This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

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Nitrous acid Reduction
Purex 1B - Bank

TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

DPST-86-694

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October 1, 1986

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RELATIVE REACTION RATES OF SULFAMIC ACID AND HYDROXYLAMINE WITH NITRIC ACID

INTRODUCTION

Sulfamic acid (HSO_3NH_2, "HSA") and hydroxylamine nitrate ($NH_2OH \cdot HNO_3$, "HAN") are used in SRP solvent extraction and ion exchange processes to prevent the oxidation of Fe^{2+}, Pu^{3+} and Np^{4+} by nitric acid. In the absence of nitrous acid (HNO_2), nitric acid oxidation of Fe^{2+}, Pu^{3+}, or Np^{4+} is very slow, but when HNO_2 is present to provide a kinetic path, the reaction is quite rapid. Since HNO_2 is a product of HNO_3 oxidation of Pu^{3+} or Np^{4+}, the reaction becomes autocatalytic. The effectiveness of holding reductants depends on their rate of reaction with the radiolytically or chemically generated HNO_2. The report describes a study of comparative reaction rates where the reductant is in excess, as in the 1B bank in the Purex process. The results of this work apply to planned plant tests to partially substitute HAN for the ferrous sulfamate reductant in the Purex 1B bank.

SUMMARY

The comparative reaction rates of HSA and NH_2OH with nitrous acid were measured at room temperature over the acid range 0.3 to 3.5M HNO_3 and the ratio of the reaction rate constants found to be $k(NH_2OH)/k(HSA) = 0.056 + 0.082\ [H^+]$. Application of these results to plant processes allows a calculation of relative amount of reductant to achieve the same rate of nitrite destruction. For example, with a 1B bank acidity of 1.5M, a reduction of 0.02M HSA requires a calculated 0.11M HAN to maintain the equivalent nitrite destruction rate. The solid waste saving for the reduction of ferrous sulfamate in the Purex 1BX is calculated to be $600M/1000 MTU for each 0.01M reduction.

BACKGROUND

The reactions of HNO_2 with HSA and NH_2OH in acid solution proceed through intermediate species to yield only gaseous products. The reactions are extremely rapid and, in a superficial sense, are complete during the time of mixing. These reactions have been studied kinetically by stopped flow techniques and under conditions where the reactions are slow enough for conventional kinetic methods (low concentration; low acidity, 0°C). In this study, the reductants were studied in competition with each other and the relative rates determined from analyses of the gaseous products.

This method is based on the different products produced by the reaction between HNO_2 and the different reductants. The net reactions are:[1,2]

$$HSO_3NH_2 + HNO_2 \longrightarrow SO_4^{=} + 2H^+ + N_2 + H_2O \qquad (1)$$

$$NH_3OH^+ + HNO_2 \longrightarrow N_2O + 2H_2O + H^+ \qquad (2)$$

From equations 1 and 2, the reaction of HSA with HNO_2 produces N_2, and the reaction of NH_2OH with HNO_2 produces N_2O. Thus, the relative reaction rates of two reductants in competition for HNO_2 can be determined from the ratio of N_2 to N_2O.

EXPERIMENTAL

Reagents

$NaNO_2$ and HSO_3NH_2 were c.p. grade; $NH_2OH \cdot HNO_3$ was obtained from SRP as a 1.8M solution.

Apparatus

The reaction vessel was a standard 100 mL flask fitted with a small side neck. The principal neck of the flask was connected through Tygon tubing to a gas sample tube and then a water filled flask. Evolution of the gas from a reaction displaces the gas in the system and forces water from the water flask for measurement of the total gas evolved.

Procedure

A solution of HSA and $NH_2OH \cdot HNO_3$ in nitric acid (total volume, 60 mL) was added to the flask, the side neck closed with a rubber septum and the gas sample tube connected to the reaction flask. The reaction flask and gas sample tube were flushed for about 15 minutes with argon introduced via a hypodermic needle through the rubber septum. After flushing, the water filled flask was connected to the system and the reaction initiated by discharging 6 mm of $NaNO_2$ (1 mL of 6M $NaNO_2$) by hypodermic needle through the rubber septum. The volume of water displaced was measured by a graduated cylinder, and the contents of the gas sample tube were analyzed by gas chromatography. The analytical method was tested with gas samples produced by reacting NaN_3 with HNO_2 and found to be within 8% of the theoretical ratio of $N_2/N_2O = 1$.[2] All reactions were initiated at room temperature, 25 ± 3°C, but the heat released by the reaction raised the solution temperature to about 30°C.

RESULTS AND DISCUSSION

Experiments on the relative reaction rates of HSA and $NH_2OH \cdot HNO_3$ with HNO_2 were studied over the acid range 0.3 to 3.5M HNO_3 with (1) 0.27M $NH_2OH \cdot HNO_3$-0.20M HSA ($HSA/NH_2OH = 0.75$) and (2) 0.27M $NH_2OH \cdot HNO_3$-0.133M HSA ($HSA/NH_2OH = 0.50$). The results are shown in Figures 1 and 2 and Table 1.

In this system, where $NH_2OH \cdot HNO_3$ is ~ 300% excess and HSA is 200% excess (Figure 1) or HSA is 135% excess (Figure 2), the reaction rate of HSA with HNO_2 ranges from 6 to 9 times faster than $NH_2OH \cdot HNO_3$ at 0.3-0.4M HNO_3 to about 1.8 times more rapid at 3.5M HNO_3.

The reaction rate law for the NH_2OH-HNO_2 reaction has been found in previous studies[3,4] to be

$$-d(HNO_2)/dt = k_1(HNO_2)(NH_3OH^+)(H^+) \quad (3)$$

where k_1 is the rate constant.[5-7] The rate law for the HSA-HNO_2 reaction has been determined to be

$$-d(HNO_2)/dt = k_2(HNO_2)(SO_3NH_2^-)(H^+) \tag{4}$$

where k_2 is the rate constant. The N_2/N_2O ratio (Table 1) is the ratio of reaction 4 to reaction 3, or

$$N_2/N_2O = k_2(SO_3NH_2^-)/k_1(NH_3OH^+) \tag{5}$$

From the values of N_2/N_2O in Table 1 and the ratio of the reactants, the ratios k_1/k_2 were determined and are shown in Figure 3. The straight line (Figure 3) is the least-squares fit of the k_1/k_2 ratio as $k_1/k_2 = 0.056 + 0.082\ (H^+)$ with an average standard error of 5%. These values of k_1/k_2 may be compared to the value of 0.016 reported[8] for the competitive reactions in perchloric acid at 0°C.

Figures 1, 2, and 3 all demonstrated an apparent increase in NH_2OH-HNO_2 reaction rate relative to the HSO_3NH_2-HNO_2 reaction rate as the acidity increases. However, the actual cause of the relative rate increase is the increase in ionic strength,[3] which allows easier approach between the positively charged species NH_3OH^+ and H^+ in the HNO_2-NH_2OH rate law. The rate law for the HNO_2-HSA involves the reaction between a positively and negatively charged species and, thus, is affected only slightly by a change in ionic strength. The ionic strength was varied with the acidity in these experiments to be applicable to SRP processes.

NH_2OH reacts with HNO_3 at acid concentrations above 2M, reaching a maximum rate at 5M HNO_3.[9] This reaction is autocatalytic with a 10-15 second induction period and is usually complete within 30 seconds.[9] The products of the reaction are N_2O and HNO_2, which is believed to be involved in the reaction mechanism. The induction period represents the time necessary for the HNO_2 concentration to cause a perceptible reaction. Under the conditions of the experiments reported here, the presence of HSA prevents the autocatalytic increase in HNO_2, and the reaction is initiated only when HNO_2 is added.

APPLICATION TO PLANT PROCESSES

SRP has successfully tested the substitution of HAN for a portion of the ferrous sulfamate (FS) reductant in the Purex 1B bank and plans further tests with the object of minimizing the iron and sulfate in the solvent extraction waste.[10] Each 0.01M reduction of the FS concentration in the Purex 1BX stream represents a savings of $600M/1000 MTU processed in solid waste processing at DWPF. The amount of reductant required is determined by the Fe^{2+}

required to reduce Pu^{4+} to Pu^{3+} and the amount of HSA and HAN necessary to suppress HNO_2 oxidation. At 0.07M FS and 7 g Pu^{3+} in the 1BP, Fe^{2+} is 140% in excess of the stiochiometric amount required. A reduction of 0.01M FS corresponds to a reduction of 0.02M in HSA. If the acid profile of the 1B bank averages 1.5M HNO_3, $k(NH_2OH)/k(HSA)$ is calculated to be 0.18 and an increase in the HAN concentration by 0.02/0.18 = 0.11M HAN is required to have the equivalent nitrite suppression. This value would be reduced because of the ionic strength contributed by the $UO_2(NO_3)_2$ in the aqueous phase, but does provide a guide for future plant tests.

ACKNOWLEDGEMENT

The author is indebted to R. H. Young of ADD for the many gas analyses required in this work.

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Table 1.

Reaction Products: HSO_3NH_2-$NH_2OH \cdot HNO_3$ versus HNO_2

	Initial Concentrations, M[a]		Gas, %		
Run	HNO_3	HSO_3NH_2	N_2	N_2O	N_2/N_2O
75	0.40	0.20	90	10	8.8
51	0.63	0.20	87	13	6.8
71	1.00	0.20	87	13	6.8
53	1.23	0.20	80	20	4.0
61	2.20	0.20	82	18	4.7
70	2.23	0.20	70	30	2.27
63	2.7	0.20	76	23	3.3
74	3.5	0.20	65	35	1.86
76	0.30	0.135	86	14	6.0
50	0.63	0.135	84	16	5.2
72	0.90	0.135	81	19	4.3
52	1.23	0.135	71	29	2.4
60	2.13	0.135	67	33	2.0
62	2.63	0.135	70	30	2.3
73	3.50	0.135	63	37	1.7

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[a] Initial concentration of $NH_2OH \cdot HNO_3$ was 0.27M for all runs.

FIG 1 RELATIVE HSA/NH2OH RATES

HSA/NH2OH=0.75

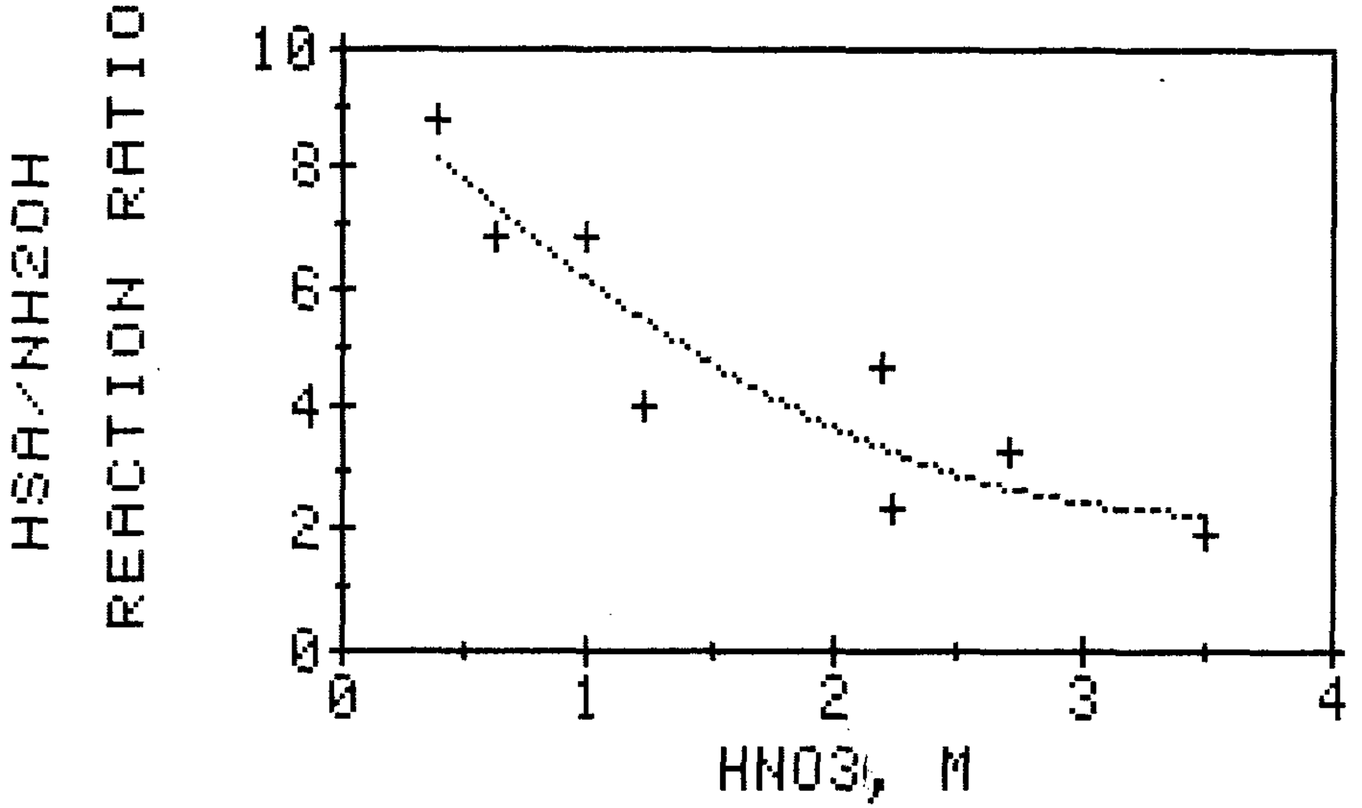

FIG 2 RELATIVE HSA/NH2OH RATES

HSA/NH2OH=0.5

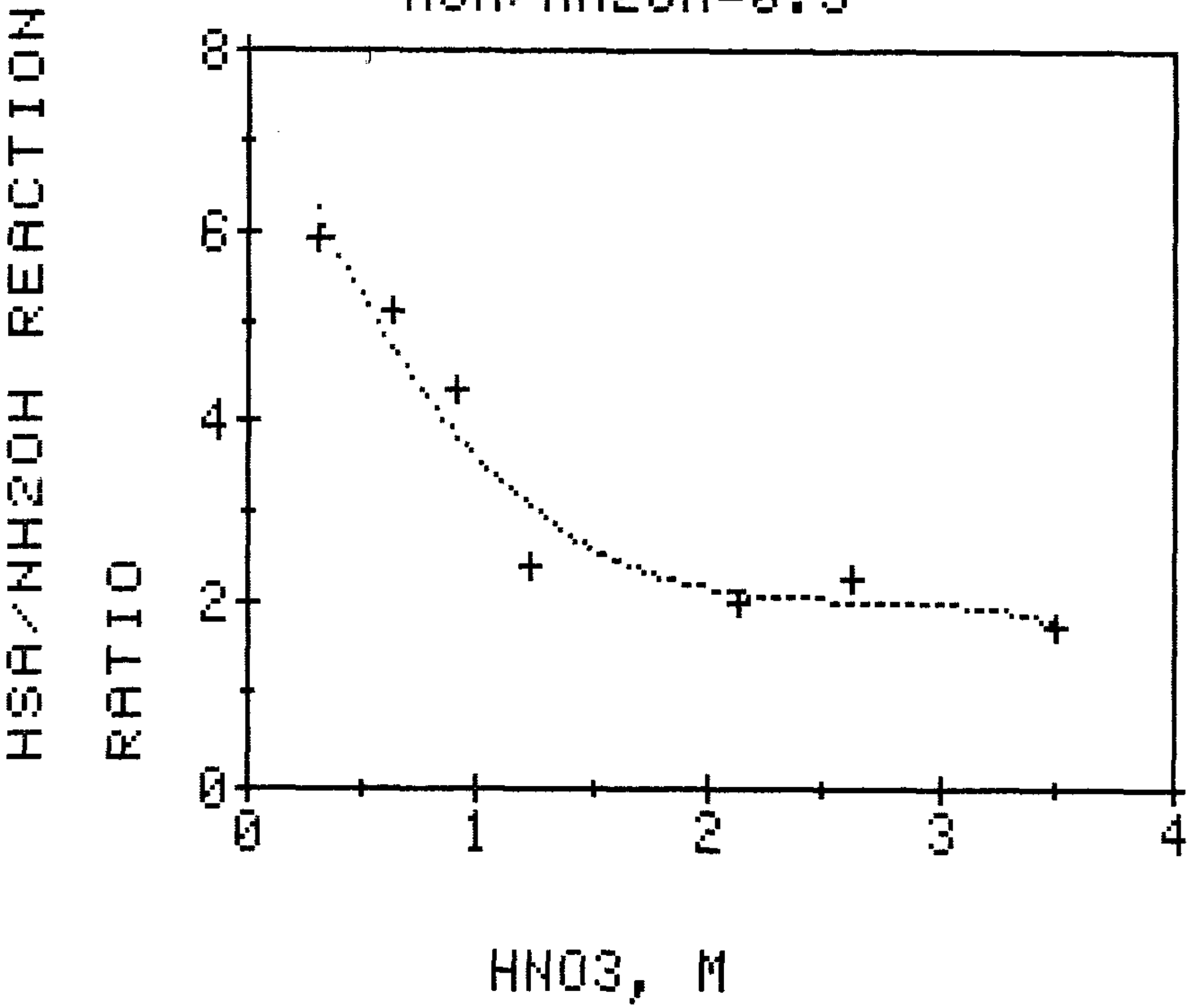

FIG 3 NH2OH/HSO3NH2 REACTION
RATE RATIO VS HNO3