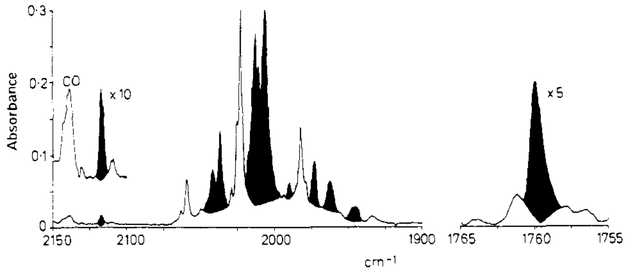

Figure 1. IR spectrum in the ν(CO) region after UV photolysis (λ = 290 ± 10 nm) of $MnRe(CO)_{10}$ in an argon matrix at 12 K (matrix ratio ~1:5000). Bands due to $MnRe(CO)_9$ are shown in black. Note that the low-wavenumber ν(CO) region is shown with expanded wavenumber and absorbance scales to emphasize the presence of a bridging CO group in $MnRe(CO)_9$.

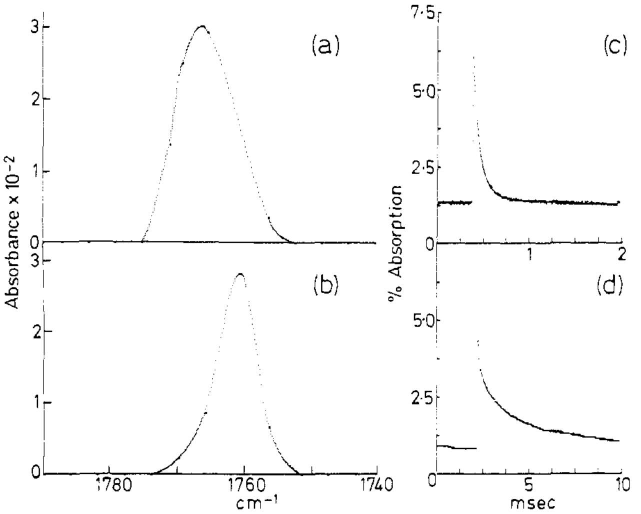

Figure 2. Time-resolved IR spectra in the ν(CO) bridging region (1790–1740 cm^{-1}) obtained 15 μs after UV flash photolysis (5×10^{-4} M cyclohexane solution, 25 °C): (a) $MnRe(CO)_{10}$; (b) $Mn_2(CO)_{10}$. Kinetic traces showing formation and decay: (c) $MnRe(CO)_9$; (d) $Mn_2(CO)_9$. These traces were measured at 1764.1 cm^{-1} for $MnRe(CO)_9$ and 1761.3 cm^{-1} for $Mn_2(CO)_9$. Note that the time scale for (d) is expanded with respect to that of (c).

less expected is the much greater reactivity of $MnRe(CO)_9$ than $Mn_2(CO)_9$. We are now investigating the photosubstitution reactions of these compounds both in solid matrices and in liquid xenon solution in an attempt to understand these differences in reactivity.

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Contribution from Lawrence Berkeley Laboratory,
University of California, Berkeley, California 94720

Kinetics of Acid Hydrolysis of the Nitridotrisulfate Ion

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

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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. The hydrolysis reactions of nitridotrisulfate (NTS) and hydroxysulfamate (HSA) have not been thoroughly investigated. Sisler and Audrieth[2] observed the hydrolysis reaction of NTS at several temperatures:

$$N(SO_3)_3^{3-} + H_2O \rightarrow HN(SO_3)_2^{3-} + H^+ + SO_4^{2-} \quad (1)$$

They found that the NTS hydrolysis reaction occurred much more quickly than the iminodisulfate hydrolysis reaction but did not obtain any quantitative results. We have studied the hydrolysis of NTS over a temperature range of 283–333 K at solution pHs ranging from 4.1 to 6.7. The influence of ionic strength was determined over a range of μ = 0.03–0.5 M.

Experimental Section

The potassium salt of NTS was prepared by a modification of the method of Sisler and Audrieth.[2] A 12.5-g sample 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 prepn. 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 compounds were stored in an evacuated desciccator 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. The procedure is described elsewhere in more detail.[3] With the system used, the response to SO_4^{2-} was linear up to 4×10^{-4} M and the response to IDS was linear up to 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 deionized water made alkaline with a small amount of NaOH. These were then mixed with buffer solutions, also prepared from deionized water, to initiate the hydrolysis reaction. The potassium salt of NTS has limited solubility at room temperature (<0.02 M). The concentrations of NTS in the reacting solutions ranged from 1×10^{-3} 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. The choice of buffer did not appear to influence the hydrolysis rate. Most runs were done with a buffer concentration of 0.025 M.

The pH values of the reaction mixtures at 25 °C were measured with a pH meter that 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.[4]

After the NTS and buffer solutions were mixed 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. 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

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(1) Chang, S. G.; Littlejohn, D.; Lin, N. H. *ACS Symp. Ser.* **1982**, *No. 188*, 127.

(2) Sisler, H.; Audrieth, L. F. *J. Am. Chem. Soc.* **1938**, *60*, 1947.

(3) Littlejohn, D.; Chang, S. G. *Anal. Chem.* **1986**, *58*, 158.

(4) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*; Chemical Rubber Publishing Co.: Boca Raton, FL, 1985.

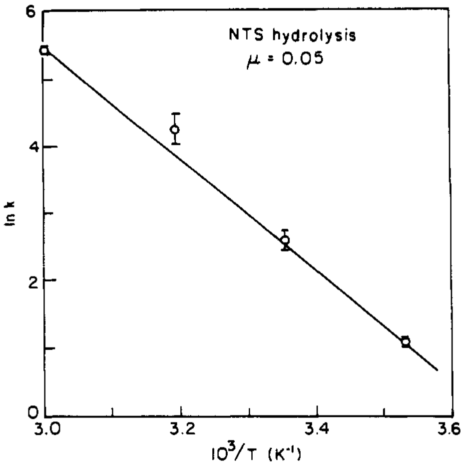

Figure 1. Arrhenius plot for the hydrolysis rate constant for NTS.

dependence was correct.[1] Using buffers to maintain the solutions at pH 5.0, runs were made in which the NTS concentration was varied from 1×10^{-3} to 10×10^{-3} M. 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.

The hydrolysis rate dependence of H^+ concentration was studied at both 298 and 313 K. The runs were done with 2.5×10^{-3} M NTS, and the solution pH ranged from 4.1 to 6.7. 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. Since the H^+ concentration was maintained at a nearly constant level by the buffer solution, the rate equation can be expressed as

$$\ln\left([\mathrm{NTS}]_0/[\mathrm{NTS}]_t\right) = k[\mathrm{H}^+]_t$$

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

T, K	k, L mol^{-1} s^{-1}
283	3.03 ± 0.17
298	12.7 ± 2.0
313	70 ± 18
333	227 ± 12

An Arrhenius plot of these values is shown in Figure 1. 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}, s^{-1} and $E_a = 16.5 \pm 0.3$ kcal/mol.

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

Brønsted's equation for the influence of ionic strength on a reaction rate constant can be written as[5]

$$\log k = \log k_0 + 2Az_1z_2\frac{\mu^{1/2}}{1 + \mu^{1/2}}$$

where k_0 is the limiting rate constant as the ionic strength approaches zero, A is the Debye–Hückel coefficient (0.5065), 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 2. 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^+. The intercept gives a value of $k_0 = 44.8$ L mol^{-1} s^{-1} at 298 K.

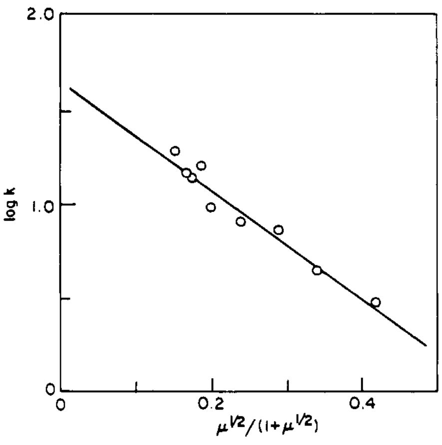

Figure 2. Dependence of the hydrolysis rate constant on ionic strength.

The decomposition of NTS under alkaline conditions was also checked. Solutions of NTS in the range of pH 8–10 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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Registry No. $N(SO_3)_3^{3-}$, 72198-01-7.

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(5) Doyle, G. J.; Davidson, N. *J. Am. Chem. Soc.* **1938**, *60*, 1947.

Contribution from the Department of Chemistry,
University of California at Santa Cruz,
Santa Cruz, California 95064

Circular Dichroism of the Reduction Products of $Ru(bpy)_3^{2+}$

Jon S. Gold and Steven J. Milder*

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The nature of the metal-to-ligand charge-transfer (MLCT) state of $Ru(bpy)_3^{2+}$ has been of considerable interest for some time. Of particular interest is the degree of ligand localization of the promoted electron. There is an abundance of data, including resonance Raman,[1] absorption,[2] circular dichroism,[3] and excitation photoselection[4] spectra, that strongly argue for ligand localization. Other data suggest a delocalized description when the complex is in a rigid medium.[5,6] However, this result is open to question.[2d,4] Electrochemical reduction also appears to yield species with the added electron(s) localized on a single ligand(s).[7] Thus, an

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(1) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.

(2) (a) Lachish, U.; Infelta, P. P.; Gratzel, M. *Chem. Phys. Lett.* **1979**, *62*, 317. (b) Braterman, P. S.; Harriman, A.; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1801. (c) Creutz, C.; Chou, M.; Netzel, T. L.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309. (d) Milder, S. J.; Gold, J. S.; Kliger, D. S. *J. Phys. Chem.* **1986**, *90*, 548.

(3) Gold, J. S.; Milder, S. J.; Lewis, J. W.; Kliger, D. S. *J. Am. Chem. Soc.* **1985**, *107*, 8285.

(4) Carlin, C. M.; DeArmond, M. K. *J. Am. Chem. Soc.* **1985**, *107*, 53.

(5) Ferguson, J.; Krausz, E.; Maeder, M. *J. Phys. Chem.* **1985**, *89*, 1852.

(6) Ferguson, J.; Krausz, E. R. *Chem. Phys. Lett.* **1982**, *93*, 21.

0020-1669/86/1325-4611$01.50/0