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HYDRAZINE, IRON

CATALYSIS OF HYDRAZINE - NITRIC ACID REACTION

TECHNICAL DIVISION
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THE IRON-CATALYZED OXIDATION OF HYDRAZINE BY NITRIC ACID

INTRODUCTION

The separations processes of the Savannah River Plant (SRP) use hydrazine as a reducing agent, a holding reductant, and, in dissolving plutonium metal, as an oxidizing agent for the H free radical. The stability of hydrazine toward oxidation by nitric acid limits the temperatures and time that solutions of hydrazine can maintain their effectiveness in processing, and is particularly critical in dissolving plutonium in HNO_3-KF-$N_2H_4 \cdot HNO_3$ solutions. A previous study[1] found the rate of oxidation of hydrazine in nitric acid to be less than expected; the half-life of $N_2H_4 \cdot HNO_3$ in 5.4M HNO_3 at 80° was measured as 8 hours, which could safely allow an increase in the temperature limit imposed on plutonium dissolving with a consequent increase in dissolving rate.

However, the previous study also found that the oxidation of hydrazine by nitric acid was catalyzed by adding ferric nitrate to the solution. Iron is not normally a major impurity in plutonium metal, but might be present in an unusual alloy, and the solution stability could also be affected by iron dissolved during equipment corrosion. In other process solutions, iron is often present from ferrous sulfamate use in prior processing. To assess the importance of iron to hydrazine stability, the study of hydrazine oxidation by nitric acid has been extended to investigate the iron-catalyzed oxidation. This report describes the results of these studies.

SUMMARY

Measurements of the kinetics of the iron-catalyzed oxidation of hydrazine by nitric acid were found to correlate with the empirical rate law

$$\ln \left[(N_2H_4)/(N_2H_4)_0\right] = -\left[(a'(Fe^{3+}) + b'(Fe^{2+})\right] (H^+)\ t$$

where concentrations are in moles per liter, $(N_2H_4)_0$ is the initial hydrazine concentration and $a' = 0.114\ M^{-2}\ min^{-1}$ and $b' = 0.065\ M^{-2}\ min^{-1}$ at 80°C, and t = minutes. Measurements at 70°C and 90°C were combined with a previous study[1] to calculate reaction rates for hydrazine oxidation in 6M NO_3^- solutions up to 5.4M HNO_3, 0.1M $Fe(NO_3)_3$ and temperatures from 60 to 100°C. The method of calculation is presented by an example.

Applying these results to the dissolving of impure Pu metal with HNO_3-$N_2H_4 \cdot HNO_3$-KF, it is recommended that the maximum dissolving temperature be limited to 60°C for a 2.2 wt % Fe impurity, 70°C for a 0.9 wt % Fe, and 80°C for a 0.16 wt % Fe.

EXPERIMENTAL

The experimental methods were those described in the previous study[1]. An additional measurement for the concentration of ferrous ion was made by titration with ceric sulfate solution in 2M H_2SO_4 with "ferroin" indicator. Tests show no appreciable interference from N_2H_4 or HN_3 in these titrations provided the sample was diluted by a factor of 50 to 100 with 2M H_2SO_4.

The reaction mixture was made up as previously reported[1]. A constant volume was maintained by pipetting concentrated nitric acid, water, 10M NaOH, 1.35M $Fe(NO_3)_3$ and 3.6M $N_2H_4 \cdot HNO_3$ solutions. A constant volume of concentrated HNO_3 was added to each reaction mixture and the acidity adjusted by adding varying volumes of 10M NaOH. This makeup method served to keep the ionic strength of the mixture constant for all reactions; the ionic strength (μ) was in the range 6.0-6.3M during this study, from 5.44M (HNO_3 + $NaNO_3$), 0.55M $N_2H_4 \cdot HNO_3$ and 0.10 to 0.01M $Fe(NO_3)_3$. During the reaction, the oxidation of hydrazine and the formation of NH_4^+ and HN_3 reduces the ionic strength to approximately 5.7M.

Throughout this report, it will be assumed that the sum of H^+ and Na^+ ions is 5.44M, and, as an example, "a reaction in 3.9M HNO_3" is actually a reaction in 3.9M HNO_3 - 1.54M $NaNO_3$.

RESULTS

General

The catalytic effect of iron ions was studied primarily at 80°C and with an initial iron concentration of 0.1M. These conditions were chosen to keep the reaction rate in a measurable range for the sampling techniques used, to have iron concentrations in a measurable range by titration techniques and to assure that the main route of the hydrazine oxidation would be by the iron-catalyzed reaction, rather than nitric acid oxidation. The previous study found reaction half-times of 0.33 hr, 2.7 hr, and 8 hr for 0.1M, 10^{-2}M, and zero ferric nitrate, respectively, added initially to the reaction mixture. From these data, it can be calculated that 97% of the hydrazine oxidation occurs by the iron-catalyzed route at 80°C with 0.1M $Fe(NO_3)_3$ initially present, but only 55% of the oxidation proceeds through a catalytic path when the initial $Fe(NO_3)_3$ concentration is 10^{-2}M.

Nature of the Reaction

Preliminary experiments found that not only were the iron ions oxidized and reduced during the reaction, but also the first-order oxidation of hydrazine accelerated as the ferric concentration increased. (Figure 1) Iron ions were added both as $Fe(NO_3)_3$ and hydrazine-stabilized $Fe(NO_3)_2$. When 0.1M Fe^{3+} was added initially, there was a rapid evolution of gas during the first 10 minutes of the reaction at 80°C in 2.93M HNO_3, but only a minor gas evolution when the initial iron addition was 0.1M Fe^{2+}. (Figure 2) The measured difference between initial additions of Fe^{3+} and Fe^{2+} was 2.3 millimoles of gas. This initial reaction was expected from the results of earlier investigators[2-4], and is due to

$$N_2H_5^+ + Fe^{3+} \longrightarrow N_2H_3 + Fe^{2+} + 2H^+$$

followed by

$$2N_2H_3 + 2H^+ \longrightarrow 2NH_4^+ + H_2$$

The reduction of the 5.2 millimoles of Fe^{3+} initially added could produce 2.6 millimoles (m moles) of N_2. As the reduction of Fe^{3+} in the first 10 minutes was 87% complete, the expected yield of N_2 is 2.26 m moles. The 2.3 m mole experimental value agrees well with the calculated value.

The initial reduction of Fe^{3+} depends on both the acid concentration and the temperature. Higher acidities and higher temperatures result in a higher Fe^{3+} concentrations in the initial stage of the reaction. The concentration of Fe^{3+} 10 minutes after reaction initiation at varying acidities is shown in Figure 3; data on Fe^{3+} concentration and initial reaction half-times are shown in Table I.

TABLE 1

Initial Fe^{3+} Concentration$^{(a)}$ and Reaction Half-Times

HNO_3,M	T, °C	Fe^{3+}, M	Reaction Half-Time, min
5.44	80	0.040	16
4.67	80	0.030	18
3.90	80	0.027	22
3.30	80	0.010	26
2.93	80	0.014	28
1.99	80	0.005	48
5.44	70	0.038	60
3.90	70	0.039	62
3.90	90	0.039	14
2.93	90	0.01	9
5.44^{b}	90	nd	33
3.90^{b}	90	nd	84
5.44^{c}	90	-	160

(a) Initial Concentration: 0.54M $N_2H_4 \cdot HNO_3$, $Fe^{3+} + Fe^{2+} = 0.1M$

(b) $Fe^{3+} + Fe^{2+} = 0.013M$

(c) No added $Fe(NO_3)_3$

The Fe^{3+} concentration measured 10 minutes after the start of the reaction is normally the minimum concentration and increases during the hydrazine oxidation. The Fe^{3+}/Fe^{2+} ratio maintains a steady-state between the reduction of Fe^{3+} by hydrazine and reducing intermediates and the oxidation of Fe^{2+} by HNO_3. When the hydrazine concentration becomes small, the Fe^{3+} concentration increases and the reaction rate increases, as in Figure 1.

Reaction Rates

Table I shows the reaction half-times as measured by the initial slope of a graph like Figure 1. Between 5.43M and 2.93M HNO_3 at 80°C, the reaction has a first-power dependence on acidity (Figure 4). The reaction rate increases about a factor of three for each 10° increase in the temperature.

A more detailed analysis of the data involved a computer fit of the data to a two-path model. Of the several fits attempted, the best fit was achieved for the model

$$-\ln\left[(N_2H_4)/(N_2H_4)_0\right] = \left[a(Fe^{3+}) + b(Fe^{2+})\right] t$$

where $(N_2H_4)_0$ is the initial concentration of hydrazine and the values for (N_2H_4), (Fe^{3+}), and (Fe^{2+}) are the experimental values measured at time t (minutes).

The run data were fit with a nonlinear least-square program (PROC NLIN)[5] in the SAS[6] system on the IBM 3081 to determine values for the coefficients a and b. A sample of the computer fit for one data set (2.93M HNO_3, 0.1M $Fe(NO_3)_3$, 0.55M $N_2H_4{\cdot}HNO_3$, 80°C, initial conditions) is shown in Table II; values for a and b for all data are shown in Table III.

TABLE II

Computer Data Fit

OBS	Y	X	T	Z	YHAT	RHAT
1	0.213	0.013	10	0.087	0.20710	0.005904
2	0.418	0.014	20	0.086	0.41780	0.000196
3	0.658	0.015	30	0.085	0.63213	0.025875
4	0.883	0.023	40	0.077	0.90063	-0.017634
5	1.173	0.031	50	0.069	1.19804	-0.025043
6	1.480	0.035	60	0.065	1.48100	-0.001001
7	1.848	0.044	70	0.056	1.84163	0.006371
8	2.229	0.051	80	0.049	2.20587	0.023131
9	2.648	0.062	90	0.038	2.66042	-0.012423

Key: Y = ln $[(N_2H_4)/(N_2H_4)_0]$, expl; YHAT, calc.;
RHAT = YHAT - Y, X = Fe^{3+}, Z = Fe^{2+}, T = time in minutes

TABLE III

Least-Square Constants ([a], [b])

HNO_3, M	T, °C	a	$a/(H^+)$	b	$b/(H^+)$
5.44	80	0.656 ±0.029	0.121	0.348 ±0.055	0.064
4.67	80	0.448 ±0.012	0.096	0.311 ±0.026	0.066
3.90	80	0.414 ±0.008	0.106	0.239 ±0.010	0.061
3.30	80	0.416 ±0.017	0.125	0.243 ±0.017	0.073
2.93	80	0.364 ±0.004	0.124	0.184 ±0.004	0.063
1.99	80	0.402 ±0.015	0.201	0.176 ±0.003	0.086
5.44	70	0.180 ±0.005	0.033	0.098 ±0.008	0.018
3.90	90	1.02 ±0.05	0.262	0.98 ±0.14	0.025
3.90	70	0.147 ±0.002	0.038	0.073 ±0.003	0.019

(a) Initial conditions: 0.55M $N_2H_4 \cdot HNO_3$, 0.10M Fe^{3+}, $\mu = 6 \cdot 3$
(b) Constants for

$$-\ln\left[(N_2H_4)/(N_2H_4)_0\right] = \left[a(Fe^{3+}) + b(Fe^{2+})\right]t$$

The values for both a and b show a linear dependence on acidity for the data at 80°C at 2.93M HNO_3 and higher acidity. (See the first five entries in columns 4 and 6, Table III). At 80°C, $a = 0.114(H^+)$ and $b = 0.065(H^+)$; the computer-fitted data can be represented empirically by

$$-\ln \left[(N_2H_4)/(N_2H_4)_0\right] = \left\{0.114(H^+)(Fe^{3+}) + 0.065(H^+)(Fe^{2+})\right\}t$$

where t is in minutes.

Temperature Dependance

The temperature dependence of $a/(H^+)$ and $b/(H^+)$ was determined from a graph of the appropriate values from Table III vs 1/T (Figure 4). The temperature dependence of $b/(H^+)$ is about 30% greater than the temperature dependence of $a/(H^+)$.

The reaction half-time at 5.44M HNO_3 for the uncatalyzed reaction (last line, Table I) was combined with earlier data[1] to determine the temperature dependence of the uncatalyzed reaction; a graph of the inverse of the reaction half-time vs 1/K is shown in Figure 5. Figures 4 and 5 and the rate equations can be used to predict the rate of hydrazine oxidation in 6M NO_3^- solutions; an example will be shown later in the Discussion section.

Reaction Products

The reaction products (Table V) show remarkably little variation with temperature and acidity. There is an slight increase in the N_2O yield at lower acidity that may be real. However, the percentages of N_2 and N_2O change enough during a reaction that composition of the gas sample can be affected by when the gas sample was taken. In a reaction at 90°, 5.44M HNO_3, 0.10M $Fe(NO_3)_3$ gas samples showed 89%, 74% and 65% N_2 at the beginning, middle and end of the reaction, respectively. Large gas samples were taken to obtain an average value, but the gas samples did not include all the gas produced during a reaction.

The major difference between the Fe^{3+} catalyzed and the uncatalyzed reaction is the large increase in NH_4^+ produced in the catalyzed reaction. The uncatalyzed reaction (Figure 5) produces roughly equal amounts of NH_4^+ and HN_3; the Fe^{3+} catalyzed reaction produces about 5 times as much NH_4^+ as HN_3.

TABLE IV

Reaction Products for Fe^{3+}/Fe^{2+} - Catalyzed Hydrazine Oxidation

Initial			Final				
			Millimoles			%	
HNO_3, M	Fe^{3+}, M	T, °C	NH_4^+	HN_3	N_2+N_2O	N_2	N_2O
5.44	0.1	90	16.1	2.6	20.9	76	23
	0.1	80	16.6	2.5	19.0	79	21
	-	90	4.7	4.9		74	26
	0.013[a]	90	13.0	3.2	20.4		
	0.076[a]	65	14.0	3.6	13.7[b]	82	18
	0.013	90	13.5	3.2	18.5	69	31
4.67	0.1	80	15.1	2.9	19.3	72	28
3.90	0.1	90	14.0	2.0		80	20
	0.1	80	16.6		19.9	72	28
	0.01	90	16.6	3.1			
	0.1	70					
2.93	0.1	80	12.5	3.6		71	29
1.99	0.1	80	15.1	3.1	19.3	68	32

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[a] Fe^{2+}

[b] Reaction incomplete

Net Reaction

The net reaction at 80°C in 2.93M HNO_3 with 0.1M Fe^{3+} catalyst can be calculated from the data of Table IV to be

$$N_2H_4 + 1.4\ HNO_3 \dashrightarrow 0.56\ N_2 + 0.24\ N_2O + 0.15\ HN_3 + 0.70\ NH_4NO_3 + 1.5\ H_2O \tag{e}$$

For comparison, the net reaction at 90°C in 5.44M HNO_3 with no iron catalyst was calculated to be

$$N_2H_4 + 0.6\ HNO_3 \dashrightarrow 0.2\ NH_4NO_3 + 0.2\ HN_3 + 0.2\ N_2O + 0.6\ N_2 + 1.4\ H_2O \tag{f}$$

The major difference between the products of the iron-catalyzed and uncatalyzed oxidation is the increase in acid consumption and in NH_4^+ produced in the iron-catalyzed reaction.

DISCUSSION

Reaction Mechanism

In general, the Fe^{3+} catalyzed oxidation of hydrazine proceeds through the oxidation of hydrazine by Fe^{3+} and the oxidation of Fe^{2+} to Fe^{3+} by HNO_3. These reactions compete to create a steady-state concentration of Fe^{3+}, the primary oxidant for hydrazine. However, the detailed mechanism is considerably more complex. Hydrazine can react to form hydrazyl (N_2H_3) and/or diazene (N_2H_2) free radicals; where Fe^{3+} is the oxidizing agent, both free radicals are produced[2,4,7]. The products of the reaction are N_2, N_2O, NH_4^+, and HN_3, all of which are formed by reactions of the reactive intermediates N_2H_3, N_2H_2, OH, and HNO_2.

The Fe^{3+} catalyzed oxidation begins with primary reaction between Fe^{3+} and $N_2H_5^+$.

$$Fe^{3+} + N_2H_5^+ \dashrightarrow Fe^{2+} + 2H^+ + N_2H_3 \tag{1}$$

Fe^{2+} is oxidized by HNO_3

$$Fe^{2+} + HNO_3 + H^+ \dashrightarrow Fe^{3+} + HNO_2 + OH \tag{2}$$

followed by

$$Fe^{2+} + H^+ + OH \dashrightarrow Fe^{3+} + H_2O \tag{3}$$

Reactions (2) and (3) are similar to steps in the oxidation of Fe^{2+} by H_2O_2[8] and are proposed rather than the mechanism of Epstein, et al[9]. Epstein's mechanism produces NO and NO_2, which were not observed in any experiment.

HNO_2 is rapidly scavenged by $N_2H_5^+$ and HN_3[10-12].

$$HNO_2 + N_2H_5^+ \longrightarrow HN_3 + H^+ + 2\ H_2O \tag{4}$$

$$HN_3 + HNO_2 \longrightarrow N_2O + N_2 + H_2O \tag{5}$$

The hydrazyl free radical reacts[2] by

$$2\ N_2H_3 + 2\ H^+ \longrightarrow 2NH_4^+ + N_2 \tag{6}$$

$$N_2H_3 + 2H^+ + Fe^{2+} \longrightarrow N_2H_5^+ + Fe^{3+} \tag{7}$$

$$N_2H_3 + Fe^{3+} \longrightarrow N_2H_2 + Fe^{2+} + H^+ \tag{8}$$

The diazene free radical also reacts by

$$N_2H_2 + HN_3 + H^+ \longrightarrow 2N_2 + NH_4^+ \tag{9}$$

$$N_2H_2 + 2\ Fe^{3+} \longrightarrow 2\ Fe^{2+} + 2H^+ + N_2 \tag{10}$$

The relative importance of these ten reactions can be estimated from the data of Tables I and Table IV. Reactions 1-4 are largely responsible for maintaining the $Fe^{3+} - Fe^{2+}$ steady state and oxidizing N_2H_4. Reaction 5 is the only reaction that produces N_2O, and thus accounts for about 55% of the gaseous products. Reaction 6 produces up to 40% of the evolved gas; however, it is most important in the early part of the reaction. As the N_2H_4 concentration is depleted, the concentraton of N_2H_3 radicals decreases and the bimolecular reaction becomes less probable. Reactions 8, 9 and 10 become more important as the reaction nears completion.

Rate Law

Ideally, a rate law for the concentration of the reactants and the products as a function of time can be derived from reactions 1-10. However, the system is quite complicated and a number of assumptions are necessary to solve the equations. The derived rate law should have a form similar to the experimental rate law,

$$\ln\left[(N_2H_4)/(N_2H_4)_0\right] = -\left[(a'(Fe^{3+}) + b'(Fe^{2+})\right](H^+)t \tag{11}$$

where $a' = a/(H^+)$, $b' = b/(H^+)$

Under different assumptions (see Appendix) two rate laws for hydrazine were derived,

$$\ln\left[(N_2H_4)/(N_2H_4)_0\right] = -\,k_1{}' \,(Fe^{3+})\,(H^+)t - \left[k_2{}' \,(Fe^{2+})\,(H^+)^2\,(NO_3{}^-\right]/k_1{}' \,(Fe^{3+})\,(N_2H_4) \quad (12)$$

and

$$\ln\left[(N_2H_4)/(N_2H_4)_0\right] = -\,k_1{}' \,(Fe^{3+})\,(H^+)t - \left[k_2{}' \,(Fe^{2+})\,(NO_3{}^-)\,(H^+)^3t\right]/k_5\,(HN_3) \quad (13)$$

Both 12 and 13 have the same leading term as 10, and comparing with experimental rate law,

$$k_1{}' = a' = 0.114M^{-2}\ min^{-1} \text{ at } 80°C.$$

The second term on the right side of both 12 and 13 does not have the same form as 10, and attempts to computer fit experimental data to both were unsuccessful. The failure to derive a satisfactory rate equation was caused by either an inadequate mathematical treatment or by the neglect of an important reaction. In any case, it did not appear worthwhile to pursue a rate derivation.

Calculation of Reaction Rate

The oxidation of hydrazine by nitric acid can be considered to be the sum of the rate for the uncatalyzed reaction and the rate for the Fe^{3+} - Fe^{2+} catalyzed reaction. From the available data, the half-time for the oxidation of hydrazine by the combined reactions can be calculated. As an example, the reaction half-time in 5.44M HNO_3 - 0.01M Fe^{3+} at 90°C will be calculated.

- From Figure 3, assume Fe^{3+} = 0.004M and Fe^{2+} = 0.006M. From Figure 4, at 90°C, both a′ and b′ = 0.26. The reaction half-time for the Fe^{3+} - catalyzed reaction can be calculated by substituting these values and ln 0.5 = 0.693 into 11.

$$0.693 = \left[(0.004)(0.26)(5.4) + (0.006)(0.26)(5.4)\right]t_{1/2}$$

Solving, the reaction half-time, $t_{1/2}$ = 50 min

- For the uncatalyzed reaction path, the reaction half-time in 5.4M HNO_3 at 90°C from Figure 6 is 2.6 hr.

- Combining, by

$$1/t_{1/2}\text{ (total)} = {}^{1}/t_{1/2}\text{ (Fe)} + {}^{1}/t_{1/2}\text{ (HNO}_3\text{)}$$

$$t_{1/2}\text{ (total)} = 0.6\text{ hr. or }36\text{ min.}$$

The measured value (Table I) is 33 min.

These approximate calculations can be used to estimate the half-life of hydrazine to about 20% within the range of the measurements in solutions of about 6M NO_3^-. It should be cautioned that the data of Figure 6 are acid-dependent, and must be corrected from 5.44M HNO_3 by the inverse ratio of the squares of the acid concentration.

Process Application

These data and those of the previous study[1] are most applicable to the dissolving of plutonium metal in HNO_3-N_2H_4•HNO_3-KF solutions. As under test in SRP[13], the dissolving temperature is limited to 70°C or less to prevent destruction of the hydrazine by reaction with nitric acid which would be followed by oxidation of Pu^{3+} to Pu^{4+} and the rapid release of a large quantity of nitrogen oxides. In practice, SRP has operated the dissolving to allow only a 60°C maximum temperature. Since the dissolving process normally operates at 50°C, this has resulted in frequent quenches of the dissolving that reduce the production rate substantially.

The data of this study shows that an iron impurity has a serious effect on hydrazine stability. At 80°C, the calculated half-lives for hydrazine in 3M HNO_3 are 1.1 hr and 4.8 hr with 0.05M and 0.02M (Fe^{3+} + Fe^{2+}) present respectively. These concentrations correspond to 1 wt % Fe and 0.4 wt % Fe impurities. The loss of hydrazine with 0.02M (Fe^{3+} and Fe^{2+}) is 18% per hour, and could be compensated for by increasing the hydrazine concentration; the hydrazine loss with 0.05M (Fe^{3+} + Fe^{2+}) present is 47% per hour and is clearly exceeds practical operating conditions.

The maximum amount of iron impurity that can be tolerated during dissolving Pu metal with HNO_3-N_2H_4•HNO_5-KF has been calculated for operating temperatures over the range 60 to 80°C, on the assumption that a 5 hour reaction half-time is an acceptable hydrazine loss.

The calculated maximum iron impurity is 2.2 wt % at 60°C, 0.9 wt % at 70°C, and 0.16 wt % at 80°C. It is recommended that SRP dissolving of impure Pu metal limit their maximum operating temperatures to these limits when an iron impurity is known to be present.

In the absence of a iron impurity, hydrazine is sufficiently stable to permit safe operation up to 80°C. At 80°C, the reaction half-time for hydrazine oxidation is 8 hours in 5.4M HNO_3, which corresponds to only an 8% loss per hour. In 3M HNO_3, the hydrazine loss is only 2.5% per hour. In the absence of catalytic metal ions, dissolving operations up to 80°C are practical, and should be considered when an increased production rate is desired. Copper ions would be expected to show catalytic activity, and the catalytic oxidation of hydrazine by technicium has been reported.[15]

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Appendix: Derivation of Rate Law

From reactions 1 and 4, the rate law for N_2H_4 is

$$d(N_2H_4)/dt = -k_1\ (Fe^{3+})(N_2H_5^+) \\ -k_4\ (N_2H_5^+)(HNO_2) \qquad (A\text{-}1)$$

$$(N_2H_5^+) = K_1\ (N_2H_4)(H^+) \qquad (A\text{-}2)$$

where $K_1 = 8.5 \times 10^7$ at 25°C.[14] Substituting into A-1,

$$d\ \ln\ (N_2H_4)/dt = -k_1{}'\ (Fe^{3+})(H^+)\ -k_4{}'(H^+)(HNO_2) \qquad (A\text{-}3)$$

where $k_1K_1 = k_1{}'$ and $k_4K_1 = k_4{}'$

From reactions 2, 4 and 5, the rate law for (HNO_2) is

$$d(HNO_2)/dt = k_2\ (Fe^{2+})(HNO_3)(H^+) \\ -k_4{}'(N_2H_4)(HNO_2) - k_5(HN_3)(HNO_2) \qquad (A\text{-}4)$$

In steady-state conditions, $d(HNO_2)/dt = 0$.

Then,

$$(HNO_2) = \frac{k_2(Fe^{2+})(HNO_3)(H^+)}{k_4{}'(N_2H_4)(H^+) + k_5(HN_3)} \qquad (A\text{-}5)$$

Substituting A-5 into A-3 and approximating the denominator of A-5 by $k_4{}'(N_2H_4)(H^+)$ results in

$$d(N_2H_4)/dt + k_1{}'(Fe^{3+})(H^+)(N_2H_4) \\ = -k_2{}'(Fe^{2+})(NO_3^-)(H^+)^2 \qquad (A\text{-}6)$$

where $k_2{}' = k_2K_2$, and $K_2(NO_3^-)(H^+) = (HNO_3)$

Integrating and evaluating the integration constant yields

$$(N_2H_4) = -(N_2H_4)_0\ \exp\ (-\ ft) - g/f \qquad (A\text{-}7)$$

where $f = k_1{}'(Fe^{3+})(H^+)$

$g = k_2{}'(Fe^{2+})(H^+)^2(NO_3^-)$

Rearranging and taking the natural log of the equation results in

$$\ln \left[(N_2H_4) + g/f)/(N_2H_4)_0\right] = -ft \qquad \text{(A-8)}$$

Using the series expansion for the logarithm,

$$\ln \left[(N_2H_4)/(N_2H_4)_0\right] = -\ ft - 2 \left(\frac{g/f}{2(N_2H_4) + g/f}\right) \qquad \text{(A-9)}$$

$$\approx -\ ft - g/f\ (N_2H_4)$$

or

$$\begin{aligned} \ln \left[(N_2H_4)/(N_2H_4)_0\right] = -k_1'\ (Fe^{3+})(H^+)t & \\ & \qquad \text{(A-10)} \\ \left[k_2'\ (Fe^{2+})(H^+)^2(NO_3^-\right]/k_1'\ (Fe^{3+})(N_2H_4) & \end{aligned}$$

A second derivation of the rate law for hydrazine oxidation can be made by making the assumption that the denominator of A-5 is approximately $k_5(HN_3)$. Then,

$$\begin{aligned} \ln \left[(N_2H_4)/(N_2H_4)_0\right] = -k_1'(Fe^{3+})(H^+)t & \\ \left[k_2'(Fe^{2+})(NO_3^-)(H^+)^3t\right]/k_5(HN_3) & \qquad \text{(A-11)} \end{aligned}$$

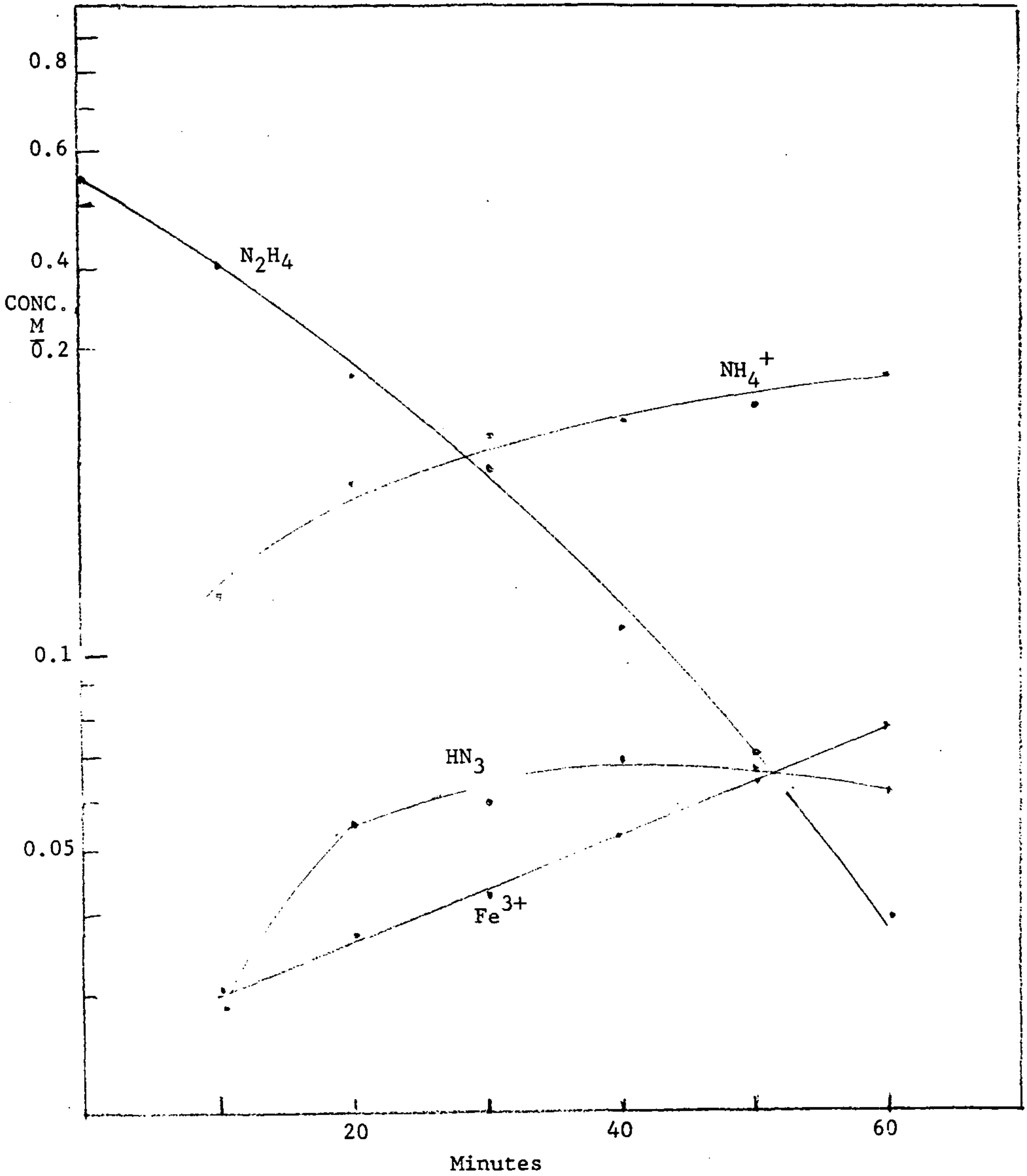

FIGURE 1. Reactant Concentrations Initial Conditions, 4.67M HNO_3, 0.1M $Fe(NO_3)_3$, 0.54M $N_2H_4 \cdot HNO_3$, 80°C

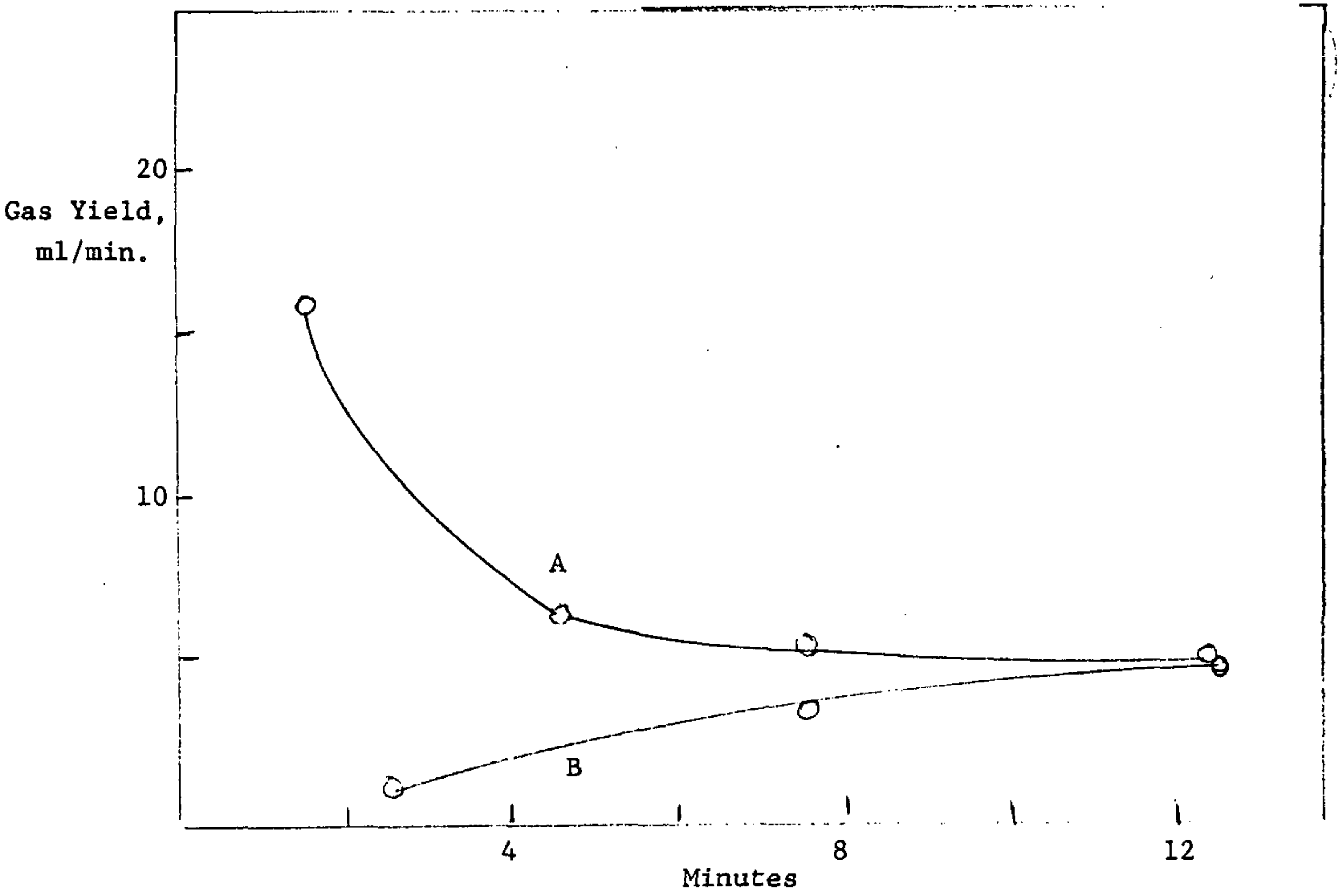

FIGURE 2. Gas Evolution from 2.93M HNO_3-0.55M $N_2H_4 \cdot HNO_3$ at 80°C with an Initial Addition of (A) 0.1M $Fe(NO_3)_3$ or (B) 0.1M $Fe(NO_3)_2$

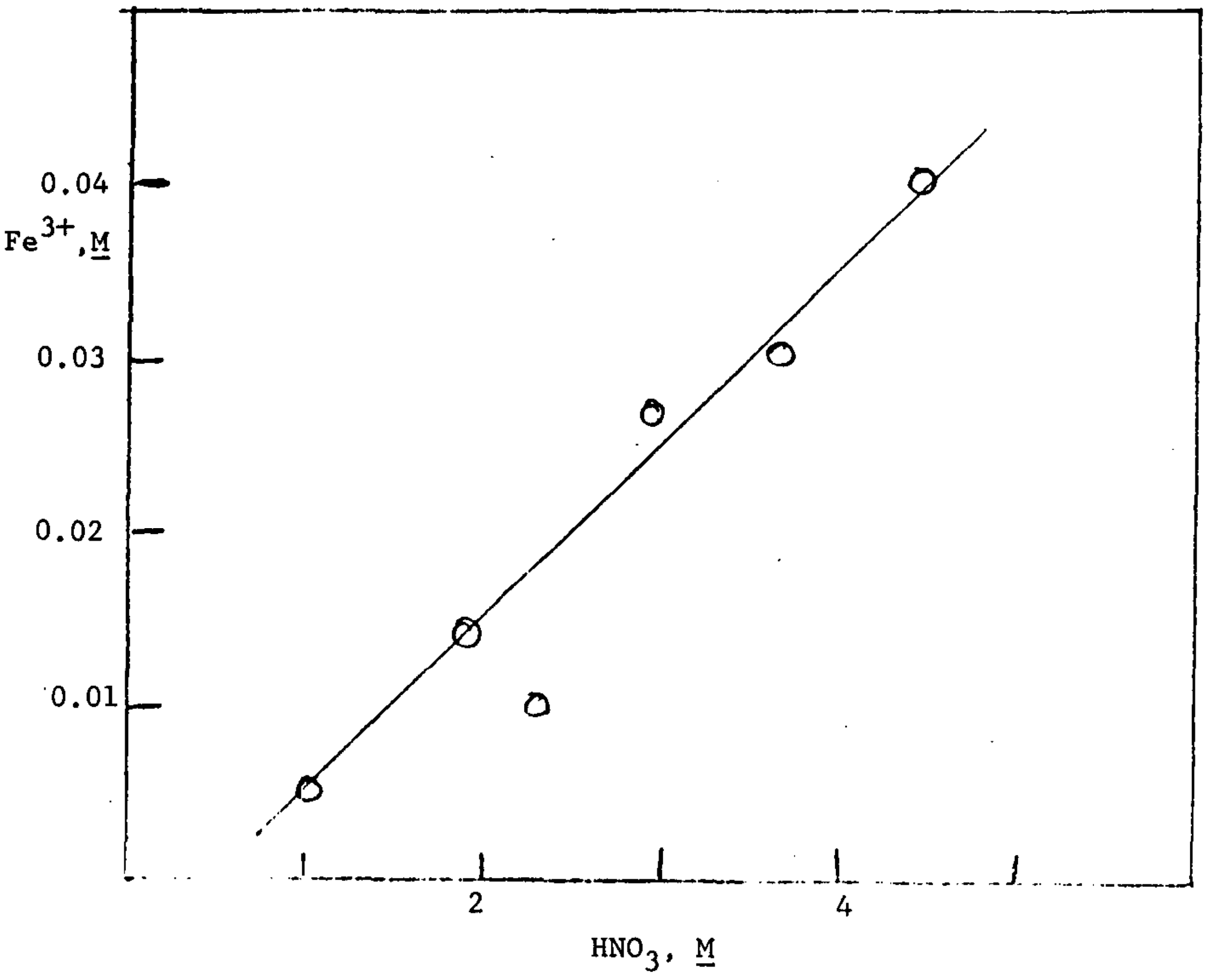

FIGURE 3. Fe^{3+} Concentration 10 Minutes After Reaction Initiation

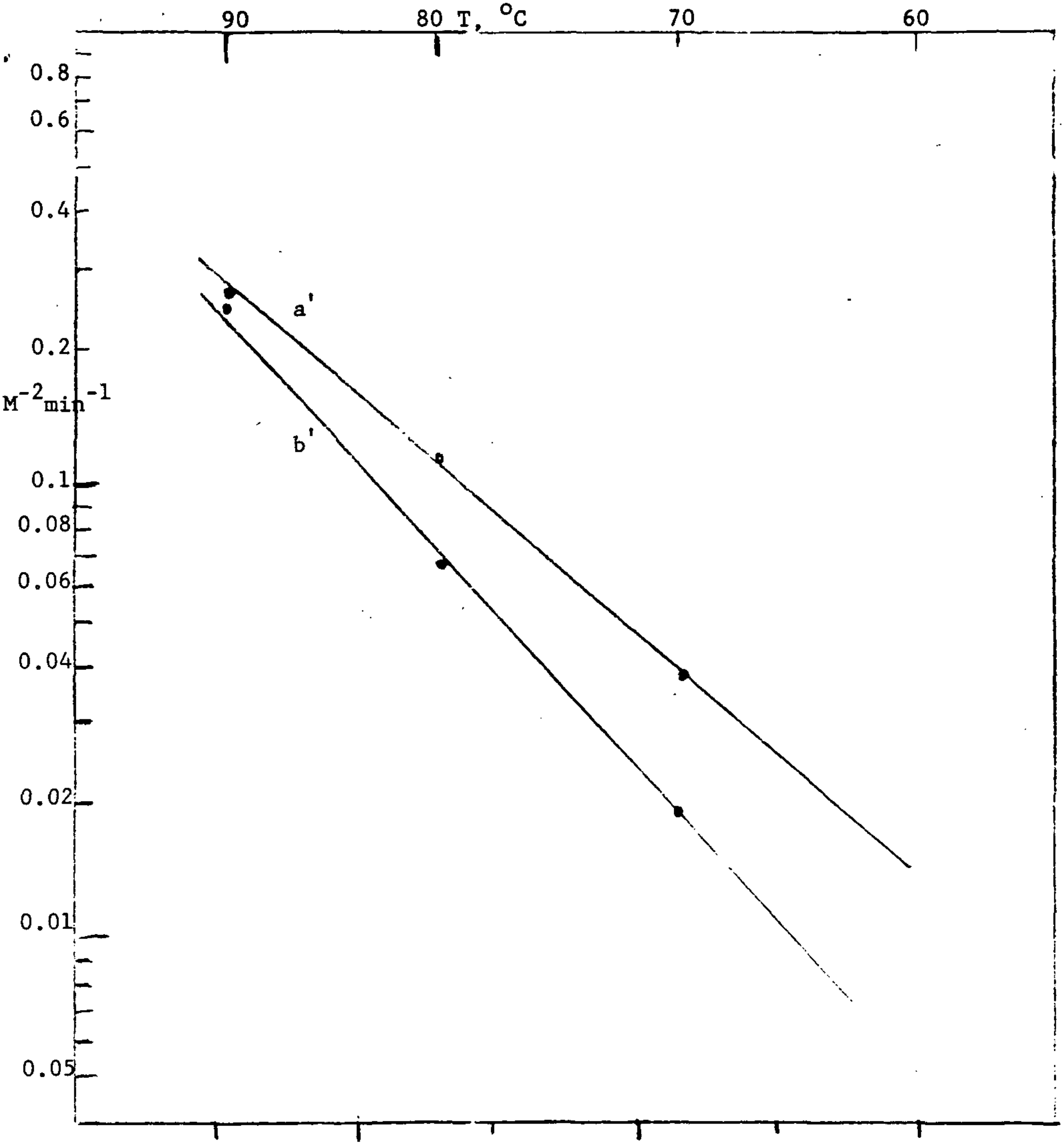

FIGURE 4. Temperature Dependence of Constants a' and b'

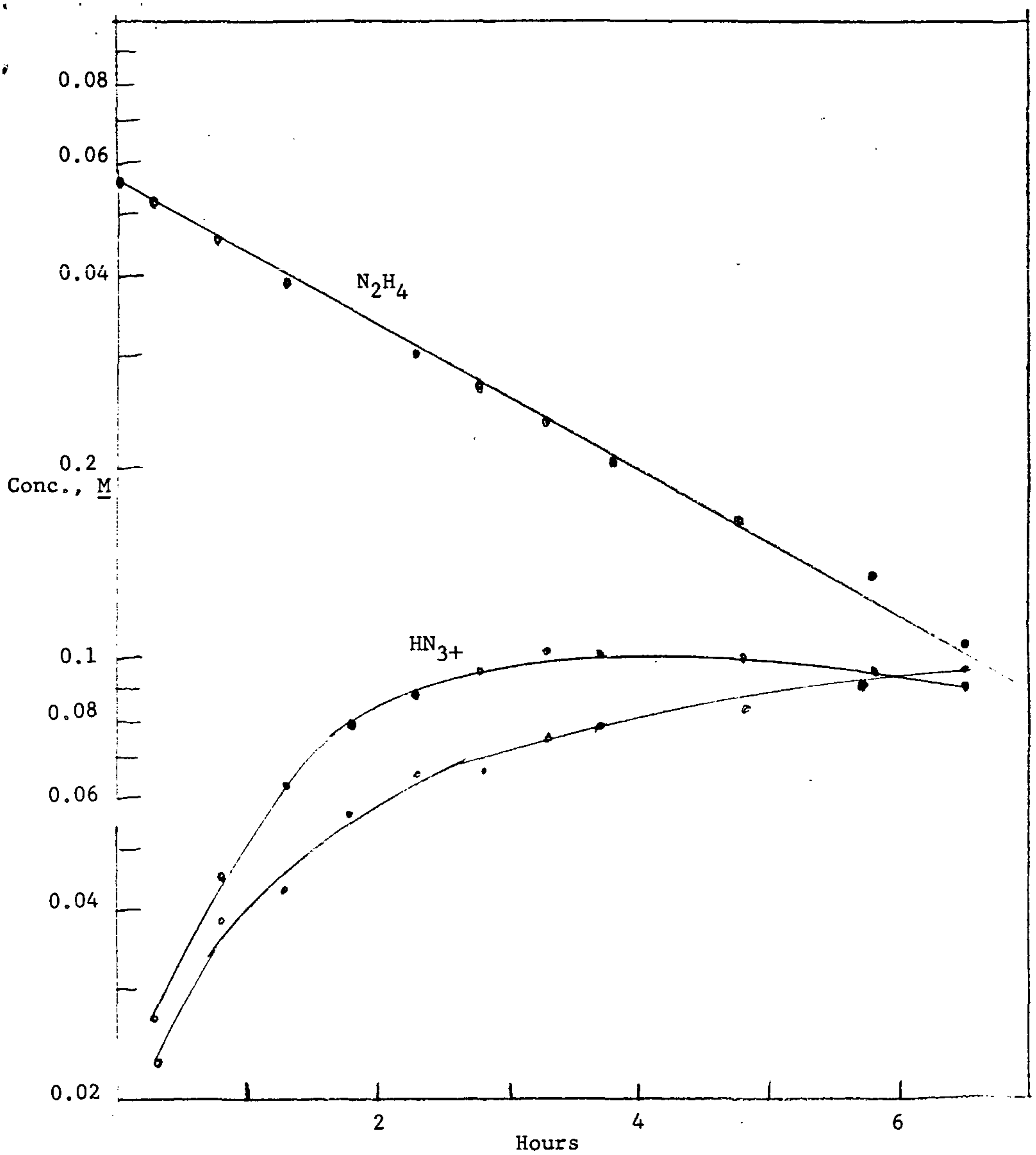

FIGURE 5. Reactant Concentrations. Initial Concentrations, 5.44M HNO_3, 0.54M $N_2H_4 \cdot HNO_3$·90°C

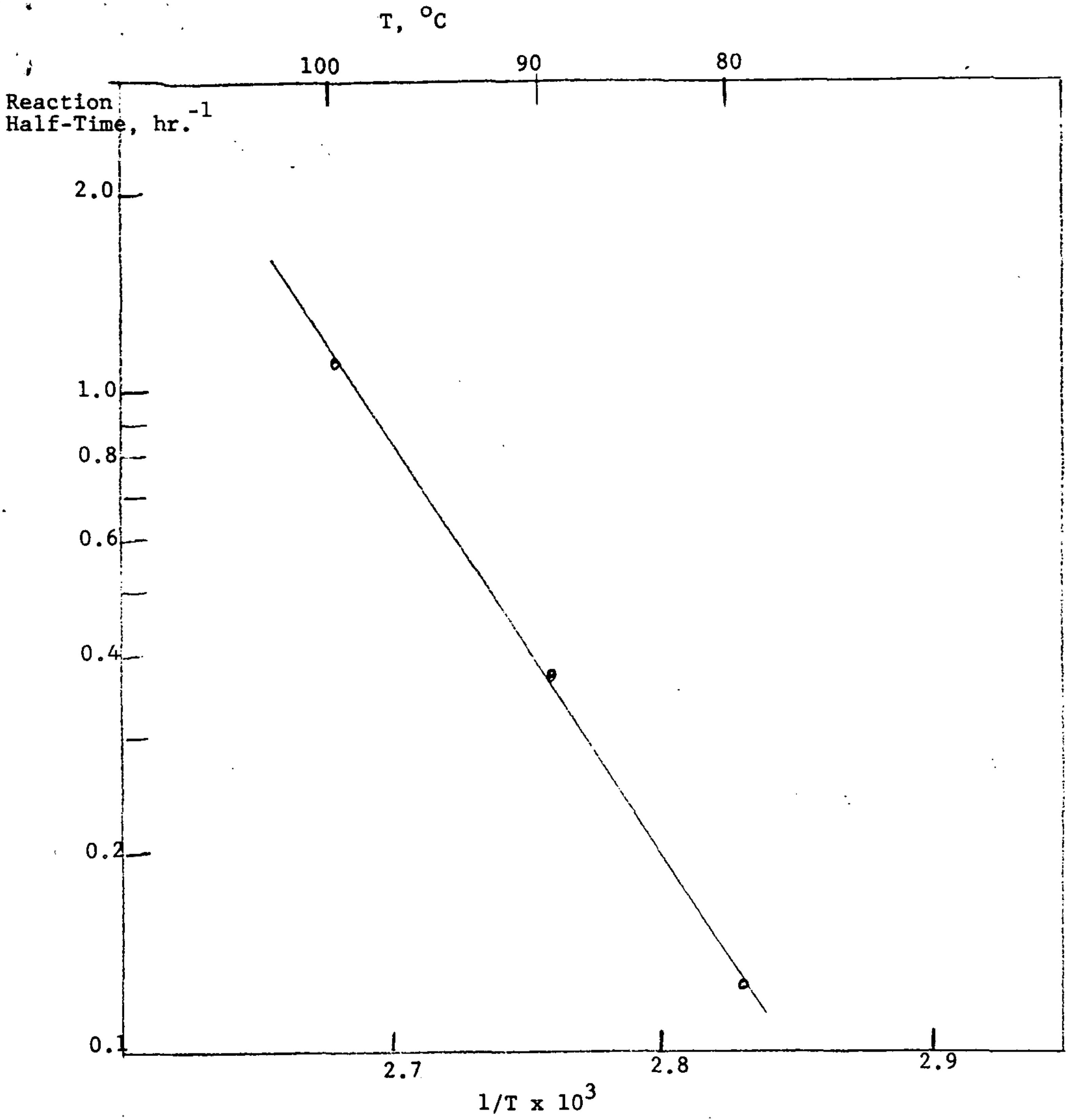

FIGURE 6. Temperature Dependence of the Uncatalyzed Hydrazine Oxidation