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CATALYTIC DEOXYGENATION OF AQUEOUS SOLUTIONS BY HYDRAZINE

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FOR THE COMMANDER

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The catalytic effect of metallic ions at their reported maximum environmental water concentrations were studied in the deoxygenation by hydrazine in aqueous solutions. Fe(III), Fe(II), Zn(II), Co(II), and Ni(II) ions did not significantly enhance the deoxygenation of aqueous solutions. The thermal effects of the kinetic deoxygenation rate for hydrazine, MMH, and UDMH by the catalytic reactions with copper were studied. Previous work at this Lab established a predictive model for the deoxygenation kinetic rate constant as a function of propellant and copper concentration. This was expanded to include a

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thermal ratio parameter.

PREFACE

This study was conducted at the Toxic Hazards Division of the Aerospace Medical Research Laboratory. The research was performed in support of Project 6302 "Toxic Hazards of Propellants and Materials;" Task 04, from December 1974 to January 1976.

The author acknowledges the guidance and encouragement of Captain William T. Gormley who initiated this study prior to reassignment.

INTRODUCTION

Hydrazine is used in combination with monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) as fuels in several Air Force missile systems. Because of its extensive deoxygenation properties, the environmental impact of an accidental spill of these materials is of great concern to the Air Force. Previous work from our laboratory (Gormley and Ford, 1973) included a mathematical model describing the degradation of hydrazine-type fuels by the catalytic action of copper. The use of this deoxygenating property of hydrazine in boiler feedwater systems is now a standard commercial method to eliminate corrosion. This deoxygenation phenomenon was studied (Gaunt and Wetton, 1966) at low temperatures (25° to 70°F) in alkaline solutions. Their evidence revealed that the observed degradation rate was due to catalysis by traces of impurities. Their report proposed that the copper (II) - catalyzed reaction appeared to be homogeneous. However, only in the earlier stages did their reaction data fit the simple first order kinetic equations assumed by Gormley and Ford (1973).

Ellis and Moreland (1957) reported that this reaction was heterogeneous catalysis of the surface finely dispersed precipitate, formed when traces of the metal salts are added to the hydrazine solution. Ellis, Jeffreys, and Hill (1960) reported that there is more than one rate controlling stage which varies with the hydrazine concentration.

Audrieth and Ogg (1951) warned of discordant results when studying the reaction of the oxidation of hydrazine in alkaline solution by oxygen. They cautioned about the requirement to prevent access of oxygen in the atmosphere to a hydrazine solution. In environmental waters, once the dissolved oxygen is depleted by the reacting hydrazine, the only means of continuing the reaction is by diffusion of the atmospheric oxygen across the air-water interface. Work reported in this paper as well as previously did not consider this diffusional source of oxygen. It is readily apparent that future work is required with the need to consider this diffusional oxygen rate in order to provide a more valid environmental model. The work presented in this report concerns the effects of other catalysts besides copper at environmental water concentrations to determine the possibility of hydrazine degradation in an actual hydrazine spill. This report also presents preliminary experimental work on the thermal effects of the kinetic rate and how to incorporate this data into a predictive model.

THEORY

As reported by Gaunt and Wetton (1966), the copper (II) - catalyzed reaction has been shown to be complex, but as the reaction approached 25% completion their data indicated a simple rate-determining step, which was most likely:

$$\mathrm{Cu\ (II)} + N_2H_4 \rightarrow \mathrm{Cu}^{(I)} + N_2H_3 \qquad (1)$$

The stoichiometry of the copper (II) - catalyzed reaction has been determined and corresponded to the equation:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \tag{2}$$

The mathematical model, as reported in Gormley and Ford (1973) assumed the following relationship:

$$-V \frac{d\ DO}{dt} = -V \frac{d\ P}{dt} = K\ DO^N \tag{3}$$

where V is the volume, DO is the dissolved oxygen concentration, P is the propellant concentration, K is the kinetic rate constant and N is the order of the reaction. Equation 3 can be integrated for n=1 and n≠1:

N=1

$$\ln DO = -\frac{k}{v} t + \ln DO_o \tag{4}$$

N≠1

$$\frac{DO^{1-N}}{1-n} = \frac{-k}{v} (t) + \frac{(DO)_o^{1-N}}{1-N} \tag{5}$$

where DO_o is the initial dissolved oxygen concentration. The experimental data of dissolved oxygen concentration versus time was evaluated with a Hewlett-Packard Model 9810 calculator system to yield a kinetic rate constant. A searching technique evaluated the rate constant for any order and the best fit was tested by the correlation coefficient. Gormley and Ford (1973) already established first order kinetic degradation for the deoxygenation of hydrazine at 25°C by copper.

MATERIALS AND METHODS

Each experimental run was repeated four times and the average kinetic rate compared with a control without any catalyst present. The control and samples began with glass-distilled water (2-4 µmho/cm conductivity), which was aerated to at least 90% of the saturated dissolved oxygen level. An Erlenmeyer flask containing two-liters of aerated and distilled water was set-up on a magnetic stirrer. The top of the flask was sealed with paraffin film and slitted to allow a pH electrode and DO/temperature probe to be submerged in the water. After a five minute stirring time with the catalyst present, the hydrazine was added to the reaction flask and the paraffin film top sealed with tape to prevent atmospheric oxygen diffusion. The pH probe was attached to a Corning Model 12 pH meter and the pH readings were read prior to hydrazine addition and immediately afterward. The pH change was a step function from pre-addition to addition and remained constant throughout the experiment. The DO/temperature probe was an attachment of a Model 54 BP YSI oxygen meter. Its sensing element is a Clark-type membrane covered polarographic probe. This oxygen meter was attached to a Varian 20 strip chart recorder and the DO changes with time were recorded.

The reaction rate for the glass-distilled water without catalysts was found to be measurable. Gaunt and Wetton (1966) reported that this reaction rate could be increased by soaking the glass flask in "chromic acid mixture," then rinsed with cold water followed by a 15 minute period when water was boiled in the flask. Our experiments were involved with rinsing the flask with cold distilled water after each experimental run and using the chromic acid washing technique only when changing catalysts. No boiling water treatment was used. Atomic absorption spectrophotometric analysis of the glass-distilled water for trace levels of copper indicated a 0.005 mg/l level in the control water. This glass-distilled water was from a tap distilled water system which contained a copper-lined pot.

Slonim (1975) conducted hydrazine degradation studies with hard and soft water for a 96 hour period. His studies revealed that below a hydrazine concentration of 100 mg/l there was no degradation of hydrazine or deoxygenation. Below this 100 mg/l hydrazine concentration level corresponding to a pH of 8.6 in soft water, the hydrazine is too low in concentration to increase the pH sufficiently to allow the hydrazine - oxygen interaction. This reaction will not occur in acidic to neutral solution. The hydrazine compounds used were the same as described by Slonim (1975) and were obtained from Matheson, Coleman, and Bell. The purity was reported as at least a 97% minimum with the remainder primarily consisting of water.

Reported maximum concentration levels of metallic ions within environmental waters were found in a summary of trace elements in waters of the United States by Kapp and Kroner (1967) and the Public Health Drinking Water Standards (1962). To stimulate the worst environmental conditions, double-distilled water was prepared with the environmental maximum concentration level of the metallic ions. The metallic ions were tested separately to isolate their catalytic effect on the hydrazine - oxygen reaction.

If the maximum concentration as reported in the above sources differed, the higher value was tested. Table 1 presents the ion concentration levels tested for Fe (III), Fe (II), Zn (II), Co (II), Ni (II), and Cu (II).

A second series of experiments was conducted with cobalt (II). A correlation was developed from experimental data of the kinetic rate constant as a function of the cobalt ion concentration. The DO degradation data of four experimental runs at each cobalt concentration level were averaged and a kinetic rate constant evaluated with the searching technique of the computer program.

Kinetic studies of hydrazine, MMH and UDMH were conducted at 37°C to establish the thermal effect on the rate of degradation. The only catalyst present was copper. The observed kinetic rate constant at 37°C was compared with the constant at 24°C to yield a ratio parameter R (See Table 3 a-c). A prediction for the kinetic rate constant at 37°C was developed by combining this ratio parameter and the predictive model of Gormley and Ford (1973) at 24°C, which is as follows:

$$k/v \text{ at } 24^{\circ}\text{C} = \frac{Vm \; PC}{Kc \; Kp + Kc \; P + KpC + PC} \qquad (6)$$

$$k/v \text{ at } 37^{\circ}\text{C} = k/v \text{ at } 24^{\circ}\text{C} \times R \qquad (7)$$

where k/v is the rate constant, min.^{-1}, Vm, kc, kp are correlation parameters, P is the propellant concentration in mg/l, and C is the copper concentration in mg/l.

RESULTS AND DISCUSSION

Table 1 presents the maximum environmental concentration levels of metallic ions which were tested as sources of catalysts for the hydrazine - oxygen interaction. To discuss the significance of the data, it is helpful to hypothesize a natural body of water which has the worst possible conditions. If this water is assumed to contain all the ions tested in Table 1 at the concentrations studied experimentally, then the copper (II) alone would account for 95.8% of the hydrazine degradation associated with a spill. Audrieth and Ogg (1951) discussed three methods of retardation of this copper catalytic effect (interference with Cu (II) reduction by hydrazine and oxidation of Cu (I) by oxygen). The first involved reagents which form insoluble or very slightly soluble copper salts to preclude the availability of Cu (II) or Cu (I) ions in solution. The second method was addition of complexing agents for both Cu(II) and Cu (I). It is assumed that the active agent was a hydrated or hydrazinated metal ion. Their final proposed method was colloidal materials which act as absorbents for cupric or cuprous ions. They reported that sulfides, xanthates, thiocyanates and cyanides were very effective inhibitors on the auto oxidation of hydrazine. It is assumed that none of these tested metallic ions will interfere with the catalytic action of copper in the hydrazine - oxygen reaction. A preliminary experimental study with ferric Fe (III) ion and Cu (II) ion revealed no inhibition effect by the iron ion on the copper catalysis.

Data in Table 2 consider the catalytic effect of Co (II) in the aqueous deoxygenation by hydrazine. The first order rate constants were correlated by the following equation:

$$k/v = 2.62 \times 10^{-5} [\mathrm{Co\ (II)}] \ [N_2H_4] + 17.23 \times 10^{-5} [N_2H_4] \qquad (8)$$

The k/v is in min.$^{-1}$ units and the concentrations of cobalt [Co (II)] and hydrazine [N_2H_4] are in mg/l. For cobalt concentration level of 1 mg/l, only 13% of the decomposition was due to the cobalt. The remaining decomposition was probably due to the contaminants in the glass-distilled water. Since the maximum concentration of cobalt reported in United States ground water is only 0.048 mg/l (Kapp and Kroner, 1967), we can expect a negligible cobalt effect on the degradation of hydrazine in environmental waters.

The kinetic data for 37°C and 25°C for hydrazine, MMH and UDMH can be found in Table 3. The ratio parameter R, is the observed first order kinetic rate constant at 37°C divided by the one at 25°C. Table 4 describes the parameters developed by Gormley and Ford (1973) for their predictive model at 25°C. Table 5 presents the predicted values of the kinetic rate constants evaluated by use of Equation 7. The chi-square value of 0.795 for MMH indicates these results will occur by chance 2.5% of the time. The model as developed by Gormley and Ford in combination with the R factor worked quite well in predicting the kinetic rate constants. The kinetic degradation experiments were repeated for hydrazine at 6°C. However, the ratio of the kinetic rate (first order) at 24°C versus 6°C (first order) did not yield any consistency, as shown in Table 6. This inconsistent ratio was most likely due to the use of a larger reaction flask and stirring rod in the last four runs at 6°C (502.6 mg/l hydrazine and 0.25 and 0.125 mg/l copper, 251.3 and 1005.3 mg/l hydrazine and 0.5 mg/l copper). It is important to point out the data will remain inconsistent without a uniform stirring speed within the reaction vessel. These runs at 6°C must be repeated with the same vessel size and stirrer conditions as the 24°C runs. It was observed when the stirrer was inadvertently turned off that the measured dissolved oxygen concentration was severely reduced. This is probably due to the formation of a stagnant pool of water around the oxygen probe.

CONCLUSIONS

This study has shown that ferrous Fe (II), ferric Fe (III), Zinc Zn (II), cobalt Co (II), and nickel Ni (II) metallic ions at their reported maximum environmental concentration levels did not produce a significant catalytic effect in the deoxygenation of water by hydrazine. The catalytic effect of copper was studied at 37°C to determine the thermal effect on the kinetic reaction. A consistent predictive model was developed for this reaction at 37°C by combining the model established at 24°C with a ratio parameter, R.

Data at 6°C did not confirm this approach. Consistent stirring conditions were not maintained because of non-uniform vessel size. A change in vessel size will affect the convection conditions present, even if the stirring speed is maintained as a constant throughout each experimental run. In fact, future work is required to consider convection as an independent variable to determine its effect on the kinetic rate of degradation of hydrazine and dissolved oxygen within an aqueous system. Experimental design is required to relate stirring speed to natural convection conditions within environmental waters.

TABLE 1 - FIRST ORDER RATE CONSTANTS FOR ENVIRONMENTAL CONCENTRATION LEVELS OF METALLIC IONS

Test Ion	Ion Conc. mg/1	Max. Env. Ion Conc. mg/1	1st Order Rate Const. Min^{-1}	% of Cu(II) Rate Const.	Correlation Coefficient
Fe (III)	5.0	4.6	0.00173	0.03	0.9959
Fe (II)	5.0	4.6	0.0532	1.09	0.8356
Zn (II)	5.0	5.0†	0.0137	0.28	0.9800
Co (II)	0.125	0.04*	0.0918	1.88	0.8477
Ni (II)	0.25	0.13*	0.0544	1.11	0.8198
Cu (II)	1.0	1.0†	4.8823	100.00	0.9871

† PHS Drinking Water Stand. (1962).

* Kapp - FWCA (1967)

TABLE 2 - FIRST ORDER RATE CONSTANTS FOR COBALT Co (II)

Series	Co(II) mg/l	Hydrazine mg/l	1st Order Rate Min.^{-1}
1	1.0	502.6	0.0835
2	0.5	502.6	0.1079
3	2.0	502.6	0.4666
4	5.0	502.6	0.6060
5	2.0	251.3	0.1112
6	2.0	1005.2	1.0424
control	0	251.3	0.0351
control	0	502.6	0.2104
control	0	1005.2	0.5977

TABLE 3(a) - KINETIC RATES AT 25°C AND 37°C FOR HYDRAZINE

Copper mg/1	Hydrazine mg/1	k/v at 24.8 ± 0.30°C min.^{-1}	k/v at 37.17 ± 0.31°C min.^{-1}	R
1	502.6	4.8823	9.0754	1.86
0.5	502.6	4.0458	7.3943	1.83
0.25	502.6	3.3922	5.5287	1.63
0.125	502.6	2.1701	4.1760	1.92
0.5	251.3	3.6173	6.6856	1.85
0.5	1005.2	4.3785	9.8471	2.25
				1.89
				±0.20

TABLE 3(b) - KINETIC RATES AT 25°C AND 37°C FOR MMH

Copper mg/l	MMH mg/l	k/v at 24.6 ± 0.65°C min.$^{-1}$	k/v at 36.93 ± 0.31°C min.$^{-1}$	R
1.0	443.8	5.1176	10.5915	2.07
0.5	443.8	3.6703	8.3856	2,28
0.25	443.8	2.4444	5.6505	2.31
0.125	443.8	1.1738	3.1137	2.65
0.5	221.9	3.2534	8.2678	2.54
0.5	887.6	3.6782	8.8944	2.42
				2,38
				±0.21

TABLE 3(c) - KINETIC RATES AT 25°C AND 37°C FOR UDMH

Copper mg/l	UDMH mg/l	k/v at 25.4 ± 0.29°C	k/v at 36.55 ± 0.14°C	R
1.0	393.2	2.4703	6.0837	2.46
0.5	393.2	1.8689	4.0792	2.18
0.25	393.2	1.1725	2.5855	2.21
0.125	393.2	0.5863	1.4146	2.41
0.5	196.6	1.3140	3.2739	2.49
0.5	786.4	2.7627	4.9363	1.79
				2.26
				±0.26

TABLE 4 - PARAMETERS FOR EQUATIONS 7 AND 8

	Hydrazine	MMH	UDMH
Vm	6.79	13.63	12.56
R	1.89 ± 0.20	2.38 ± 0.21	2.26 ± 0.26
RVm	12.83	32.44	28.39
Kc	0.22	1.19	1.12
Kp	24.43	44.09	411.08
KcKp	16.37	52.47	460.41

TABLE 5 - DEGRADATION AT 37°C

Propellant Conc. mg/l	Copper Conc. mg/l	Hydrazine		MMH		UDMH	
		0*	C**	0	C	0	C
502.6	1.0	9.0754	9.1622	10.5915	13.4739	6.0837	6.5459
502.6	0.5	7.3943	7.7623	8.3856	8.7301	4.0792	4.2831
502.6	0.25	5.5287	5.9457	5.6505	5.1229	2.5855	2.5324
502.6	0.125	4.1760	4.0500	3.1137	2.8049	1.4146	1.3933
251.3	0.50	6.6856	6.8756	8.2678	8.0065	3.2739	2.9420
1005.2	0.5	9.8471	8.5178	8.8944	9.1433	4.9363	5.7534

*0 = Observed Kinetic Rate at Min.^{-1}

**C = Calculated Kinetic Rate at Min.^{-1}

TABLE 6 - DEGRADATION OF HYDRAZINE AT 6° vs 24.6°C

Copper conc, mg/l	Hydrazine conc, mg/l	Kinetic rate const, min^{-1} 6 ± 1°C	Kinetic rate const, min^{-1} 24.60 ± 1°C	Ratio Parameter, R
1.0	502.6	2.1604	4.8823	2.25
0.5	502.6	1.0144	4.0458	3.99
0.25	502.6	0.2593	3.3922	13.08
0.125	502.6	0.2069	2.1701	10.49
0.5	251.3	0.3572	3.6173	10.13
0.5	1005.2	2.5884	4.3785	1.69

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