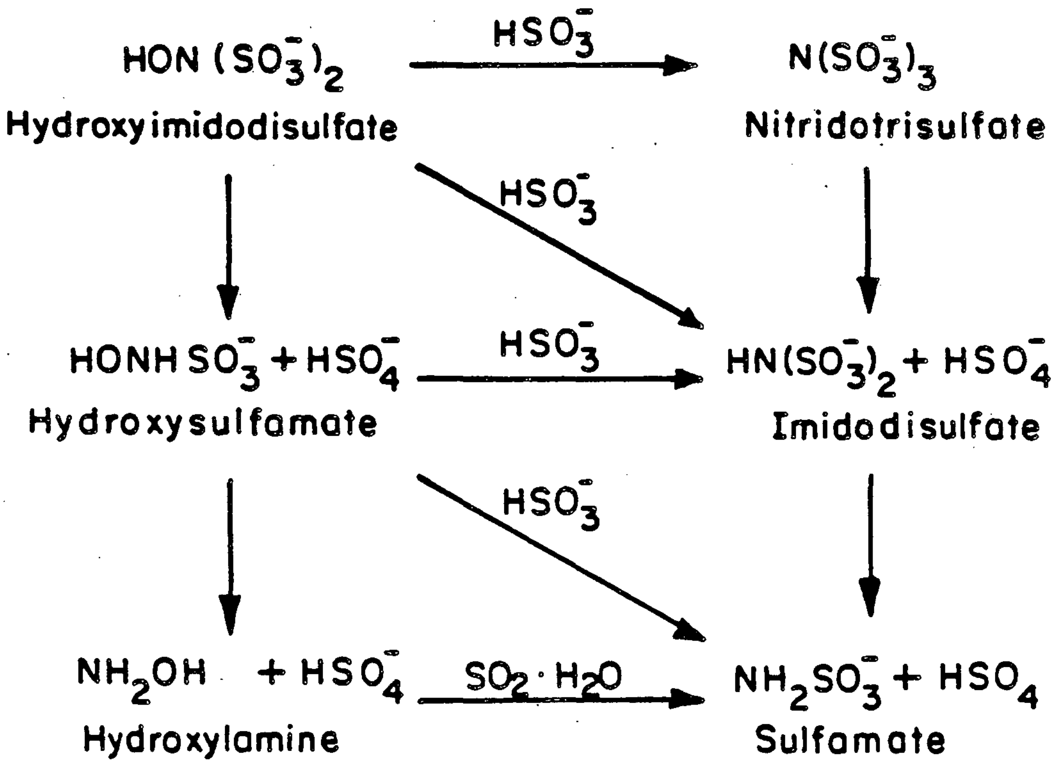
Figure 1. Some of the reactions involved with the formation and decomposition of nitrogen sulfonates.

Figure 2. Dependence of the hydrolysis rate on NTS concentration.

Figure 3. Dependence of the hydrolysis rate on H^+ concentration.

Figure 4. Arrhenius plot for the hydrolysis rate constant for NTS.

Figure 5. Dependence of the hydrolysis rate constant on ionic strength.



HON(SO3-)2
Hydroxyimidodisulfate
HSO3-
N(SO3-)3
Nitridotrisulfate
HSO3-
HONHSO3- + HSO4-
Hydroxysulfamate
HSO3-
HN(SO3-)2 + HSO4-
Imidodisulfate
HSO3-
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Hydroxylamine
SO2·H2O
NH2SO3- + HSO4
Sulfamate

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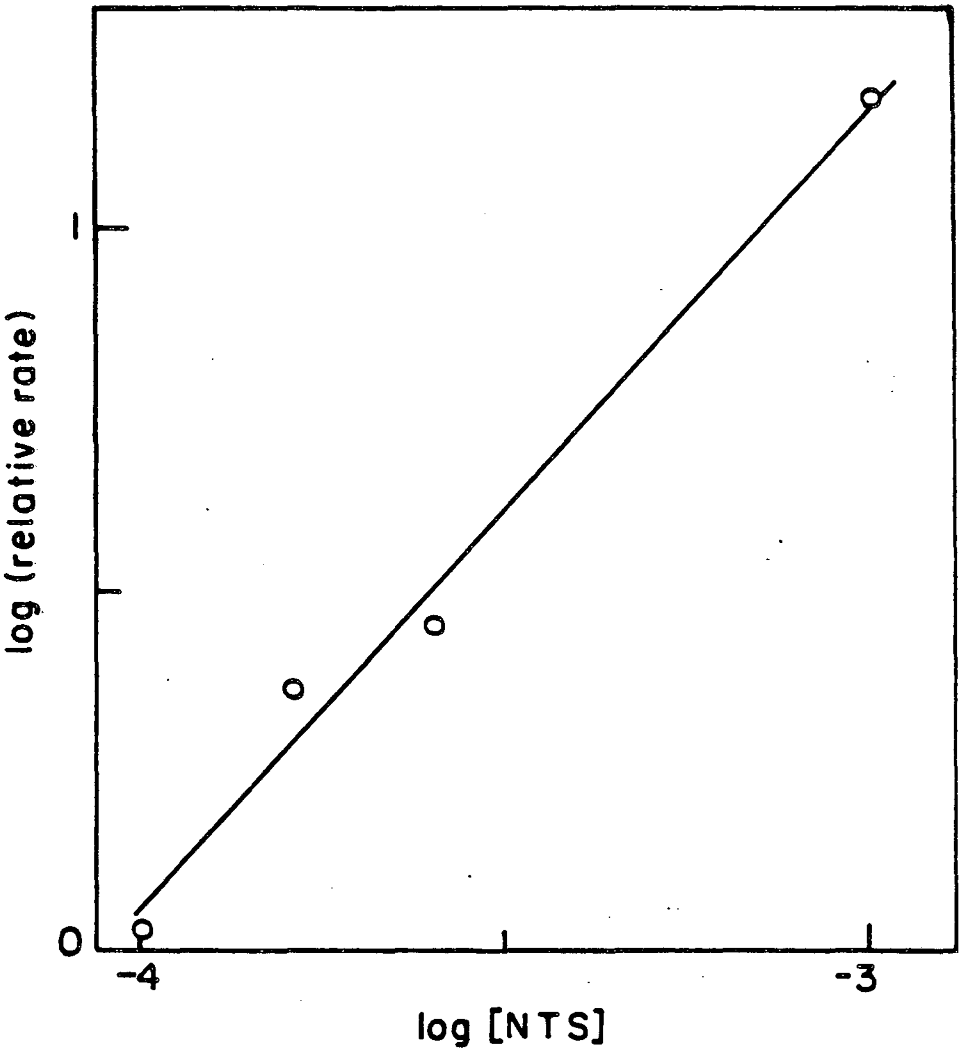

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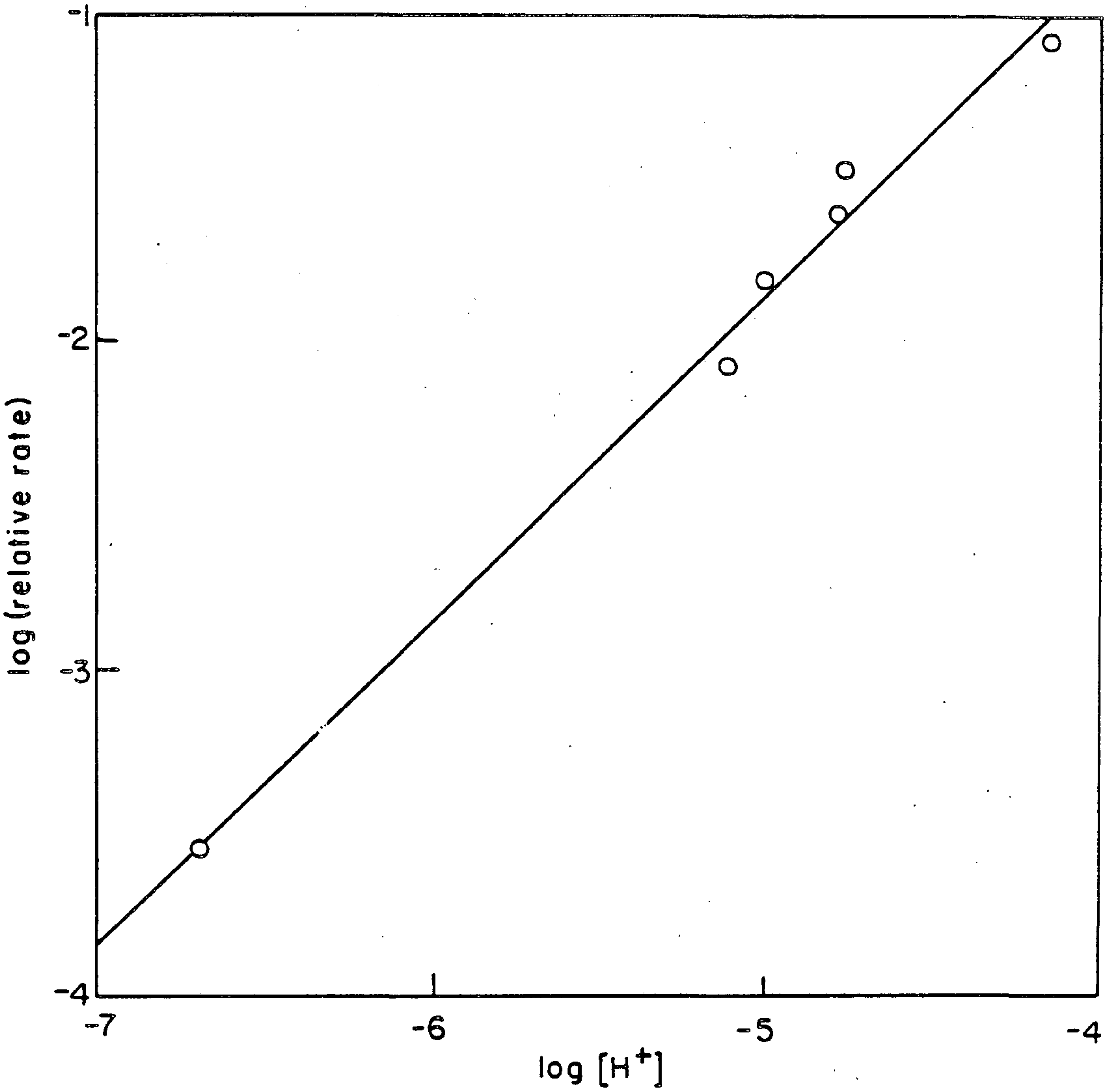

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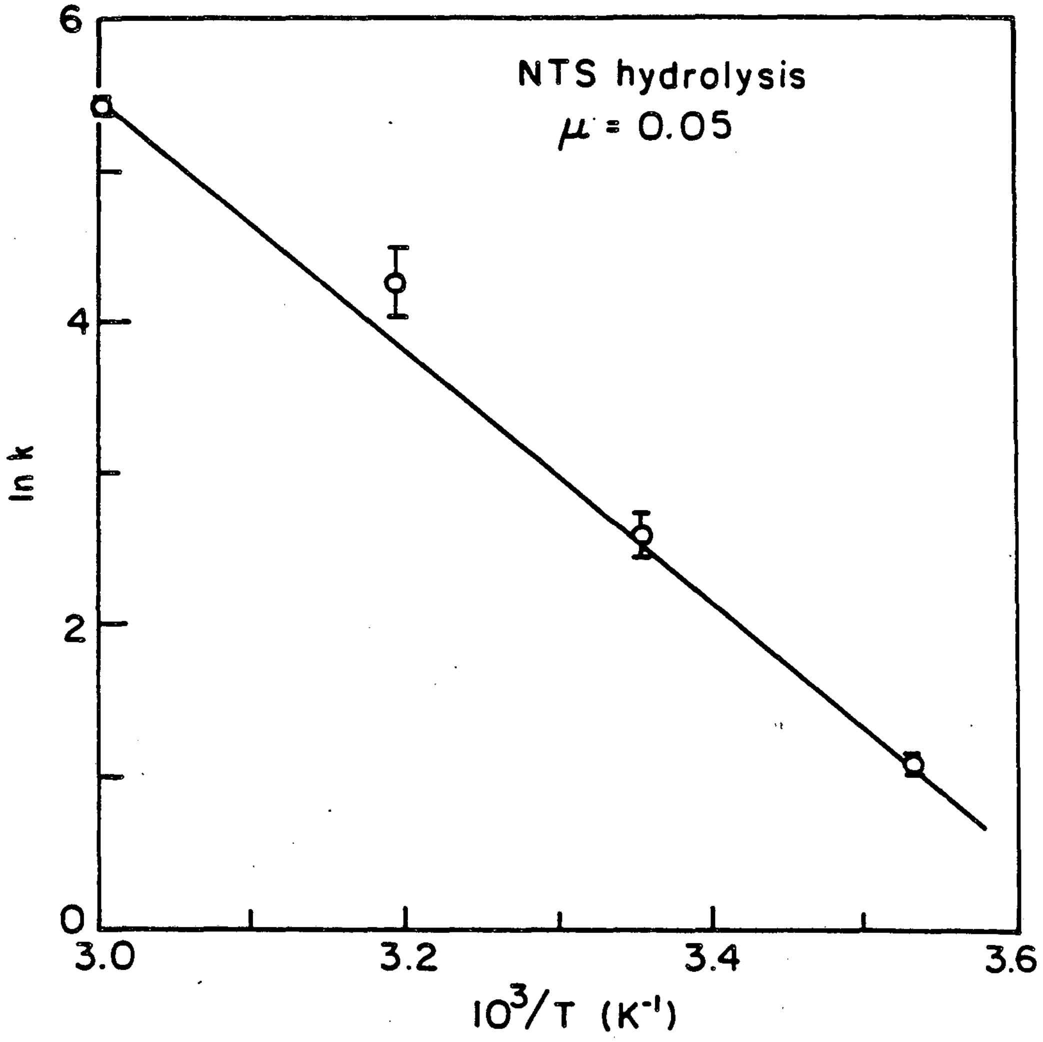

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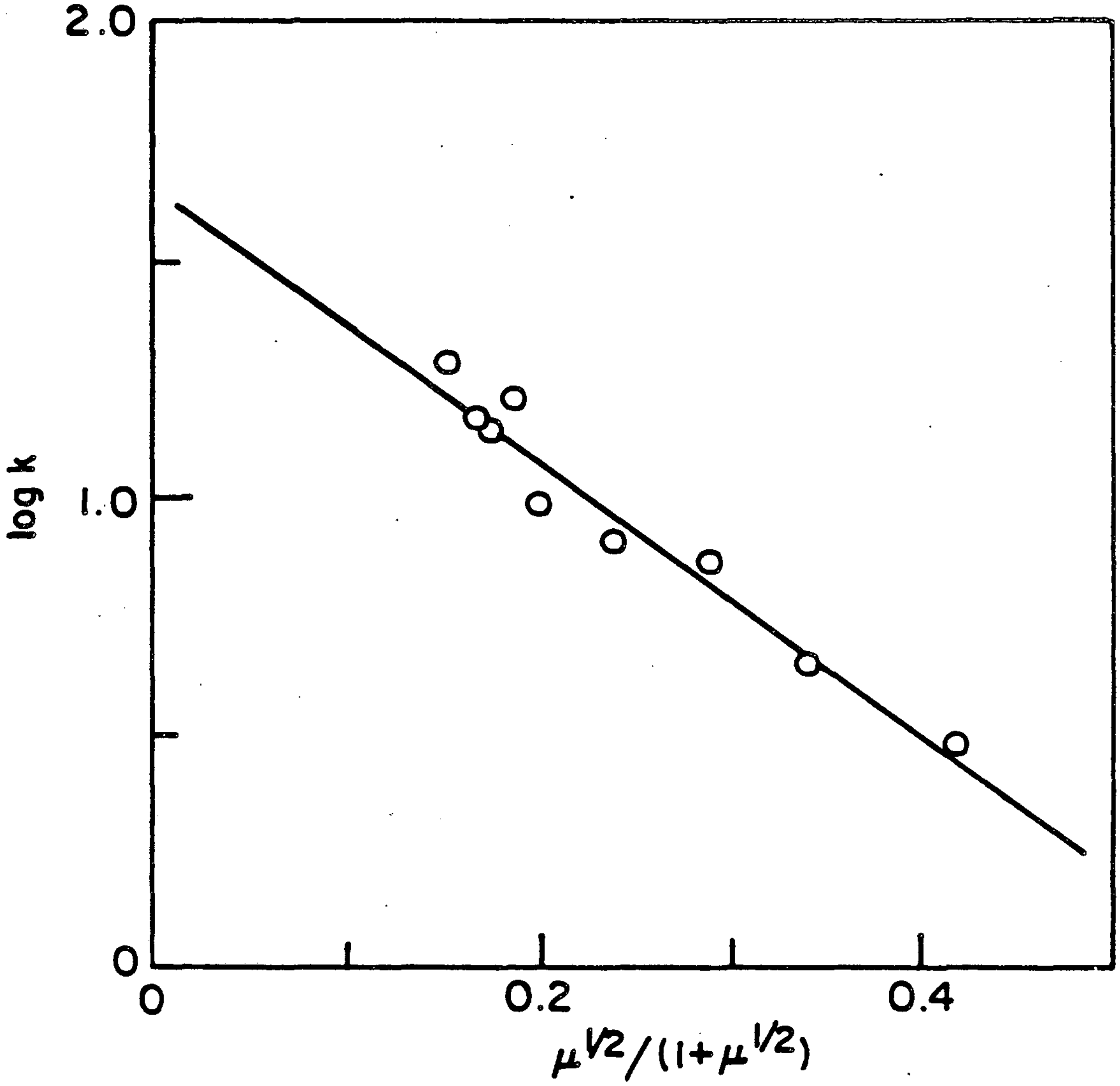

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