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DP-728

NUCLEAR TECHNOLOGY-CHEMISTRY
AND CHEMICAL ENGINEERING
(M-3679, 26th Ed.)

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FORMATION OF HYDRAZOIC ACID FROM
HYDRAZINE IN NITRIC ACID SOLUTIONS

by

E. Kenneth Dukes and Richard M. Wallace

September 1962

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ABSTRACT

A study was made of the kinetics and stoichiometry of the formation of hydrazoic acid in nitric acid solutions containing hydrazine and ferrous sulfamate. The data were used to establish safe limits for the use of hydrazine in process solutions.

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FORMATION OF HYDRAZOIC ACID FROM
HYDRAZINE IN NITRIC ACID SOLUTIONS

INTRODUCTION

Hydrazine is used to stabilize lower valence states of the actinide elements in several radiochemical separations processes. Two important applications are in the recovery of Np^{237} from aqueous Purex waste and in the separation of Pu^{238} from irradiated Np^{237} . Both are anion exchange processes and both have been described in other reports^(1,2,3). In the recovery of Np^{237} from aqueous Purex waste, the hydrazine is used in combination with ferrous sulfamate in the nitrate waste solution, to maintain the neptunium in the absorbable (IV) state. Hydrazine and ferrous sulfamate make possible the separation of Pu^{238} from irradiated Np^{237} by stabilizing absorbable Np(IV) and nonabsorbable Pu(III) in solution. In applications of this type ferrous ion is the primary reductant; hydrazine serves to supplement the sulfamate ion as a scavenger for nitrous acid. Hydrazine is advantageous because it reacts rapidly with nitrous acid and produces only a small amount of gas (gas upsets a fixed-bed ion exchange process). A disadvantage of hydrazine, however, is that one of its reaction products is hydrazoic acid, HN_3 . Under certain conditions hydrazoic acid can form explosive compounds with some metal ions, it is explosive in high concentrations in aqueous solutions, and it can form explosive mixtures with air^(4,5,6).

To evaluate the safety of process steps that employ hydrazine, it was necessary to develop analytical methods for determining the concentration of hydrazoic acid in process solutions, to investigate the mode of formation of hydrazoic acid, to study the behavior of hydrazoic acid under process conditions, and to determine safe limits of concentration to ensure against the hazards mentioned above.

SUMMARY

A study of the mechanism of formation of hydrazoic acid in process solutions revealed that hydrazoic acid is formed by the rapid reaction of hydrazine with nitrous acid, which is formed primarily from the slow reduction of nitric acid by ferrous ion. In radioactive solutions, radiolytic degradation of nitric acid is probably also a significant source of nitrous acid. Under typical process conditions - for example, in a solution containing initially 5 to 8M HNO_3 , 0.05M $\text{Fe(NH}_2\text{SO}_3)_2$, and 0.05M N_2H_4 - it was shown that the maximum conversion of hydrazine to hydrazoic acid was about 25%.

Safe limits for the concentration of hydrazoic acid in process solutions were determined. Three potential hazards were considered: the precipitation of explosive mercuric azide, the generation of explosive aqueous solutions of hydrazoic acid, and the generation of explosive hydrazoic acid - air mixtures by volatilization of hydrazoic acid from solution. A value of 0.05M HN_3 was found to be a conservatively safe

concentration limit for all these cases; this value was used as a guide in the evaluation of process steps where hydrazine was present. The maximum concentration that was found in tests with actual process solutions was a factor of five below the guide limit. This result, coupled with other conditions that were known to reduce the hazard in the proposed process, indicated that hydrazine could be safely used.

DISCUSSION

EXPERIMENTAL

Hydrazine nitrate, pH 6, was supplied by the Fairmount Chemical Company. The solution was 3.55M N_2H_4 and contained less than 0.001M HN_3 .

Ferrous sulfamate was prepared from reagent-grade iron powder and sulfamic acid. The solution was analyzed for Fe^{3+} immediately before use. All other solutions were prepared from reagent-grade chemicals.

A Beckman DU spectrophotometer with matched 1.0-cm "Corex" cells was used for all absorbance measurements.

The concentrations of ferric ion and hydrazoic acid in the test solutions were determined by measurement of the absorbance of the red ferric azide complex, FeN_3^{2+} , at 458 mμ. This procedure is described in separate reports^(7,8). The concentration of FeN_3^{2+} in highly radioactive test solutions was determined by visual comparison with standard solutions.

MECHANISM OF HYDRAZOIC ACID FORMATION

A typical process solution of interest consisted of 5 to 8M HNO_3 containing 0.05M $Fe(NH_2SO_3)_2$ and 0.05M N_2H_4 . This solution is used to reduce and elute Pu(III) from an anion exchange bed that contains both Np(IV) and Pu(IV). After the elution, this solution is heated to destroy the Fe^{2+} and reoxidize the plutonium to Pu(IV) for a subsequent anion exchange absorption. Preliminary observations of the reddish brown color of FeN_3^{2+} in this solution indicated that the HN_3 concentration reached a maximum during this heating operation, then decreased to a very low value. Detailed studies of the rate of formation of HN_3 and of the stoichiometry of the reactions involved led to the following mechanism for the formation and destruction of HN_3 in solutions of HNO_3 , Fe^{2+} , and N_2H_4 .

Reaction (1) is well known. Its stoichiometry was verified by adding known amounts of $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ to solutions of HNO_3 that contained HN_3 as a reactant for HNO_2 . The concentrations of Fe^{3+} and HN_3 were determined as a function of time. The decrease in the concentration of HN_3 , and therefore the HNO_2 production, corresponded to about one-half the concentration of Fe^{3+} formed, indicating that one-half mol of HNO_2 was produced by the oxidation of one mol of Fe^{2+} . The amount of nitrous acid that reacted with the sulfamate ion was shown to be small in other studies. A typical set of data from one of these experiments is shown in Table I.

TABLE I

Oxidation of Fe^{2+} by HNO_3 at 40°C
(6.0M HNO_3 ; 0.049M HN_3 ; 0.053M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$)

Time, min	Fe^{3+} , M	HN_3 , M	HN_3 Consumed, M	$\text{HN}_3/\text{Fe}^{3+}$ Mol Ratio
60	0.0095	0.0448	0.0042	0.44
120	0.0189	0.0409	0.0081	0.43
200	0.0292	0.0359	0.0131	0.45
1295	0.0525	0.0242	0.0248	0.47

Reaction (2) was verified by adding NaNO_2 to a solution of HNO_3 containing N_2H_4 . One mol of HN_3 was produced for each mol of HNO_2 if the ratio of N_2H_4 to HNO_2 was large. The yield of HN_3 was less than 1:1 if aliquots of a concentrated solution of NaNO_2 were added, even if the final concentration of NaNO_2 was low, because reaction (3) occurred before the NaNO_2 was diluted. The results are summarized in Table II.

TABLE II

Reaction of N_2H_4 with HNO_2 at 25°C
(1.0M HNO_3 ; 0.005M HNO_2)

<u>NaNO_2</u>		<u>N_2H_4, M</u>	<u>HN_3, M</u>	<u>HN_3/HNO_2 Mol Ratio</u>
<u>Volume, ml</u>	<u>Conc, M</u>			
5	0.01	0.355	0.0043	0.86
1	0.05	0.355	0.0036	0.72
0.05	1.0	0.355	0.0022	0.44
1	0.05	0.005	0.0021	0.42
1	0.05	0.010	0.0024	0.48
1	0.05	0.050	0.0051	1.02
1	0.05	0.34	0.0059	1.18
1	0.05	0.68	0.0053	1.06
1	0.05	1.02	0.0049	0.98
1	0.05	1.36	0.0055	1.10
1	0.05	1.70	0.0056	1.12

Reaction (3) was verified separately by adding known amounts of HNO_2 to solutions of HN_3 . There was an equimolar consumption of HN_3 and HNO_2 , and the reaction was independent of the concentration of HNO_3 . The results are shown in Table III.

TABLE III
Reaction of HN_3 with HNO_2 at 25°C

HNO_3 , M	HNO_2 , M	HN_3 , M			$\frac{\text{HN}_3 \text{ Destroyed}}{\text{HNO}_2 \text{ Added}}$
		Found	Added	Difference	
1.0	-	0.0403	0.0403	-	-
1.0	0.005	0.0349	0.0403	0.0054	1.08
1.0	0.015	0.0259	0.0403	0.0144	0.96
1.0	0.025	0.0153	0.0403	0.0250	1.00
1.0	0.005	0.0098	0.0147	0.0049	0.98
1.0	0.005	0.0147	0.0196	0.0049	0.98
1.0	0.005	0.0197	0.0245	0.0048	0.96
1.0	0.005	0.0242	0.0294	0.0052	1.04
0.1	0.010	0.0117	0.0201	0.0084	0.84
6.0	0.025	0.023	0.046	0.023	0.92

Additional support for reactions (2) and (3) was obtained by determining the amount of HNO_2 required to destroy N_2H_4 . A value of two mols of HNO_2 per mol of N_2H_4 was obtained by two different methods. In one method, a large excess of HNO_2 was added to a solution of HNO_3 that contained N_2H_4 ; the remaining HNO_2 was determined by Ce^{4+} titration. In a less quantitative method, N_2H_4 was titrated with a dilute solution of NaNO_2 . Fe^{3+} was added, and the disappearance of the color of the FeN_3^{2+} complex indicated the end point of the titration. Results from both procedures are shown in Table IV.

TABLE IV
Destruction of N_2H_4 by HNO_2 at 25°C

Procedure	N_2H_4 , M	$\frac{\text{HNO}_2/\text{N}_2\text{H}_4}{\text{Mol Ratio}}$
Ceric titration	0.1148	1.86
Ceric titration	0.1148	1.98
Ceric titration	0.1148	2.01
Ceric titration	0.1148	1.96
Ceric titration	0.1148	2.03
HNO_2 titration	0.017	2.00
HNO_2 titration	0.034	1.94
HNO_2 titration	0.051	1.85

The reduction of Fe^{3+} by low concentrations of N_2H_4 (reaction (4)) occurs very slowly at room temperature and is not important in process solutions. It was observed that the absorbance of the FeN_3^{2+} complex decreased with time in solutions that contained N_2H_4 ; only the reduction of Fe^{3+} to Fe^{2+} could account for this behavior. The results from a single measurement of the reduction rate are shown in Table V.

TABLE V
Reduction of Fe^{3+} by N_2H_4 at 25°C
(1.0M HNO_3 ; 0.10M Fe^{3+} ; 2.5M N_2H_4 ; 0.005M HN_3)

Time, min	Fe^{3+} , M
0	0.098
17	0.074
27	0.047
52	0.011

RATE OF HYDRAZOIC ACID FORMATION

In addition to a knowledge of the mechanism of formation of HN_3 in process solutions, it was important to know the rate of formation in order to evaluate the hazards from HN_3 under typical process conditions.

The rate of formation of HN_3 in 5 to 8M HNO_3 containing $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ and N_2H_4 was found to depend upon the concentrations of HNO_3 , Fe^{2+} , and N_2H_4 . The dependence of the rate of HN_3 formation at room temperature on the HNO_3 concentration is shown in Figure 1. The dependence of the rate on the Fe^{2+} concentration at 50°C is shown in Figure 2. The variation of the rate with temperature and the interdependence of the Fe^{2+} oxidation are shown in Figure 3.

FIG. 1 EFFECT OF HNO_3 CONCENTRATION ON RATE OF HN_3 FORMATION

FIG. 2 EFFECT OF Fe^{2+} CONCENTRATION ON RATE OF HN_3 FORMATION

FIG. 3 EFFECT OF TEMPERATURE AND OXIDATION OF FERROUS SULFAMATE ON RATE OF HN_3 FORMATION

In a synthetic solution initially containing 0.05M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ and 0.05M N_2H_4 , the maximum concentration of HN_3 was found to be about 0.012M. This concentration was formed under conditions of essentially complete oxidation of the initial 0.05M Fe^{2+} in about three days at 23°C, but in only about one hour at 55°C. If, in the proposed mechanism, the reaction between HN_3 and HNO_2 (reaction (3)) were extremely efficient, HN_3 would be consumed as rapidly as it was produced. In that case, after the completion of the Fe^{2+} oxidation, it would be expected that no residual HN_3 would be present in solution. For example, oxidation of 0.05M Fe^{2+} would produce 0.025M HNO_2 , which would consume 0.0125M N_2H_4 , or 25% of the initial N_2H_4 , producing and destroying 0.0125M HN_3 . The observation that HN_3 remains after the completion of the Fe^{2+} oxidation is explained by the more favorable competition of the N_2H_4 for the HNO_2 produced. For example, at 55°C 70% of the HNO_2 reacted directly with the N_2H_4 to form HN_3 , while the remaining 30% was consumed by reaction with HN_3 . At lower temperatures a larger fraction of the HNO_2 reacts with N_2H_4 ; at 23°C essentially all of the HNO_2 produced reacted with N_2H_4 . These are approximate analyses to show the relative importance of reactions (2) and (3). The actual situation is undoubtedly more complex because reaction (5) between NH_2SO_3^- and HNO_2 becomes important as the N_2H_4 is consumed.

The dependence of HN_3 formation on the oxidation of Fe^{2+} was also demonstrated by experiments in which $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ was omitted. In solutions that contained 0.05M N_2H_4 , but no Fe^{2+} , in 4 to 7M HNO_3 , less than 1% of the N_2H_4 was oxidized to HN_3 after three days at 23°C, compared with 25% in similar solutions that contained Fe^{2+} .

In other experiments it was shown that neither $\text{NH}_2\text{SO}_3\text{H}$ nor Fe^{3+} affected the rate of formation of HN_3 .

ESTABLISHMENT OF SAFE LIMITS FOR HYDRAZOIC ACID IN PROCESS SOLUTIONS

It was considered that three types of hazards might be presented by the occurrence of HN_3 in process solutions. One would be the possible precipitation of explosive metallic azides. Another hazard might be presented by the distillation of HN_3 from solutions and the condensation of explosive HN_3 solutions. Finally, HN_3 vapor can form explosive mixtures with air. It was necessary to establish safe limits for these conditions in order to compare the limits with the maximum concentrations of HN_3 expected in process solutions.

Hg^{2+} , a dissolving catalyst in the processes of interest, is the only metallic ion present in sufficient quantities to be of concern. G. S. Nichols, Savannah River Laboratory, showed that it was possible to form an explosive compound in water containing sufficient Hg^{2+} and N_3^- to form 0.02M $\text{Hg}(\text{N}_3)_2$. The precipitate apparently formed slowly and detonated spontaneously during its formation. Slow diffusional growth is reported to be essential to form explosive $\text{Hg}(\text{N}_3)_2$.

in water⁽⁴⁾. Spontaneous detonation did not occur in less than 0.02M azide in water. In acid solutions, the solubility of $\text{Hg}(\text{N}_3)_2$ is much greater because of the removal of N_3^- by the formation of weakly ionized HN_3 ; the ionization constant of HN_3 at room temperature is 1.9×10^{-5} . Fe^{3+} also competes strongly with Hg^{2+} for the N_3^- . In actual precipitation tests, a precipitate was formed in 5M HNO_3 solutions only at relatively high concentrations of Hg^{2+} and HN_3 (0.08M Hg^{2+} - 0.16M HN_3). This precipitate could not be detonated.

From these observations it can be calculated that it would be highly improbable that a precipitate of $\text{Hg}(\text{N}_3)_2$ would form under expected process conditions. Furthermore, if a precipitate were formed it would probably not be explosive. In a solution of dissolved targets⁽²⁾ containing 0.005M Hg^{2+} in 5M HNO_3 , approximately 0.05M HN_3 would be required to form a precipitate. Concentrations of N_2H_4 of about 0.05M are used under normal conditions, and, even assuming 100% conversion to HN_3 , there would not be enough HN_3 to cause precipitation. As a very conservative safe limit, it was decided that the concentration of HN_3 should never be allowed to exceed 0.05M in solutions of this type.

The minimum explosive concentration of HN_3 in aqueous solutions is given in the literature as 4.7M (17%). Measurements of the vapor pressure of HN_3 showed that a solution containing 0.05M HN_3 at 20°C can deposit condensate that contains HN_3 above this explosive limit. But at 40°C, the normal process temperature, condensation of the vapor above a 0.05M HN_3 solution will not produce an explosive solution. The normal air sweep in the process vessels and pipe gives added safety against depositing an explosive condensate.

A lower limit of hazardous concentration of HN_3 in air was estimated by calculating from the vapor pressure data the pressure increase assuming adiabatic constant volume decomposition of mixtures of HN_3 and air. These data showed that solutions containing less than 0.05M HN_3 could not evolve sufficient HN_3 into the vapor phase at any temperature to cause a damaging explosion to an ordinary steel tank. For example, it is calculated that an explosion above a solution of 0.05M HN_3 in 5M HNO_3 at 40°C would generate only seven psig, and at 60°C would generate only ten psig. Additional safety is provided by an air sweep in the process vessels to reduce the concentration of HN_3 in the vapor phase, by the small probability that a concentration of 0.05M HN_3 would ever be attained in the aqueous phase, and by the small probability that an explosive HN_3 -air mixture, if attained, would be ignited.

MEASUREMENT OF HYDRAZOIC ACID IN ACTUAL PROCESS SOLUTIONS

The studies of the mechanism of formation of HN_3 from N_2H_4 that have been discussed in foregoing sections indicated that concentrations of HN_3 greater than about 0.01M would not be formed in process solutions under normal process conditions. Furthermore, it was shown that concentrations as high as 0.05M HN_3 would be conservatively safe with respect to hazardous conditions. A final evaluation of the safety of the processes was made by measuring the concentrations of HN_3 produced in actual process solutions.

The concentration of HN_3 was determined at the most critical steps in (1) the process for the recovery of Np^{237} from Purex waste and (2) the process for the separation of Pu^{238} from irradiated Np^{237} . In the first case the most critical step occurs after the neptunium valence adjustment in the Purex waste concentrate.⁽¹⁾ A sample of high activity waste concentrate from the Purex process of the following approximate composition was used in the test:

4M HNO_3	~1000 γ curies (fission products)/liter
2M NaNO_3	0.02 g Np^{237} /liter
0.5M KNO_3	traces of Pu^{239} , Th^{234} , Th^{232}
0.2M $\text{Mn}(\text{NO}_3)_2$	
0.2M $\text{Al}(\text{NO}_3)_3$	

The sample was adjusted to 0.05M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ and 0.1M N_2H_4 at 30°C to reduce the neptunium to $\text{Np}(\text{IV})$ for absorption by anion exchange. After these adjustments, HN_3 began to form by the reaction of HNO_2 with N_2H_4 ; the HNO_2 was produced by the slow oxidation of Fe^{2+} by HNO_3 , as well as by the radiolytic degradation of HNO_3 . Analysis of the solution showed that the concentration of HN_3 increased to a maximum of 0.01M in 6 hours and then dropped to 0.001M after 20 hours.

In the process for the separation of Pu^{238} from irradiated Np^{237} , the most critical step for the production of HN_3 occurs when a solution containing the Pu^{238} after it is separated from the Np^{237} by anion exchange partitioning is heated in preparation for a subsequent anion exchange cycle⁽²⁾. A typical process sample of the following composition was used to evaluate this step.

6M HNO_3	200 mg Pu^{238} /liter
0.05M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$	2 mg Np^{237} /liter
0.05M N_2H_4	38 γ mc fission product/liter

The sample was heated to 55°C during a 30-minute period to destroy the Fe^{2+} and to oxidize $\text{Pu}(\text{III})$ to $\text{Pu}(\text{IV})$. During the heating cycle, the HN_3 concentration reached 0.004M at 40°C, then reached a maximum value of 0.012M after twenty minutes of heating from 40° to 47°C. When the temperature reached 50°C the concentration of HN_3 had decreased to 0.006M, where it remained essentially constant. These data were considered to be in good agreement with the expected behavior and to offer a wide margin of safety from any hazardous conditions.

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