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OXIDATION OF HYDRAZINE IN AQUEOUS SOLUTIONS

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The expanded use of hydrazine type fuels throughout the Air Force makes it imperative that current and accurate data be available on the potential environmental impact of these compounds. This report describes the chemistry of hydrazine in aqueous solutions under varying conditions of temperature, pH, ionic strength, salinity, hydrazine concentration, oxygen concentration, and in the presence of catalysts, and solid substrates. Results indicate that in the absence of Copper (II) as a catalyst, the degradation of hydrazine is slow. In five days a 1 x 10^{-4} molar solution of hydrazine degraded less than 2% in

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distilled water, 40% in pond water and 20% in seawater. The addition of oxide and clay solids did not change the rate of degradation. Increasing the concentration of Copper (II) caused a major increase in the oxidation rate as did increasing temperature. Salinity and ionic strength changes caused minor variations in rate. The maximum degradation rate occurs between pH8 and 9. Oxygen concentrations in the range 0.5 to 40 mg/1 had no measurable effect.

PREFACE

This study was performed under program element 62601F, JON 19004C01. The project officer was Major Michael G. MacNaughton of the Environmental Sciences Division, Civil and Environmental Engineering Development Office, ADTC, Tyndall AFB Florida 32403.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

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SECTION I

INTRODUCTION

In recent years there has been an increased use of the amine-based compound hydrazine (N_2H_4) for such diverse purposes as deoxygenation of boiler water, fuel cells, and missile propellants and as a monopropellant in gas turbine generators. The widespread usage of this material with its documented toxicity to humans and other organisms makes understanding the processes which control the fate of hydrazine in the environment most important. The studies reported here were performed to assist in preparation of environmental assessments for storage, transport, and fuel usage as well as formulating control and safety procedures. The experimental protocol was designed to produce required modeling data for the environmental transport of hydrazine released into aquatic systems. Parameters studied were the influence of pH, temperature, hydrazine concentration, oxygen concentration, salinity, and trace metals and the presence of solid substrates.

The degradation of hydrazine in aqueous solutions has been studied since the early 1900s. Browne and Shatterly (Reference 1) investigated a variety of oxidants including oxygen and ozone and found nitrogen as the only oxidation product. Bray and Cuy (Reference 2) in a footnote to their paper stated that alkaline hydrazine solutions were stable in the absence of air and, therefore, any decomposition was due to oxygen. Later in a more extensive effort to define the reaction between hydrazine and oxygen in alkaline solutions, Gilbert (Reference 3) found the maximum rate of hydrazine decomposition in the presence of oxygen occurred at hydroxyl ion concentrations between 0.01M and 0.03M. Both above and below this range, the degradation rate was found to diminish. An interesting aspect of Gilbert's work was his measurement of hydrogen peroxide as a product of the reaction, and the amount of peroxide formed was inversely proportional to the rate of oxidation. The ability of hydrazine to react with and decrease the concentration of oxygen in aqueous solutions has led many workers to study its use as a deoxygenating agent for boilers. Ellis and coworkers (References 4 and 5) studied the decrease in oxygen versus time for various initial concentrations of oxygen and hydrazine, and temperatures, and in the presence of numerous catalysts. They found the reaction to be approximately first order with respect to oxygen but dramatically accelerated with the addition of activated carbon, copper sulfate, brick, and electrode carbon. The products of the reaction, in the absence of oxygen and in the presence of carbon, were nitrogen and ammonia. Strong ultra-violet light was also found to decompose hydrazine in the absence of oxygen; however, oxygen greatly increased the degradation. Gaunt and Wetton (Reference 6) also investigated the influence of trace impurities, reporting that even rigorously cleaned glass gave much higher decomposition rates than did polythene vessesl. Of trace metals tested, only manganese (II) and copper (II) made an appreciable difference in the speed of reaction.

In the range of 5 to 40 ppm dissolved oxygen, they found the rate to be independent of the oxygen concentration; and over the temperature range 25° to 75°C, the only product was nitrogen. Lurker (Reference 7) also studied the catalytic effect of metal ions on the oxidation of hydrazine by oxygen. His studies showed that iron (II), iron (III), zinc (II), cobalt (II), and nickel (II) did not produce any significant effect on the deoxygenation of water with hydrazine. Gramley (Reference 8) in related work also studied the deoxygenation rates of water by hydrazine in the presence of copper and determined that the reaction was first order.

From the literature, the following conclusions can be drawn:

1. The products of oxygen decomposition of hydrazine are nitrogen, water, and possibly ammonia and hydrogen peroxide.

2. The reaction rate is greatly accelerated by copper, manganese, and high surface area materials.

3. The influence of oxygen on the rate of oxidation is unclear.

4. Decomposition can take place even in the absence of oxygen.

5. The reaction appears to proceed faster in alkaline solutions.

SECTION II

CHEMISTRY OF HYDRAZINE AND COPPER (II)

In water solutions, hydrazine acts as a weak base similar to ammonia in which one of the hydrogens has been replaced by a more negative amine group, NH_2. Although hydrazine can act as a polyprotic base, as shown in Figure 1, for the pH ranges of most natural waters only the first hydrolysis is important [Sillen and Martell (Reference 9); Audrieth and Ogg (Reference 10); Bannerja and Singh (Reference 11)].

(1) $N_2H_4 + H^+ \rightleftarrows N_2H_5^+$ $\quad pk_1 = 7.97$

(2) $N_2H_5^+ + H^+ \rightleftarrows N_2H_6^{2+}$ $\quad pk_{12} = 0.31$

As a base, hydrazine lies between water, pk_1 7.0, and ammonia, pk_{12} 4.75, in strength. Like ammonia, hydrazine can form coordination complexes with Lewis acids and metal ions; however, its strong reducing properties prevent most of these complexes from being stable. There are several alternative pathways for hydrazine oxidation as shown in the following examples:

(3) $2NH_4^+ \rightleftarrows N_2H_5^+ + 3H^+ + 2e$ $\quad E^o = 1.27$

(4) $N_2H_5^+ \rightleftarrows N_2 + 5H^+ + 4e$ $\quad E^o = 0.22$

(5) $N_2H_4 + 4OH \rightleftarrows N_2 + 4H_2O + 4e$ $\quad E^o = 1.17$

There are also autooxidation schemes by which hydrazine can decompose that are thermodynamically very favorable. [Audrieth and Ogg (Reference 10); Cotton and Wilkinson (Reference 12); and Latimer (Reference 13)].

(6) $3N_2H_4 \rightleftarrows 4NH_3 + N_2$ $\quad \Delta F = 157.88$

(7) $2N_2H_4 \rightleftarrows 2NH_3 + N_2 + H_2$ $\quad \Delta F = 97.92$

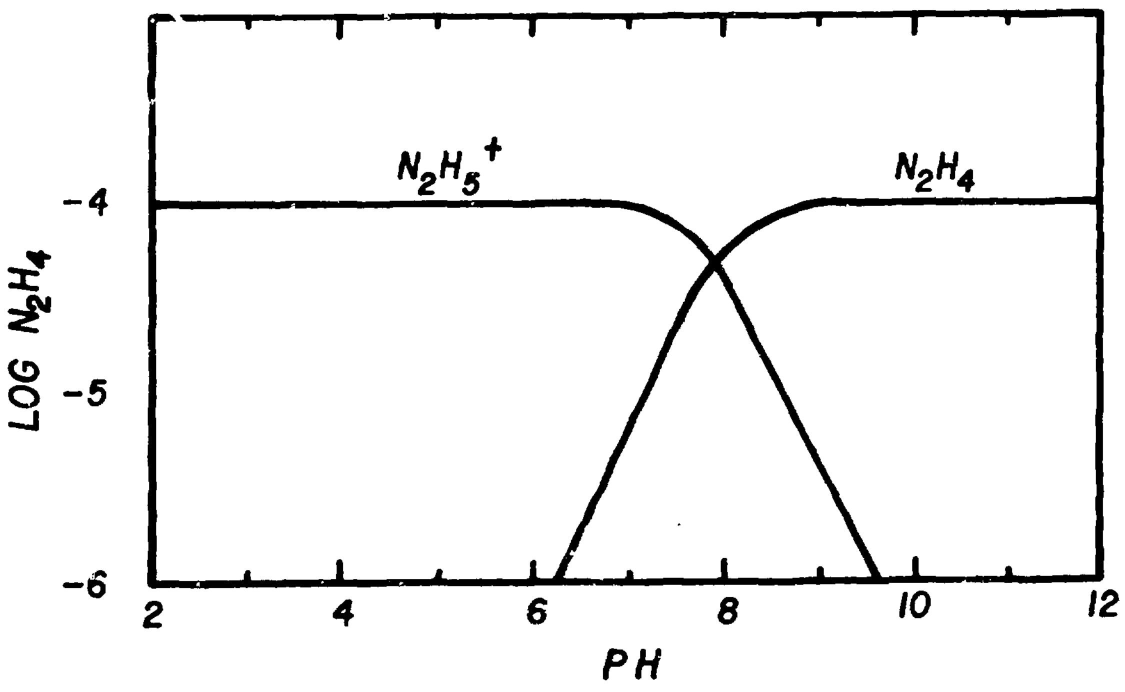

Figure 1. Hydrolysis Diagram for Hydrazine

(8) $N_2H_4 \rightleftarrows N_2 + H_2$ $\Delta F = 37.96$

Copper (II) is a weakly hydrolyzed divalent cation which has monomeric first and second hydrolysis products of insignificant concentration. As shown in the solubility diagram in Figure 2, higher hydrolysis species become important in alkaline solution [Sillen and Martell (Reference 9); Feitknecht and Schindler (Reference 14); and Arnek (Reference 15)].

(9) $Cu(OH)_2(s) + 2H^+ \rightleftarrows Cu^{2+} + 2H_2O$ $*pk_{SO} = 9.2$

(10) $2Cu\ (OH)_2(s) + 2H^+ \rightleftarrows Cu_2(OH)_2 + 2H_2O$ $*pk_{S22} = -7.4$

(11) $Cu(OH)_2(s) + H_2O \rightleftarrows Cu(OH) + H^+$ $*pk_{S3} = 17.6$

(12) $Cu(OH)_2(s) + 2H_2O \rightleftarrows Cu(OH)_4{}^2 + 2H^+$ $*pk_{S4} = 30.7$

The other important ligand in the environmental chemistry of copper besides water and OH is carbonate. The predominance diagram shown in Figure 3, from Schindler, Reinert and Gamsjager (Reference 16) illustrates the effect of P_{CO_2}, pH, and total copper on the aqueous speciation. It can be seen that, for a total copper concentration of $10^{-6}M$ and an air P_{CO_2} of 3×10^4 atm, the solid phase $Cu_2(OH)_2\ CO_3$ (Malachite) is the major copper species for these inorganic ligands.

(13) $Cu_2(OH)_2\ CO_3\ (s) + 4H^+ \rightleftarrows 2Cu^{2+} + CO_2(g) + 3H_2O$ $*pk_{so} = 6.49$

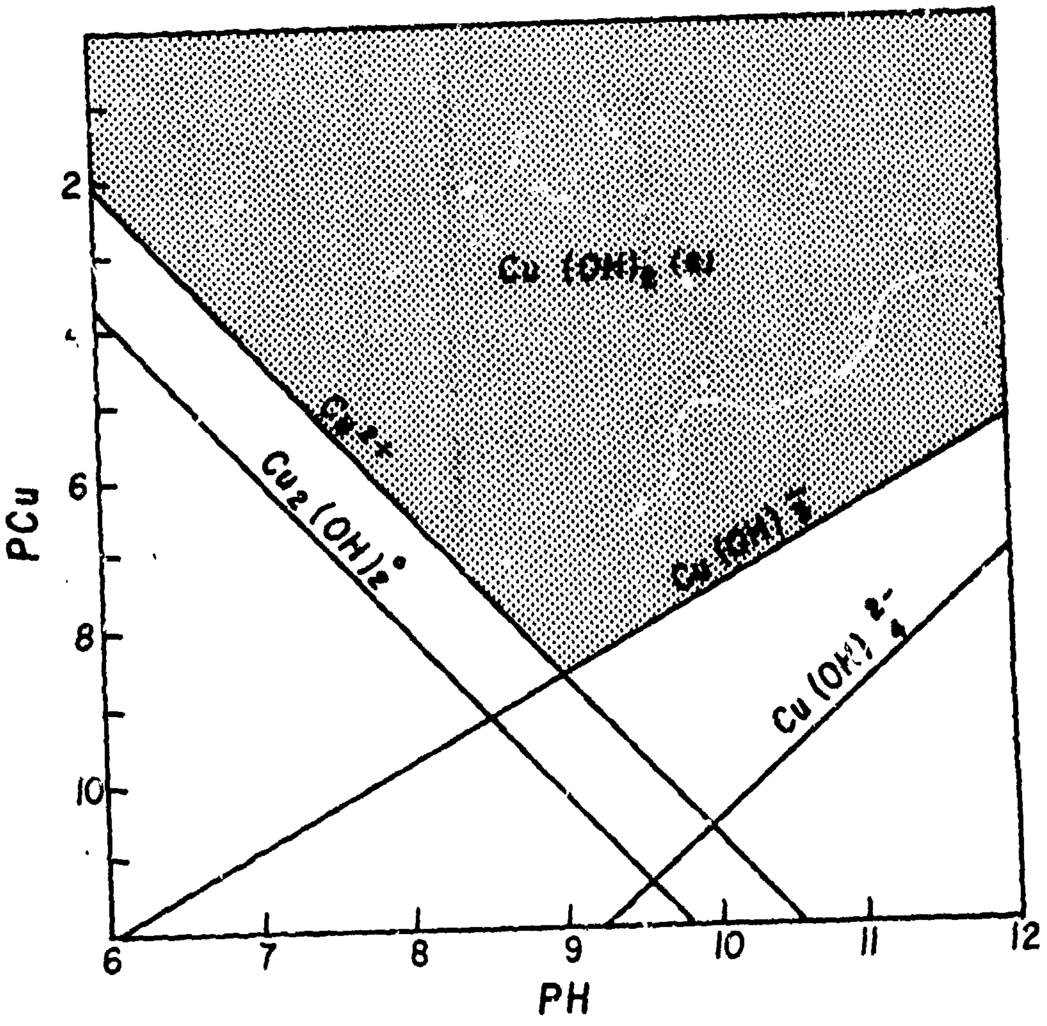

Figure 2. Solubility and Predominance Diagram for Copper Hydroxide

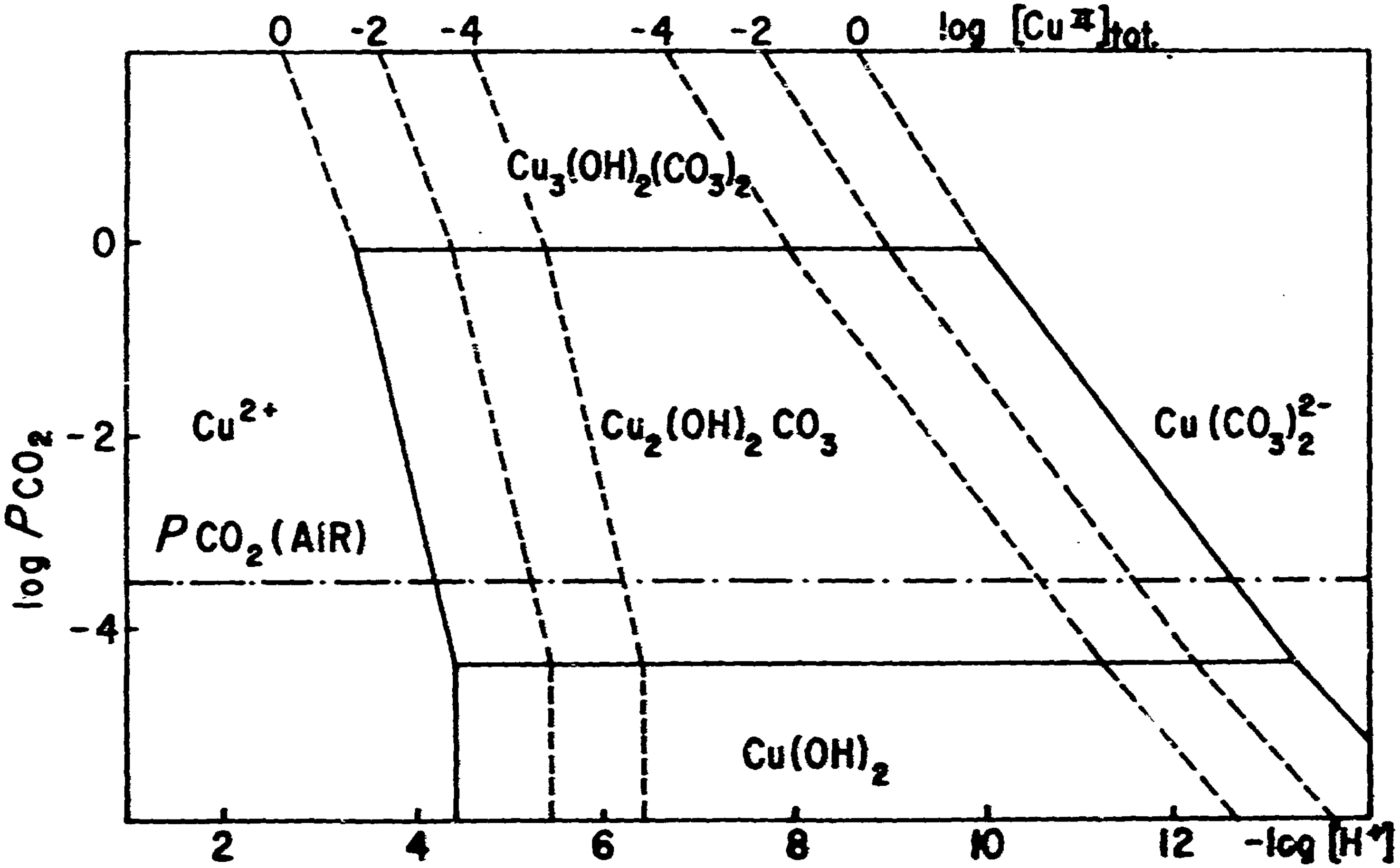

Figure 3. Predominance Diagram for the Ternary System $Cu^{2+}-H_2O-CO_2(g)$ (Ionic Strength = 0, 25°C) (Schindler, Reinert and Gamsjager, 1968)

SECTION III

EXPERIMENTAL

Long term oxidation experiments were performed in one liter Pyrex^R beakers which were slowly stirred with polyethylene stirring rods while a loose paraffin cover kept out dust. Additional experiments designed to measure the effect of temperature, pH, dissolved oxygen, and electrolyte composition were performed in a closed Pyrex ^{R} double-jacketed reaction vessel. Temperature was controlled by a Lauda K2R temperature recirculator and pH was measured, adjusted, and maintained with a Radiometer TT2 titrator and ABU12 auto burette. Experimental atmospheres were produced using water pumped nitrogen and aviator's breathing oxygen blended in the correct proportions and then passed through Ascarite^R to remove any residual carbon dioxide and a gas wash bottle filled with distilled water to humidify the gas stream and reduce evaporation of the test solution. Dissolved oxygen was monitored with a YSI 51A dissolved oxygen meter.

Reagents were ACS reagent grade or better. Both stock hydrazine and copper solutions were generated from sulfate salts and deionized, glass distilled water. The pH was adjusted using AR nitric acid and CO_2 - free potassium hydroxide. Pond water used during these experiments was collected from an isolated pond on Tyndall AFB, Florida, and seawater was collected near shore in the Gulf of Mexico. Both the pond water and seawater were filtered through Whatman GF/C glass fiber filters prior to use.

Hydrazine concentrations were determined colorimetrically using p-dimethylaminobenzaldehyde (DMBA) [Watt and Chrisp (Reference 17)]. In this procedure, hydrazine replaces the oxygen in the aldehyde group in two molecules of DMBA to form p-dimethylaminobenzalazine which shows a maximum absorbance at 460 nm. The yellow color formed is stable after 15 minutes and does not deteriorate for a least 24 hours.

SECTION IV

TEST RESULTS

EXPERIMENTS WITHOUT COPPER

As shown in Figures 4 and 5, oxidation of hydrazine in distilled water, seawater, and pondwater is relatively slow. In five days, concentrations had decreased less than 2 percent, 40 percent and 20 percent, respectively. As shown in Figure 6, the addition of excess surface area in the form of α quartz, alumina, and kaolinite did not increase the oxidation rate and, if anything, caused a small reduction in the rate. The presence of small chips of concrete, however, caused a significant oxidation of the hydrazine with nearly 100 percent degraded in 160 hours. This agrees with the rapid loss of hydrazine spilled on concrete pavement observed in spill clean-up studies [Eyl (Reference 18)].

EFFECT OF COPPER

The influence of copper as a catalyst has been described earlier by Gaunt and Wetton (Reference 6). They reported that, of all the metals tested, only manganese (II) and copper (II) acted as catalysts. Lack of catalytic ability by the other metals was explained by their high redox potential at pH 12, where the experiments took place. Kinetic data for the oxidation of hydrazine in the presence of copper reported by Gaunt and Wetton (Reference 6) have limited use for natural waters because they used a 0.1M ammonia buffer to repress the hydrolysis and precipitation of copper at pH 12 where their experiments were carried out. Both copper (II) and manganese (III) can participate in electron exchanges, and the reduced state is easily oxidized back to the high valence state by oxygen at alkaline pHs. For manganese it would be the trivalent oxidation state formed by the oxidation of manganese hydroxide ($Mn(OH)_2$) that would oxidize hydrazine. Both of these metals as well as cobalt have been reported to act as catalysts in the oxidation of iron (II) to iron (III) by oxygen [Stumm and Lee (Reference 19)]. The addition of 4 x 10^6 moles/ℓ copper (Figure 7) causes a substantial rise in the hydrazine removal rate. A more dramatic decrease in concentration with time

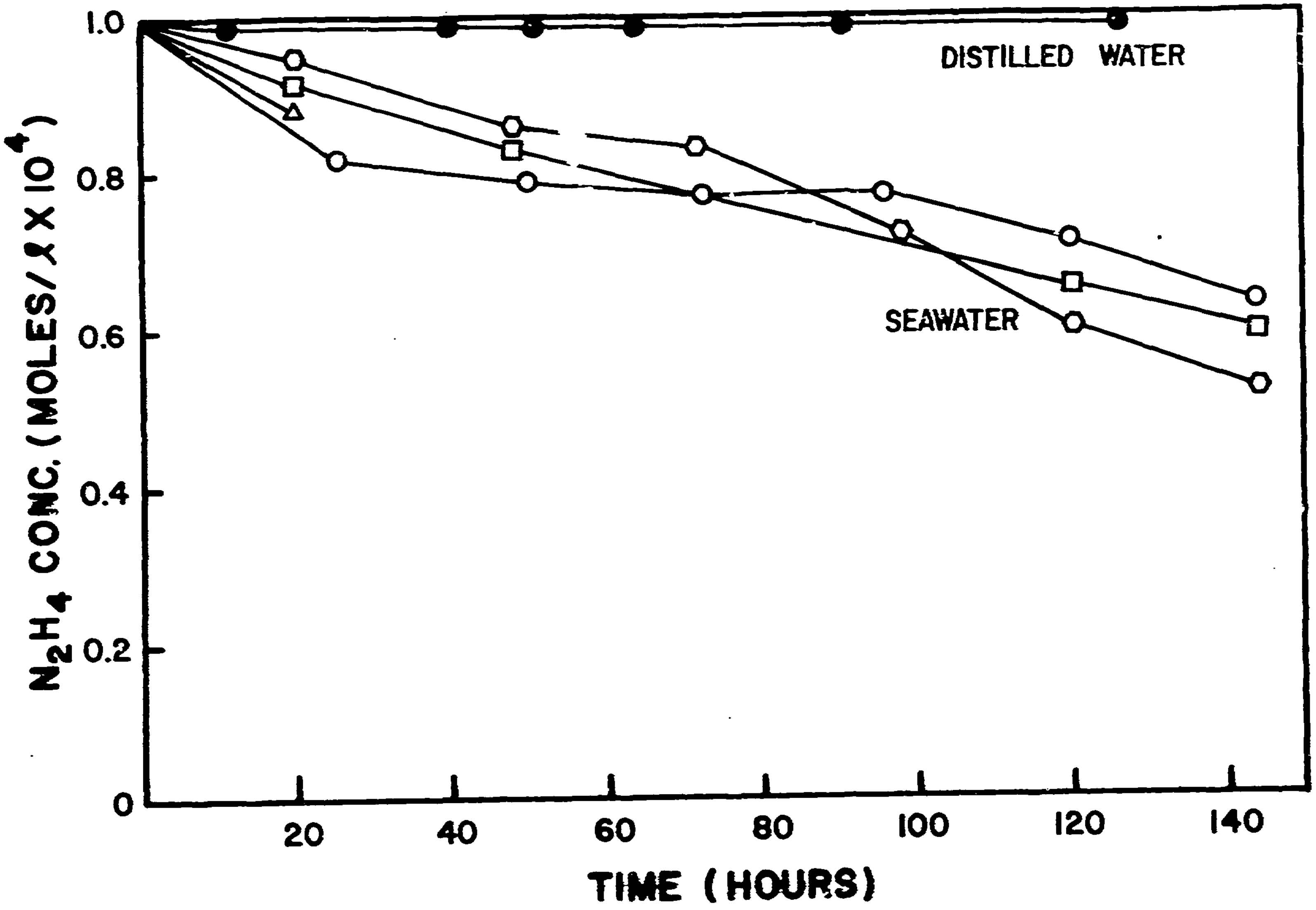

Figure 4. Concentration of Hydrazine as a Function of Time in Three Samples of Seawater and Distilled Water: Initial pH 8, 20°C, 7 ± 0.5 mg/ℓ Dissolved Oxygen

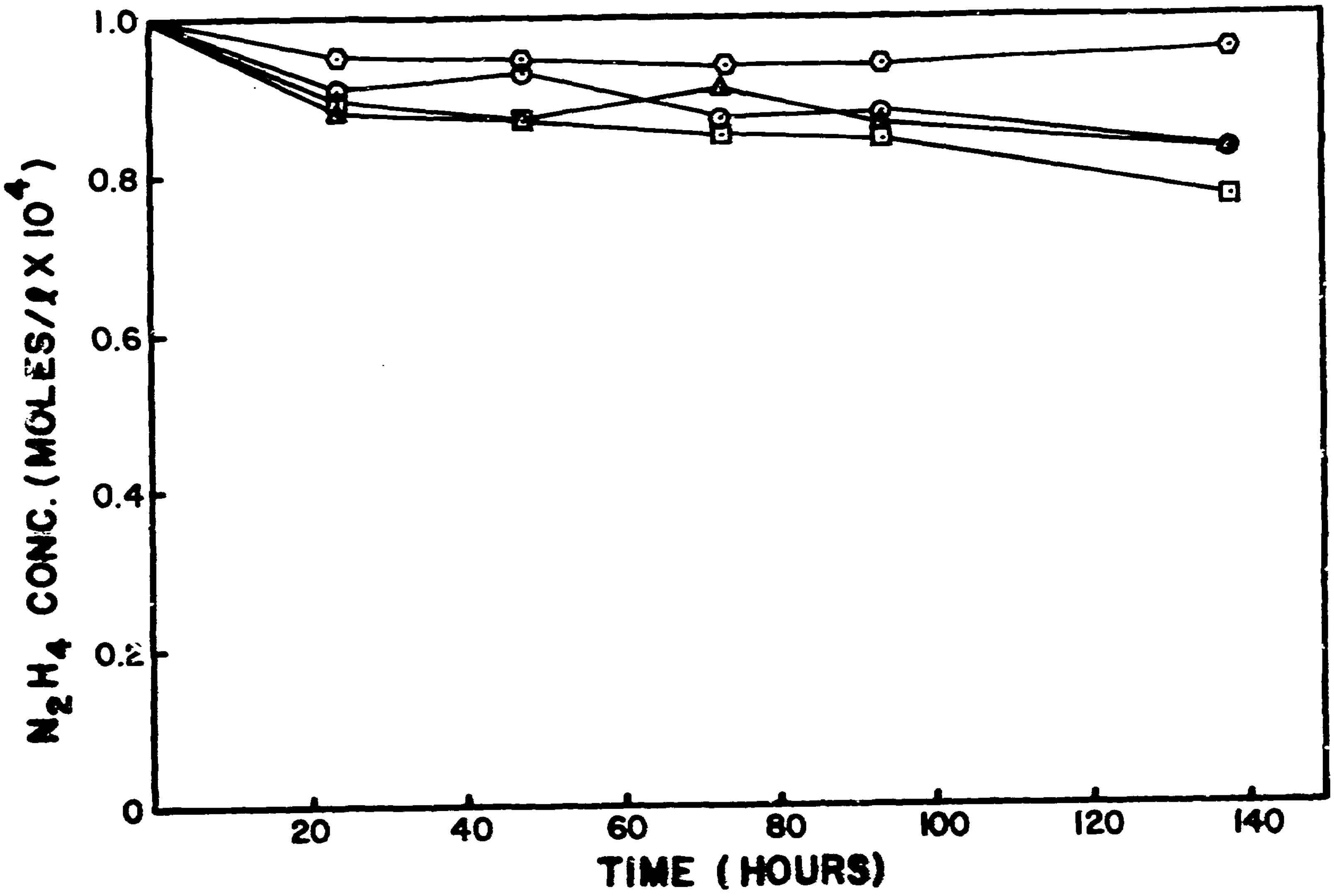

Figure 5. Concentration of Hydrazine as a Function of Time in Four Samples of Pond Water: Initial pH 8, 20°C, 7 ± 0.5 mg/ℓ Dissolved Oxygen

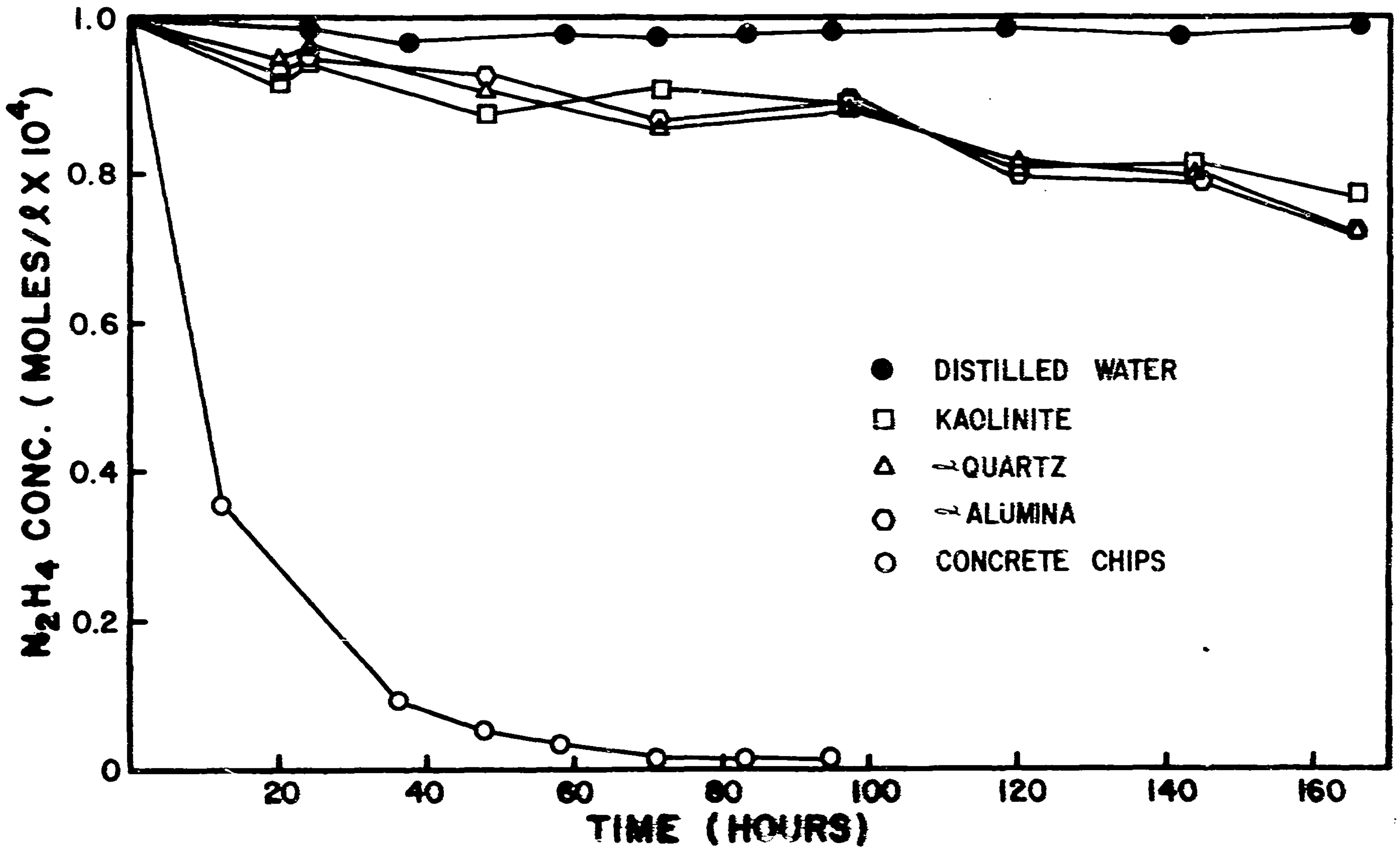

Figure 6. Influence of Added Solid Substrate on the Concentration of Hydrazine as a Function of Time: 1 g/ℓ Solid, pH 8, 20°C, 7 ± 0.5 mg/ℓ Dissolved Oxygen.

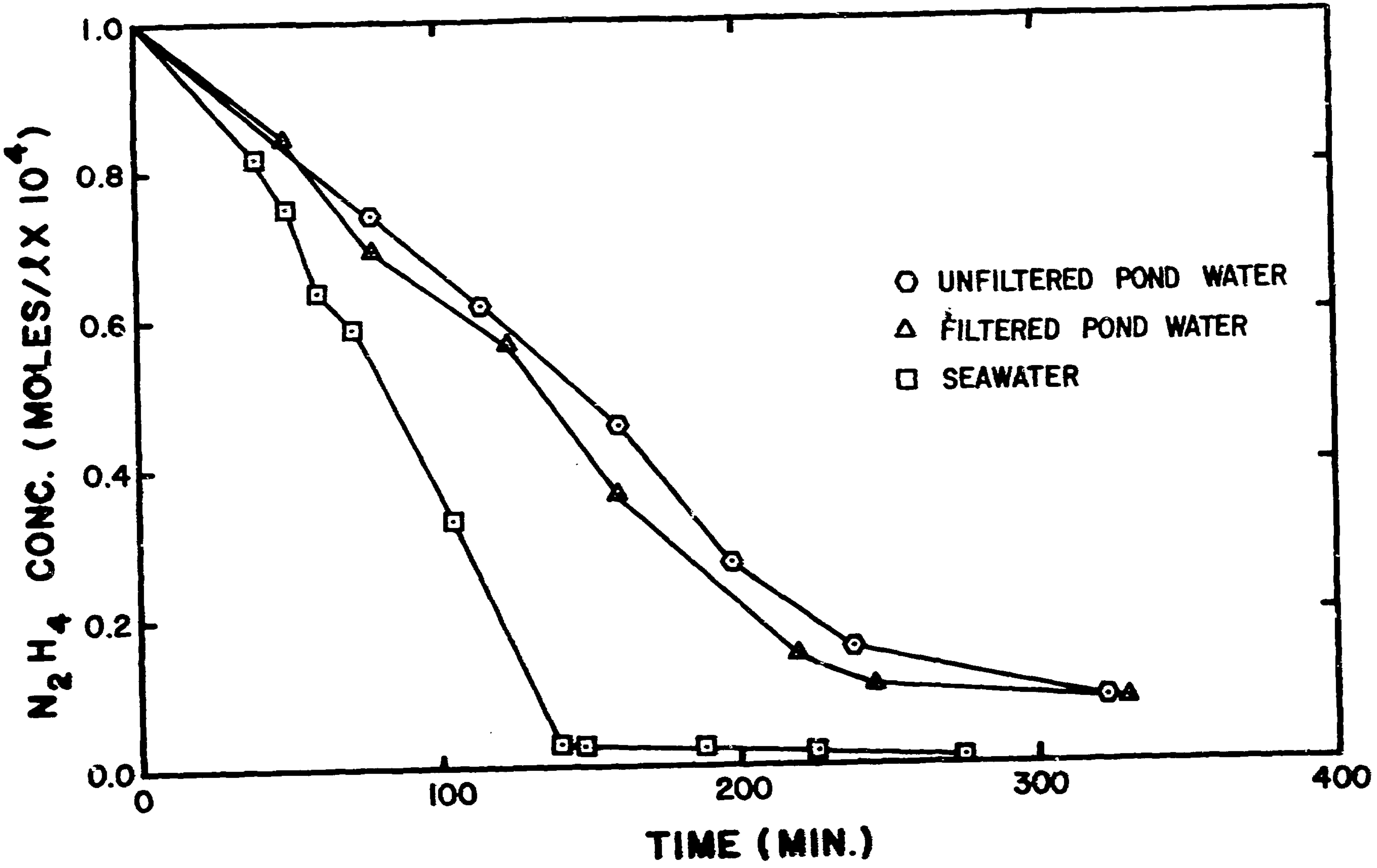

Figure 7. Concentration of Hydrazine as a Function of Time in the Presence of 4 x 10^{-6} Moles/ℓ Copper (II): pH 8.3, 20°C, 10 mg/ℓ Dissolved Oxygen

was observed with seawater; however, the higher dissolved organic content of the pond water would be expected to reduce the free copper concentration more than seawater. Filtration of the pond water resulted in no decrease or increase in oxidation rate, suggesting that the suspended material was not important in catalyzing the hydrazine oxidation or complexing the added copper (II). Figure 8 shows the effect of copper (II) concentration on the oxidation rate of a 1 x 10^{-4} mole/ℓ hydrazine solution at 10 mg/ℓ oxygen. For concentrations over 1 x 10^{-4} mole/ℓ copper (II), the response is no longer linear and additional acceleration of the reaction is minimal. The oxidation rate was unaffected by changes in oxygen concentration between $\sim$0.5 and 40 mg/ℓ measured with a dissolved oxygen meter. This suggests that the slow reaction mechanisms involving oxygen and hydrazine,

$$(14) \qquad N_2H_4 + O_2 \rightleftarrows N_2 + 2H_2O$$

is bypassed in the copper-catalyzed reaction where

$$(15) \qquad N_2H_4 + Cu^{2+} \rightleftarrows N_2H_3^{\circ} + Cu^{+} + H^{+}$$

Copper (I) can be oxidized back to copper (II) by low levels of oxygen

$$(16) \qquad Cu^{+} + O_2 + H^{+} \rightleftarrows Cu^{2+} + HO_2^{\circ}$$

and the hydroperoxyl radical can further abstract hydrogens from the hydrazyl radical to form the final products, nitrogen and water.

$$(17) \qquad HO_2^{\circ} + N_2H_3^{\circ} \rightleftarrows N_2 + 2H_2O$$

In the total absence of oxygen to recycle Cu (I) back to Cu (II), the oxidation of one mole of hydrazine would require four moles of copper. Figure 9 illustrates that this stoichiometry is nearly achieved

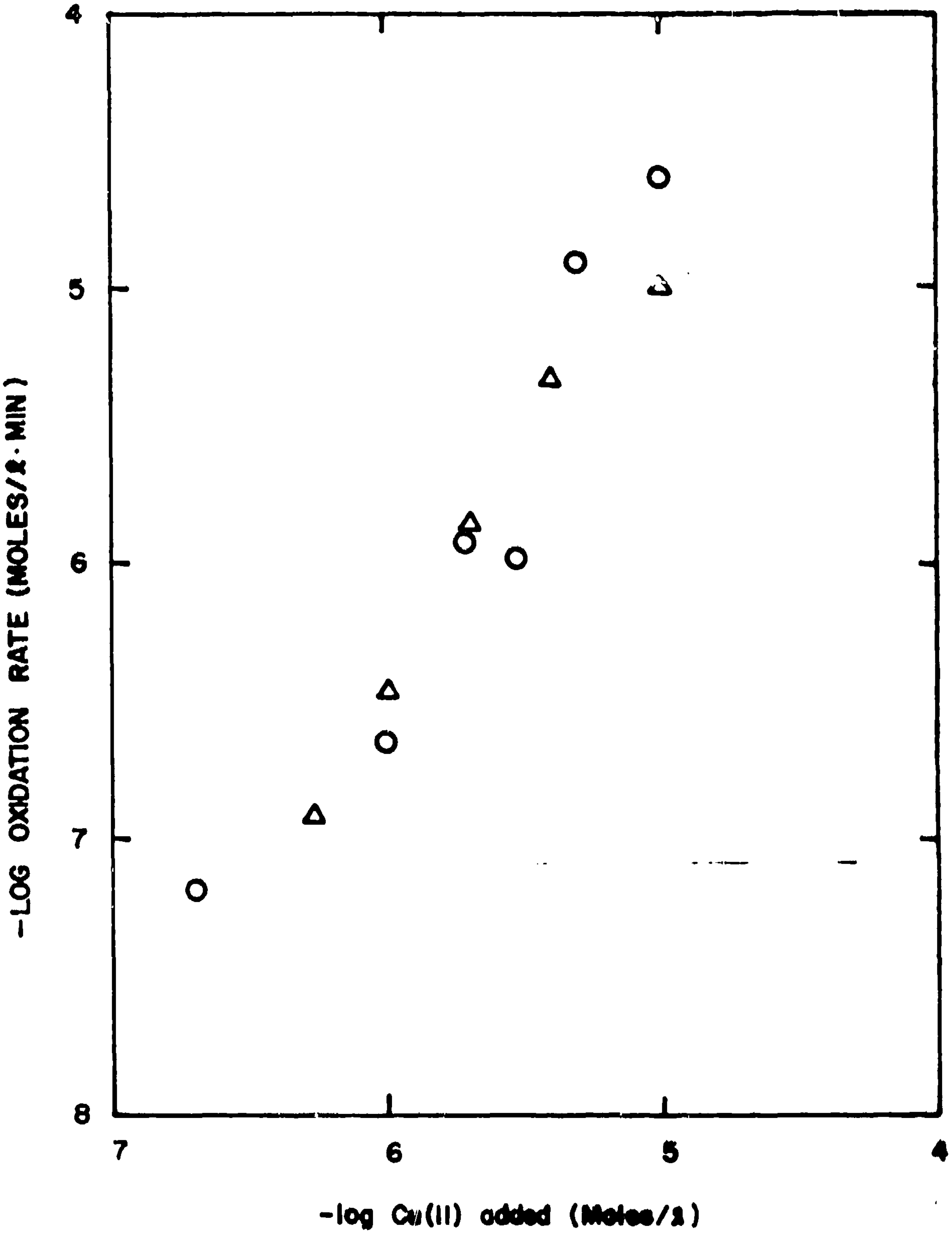

Figure 8. Influence of Copper (II) on the Oxidation Rate of Hydrazine in Two Experiments: Initial Hydrazine 1×10^{-4} Moles/ℓ, pH 8, 20°C, 10 mg/ℓ Dissolved Oxygen

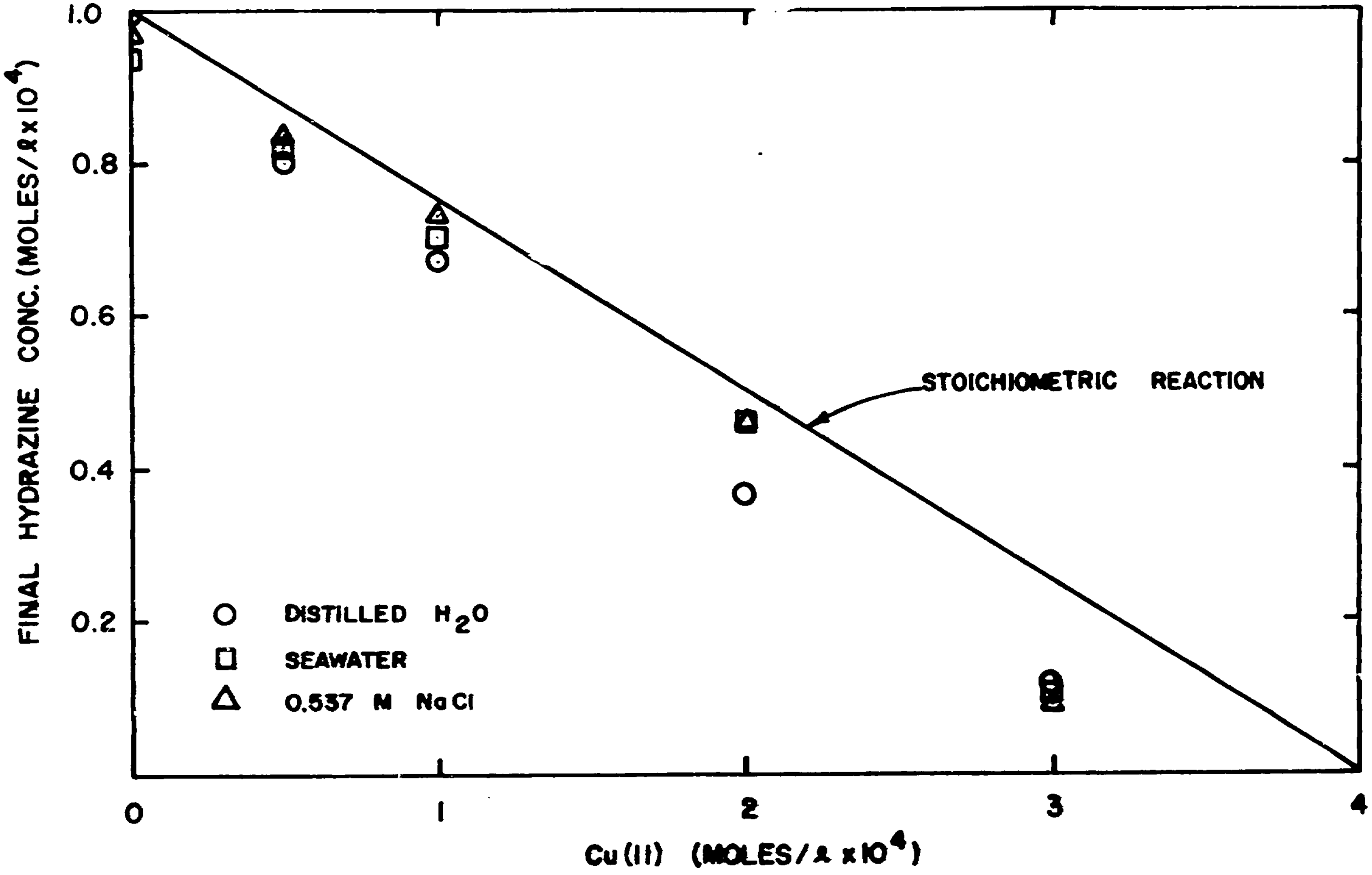

Figure 9. Influence of Copper (II) on the Oxidation of Hydrazine in the Absence of Dissolved Oxygen. Initial Hydrazine 1×10^{-4} Moles/ℓ, pH 8, 20°C

in the three electrolyte solutions studied. The small excess hydrazine oxidized in these experiments may have resulted from incomplete exclusion of all oxygen or autooxidation on walls of the pyrex vessels or electrodes.

EFFECT OF pH

As shown in Figure 1, above pH 8 the predominant hydrazine species changes from the protonated $N_2H_5^+$ to the unprotonated H_2H_4. This change in speciation is also reflected in Figure 10 by an increase in the oxidation rate as the pH is increased from 6 to between 8 and 9. The rate begins to decrease again as the pH is further increased to 10. This is not in agreement with Gaunt and Wetton (Reference 6) and Gilbert (Reference 3) who found the reaction rate increased with increasing pH from insignificant at pH 11 to a maximum at pH 12. When an ammonia solution was used to retard precipitation of the copper hydroxide, they found the maximum rate at pH 9. Ellis (Reference 4) also reported that a maximum rate occurred at a pH 9, however, provided no experimental evidence. The decrease in rate with increasing pH near neutral pH's may be the result of reduction of free available copper (Cu^{2+}) in solution due to hydrolysis and precipitation of copper hydroxide or copper carbonate. If the rate limiting step in the oxidation of hydrazine is given by Equation (6), then the rate should be a function of the reaction product of the unprotonated hydrazine, N_2H_4, and unhydrolyzed copper, Cu^{2+}. Figure 10 illustrates that a plot of calculated log $\{N_2H_4.Cu^{2+}\}$ versus pH reasonably duplicates the pH response of the oxidation rate suggesting that the two reacting species are in fact the unprotonated N_2H_4 and the unhydrolyzed Cu^{2+}.

EFFECT OF IONIC STRENGTH

The influence of ionic strength on the oxidation of hydrazine is shown in Figure 11. There is a significant increase in the oxidation date of hydrazine with increasing chloride or nitrate concentration.

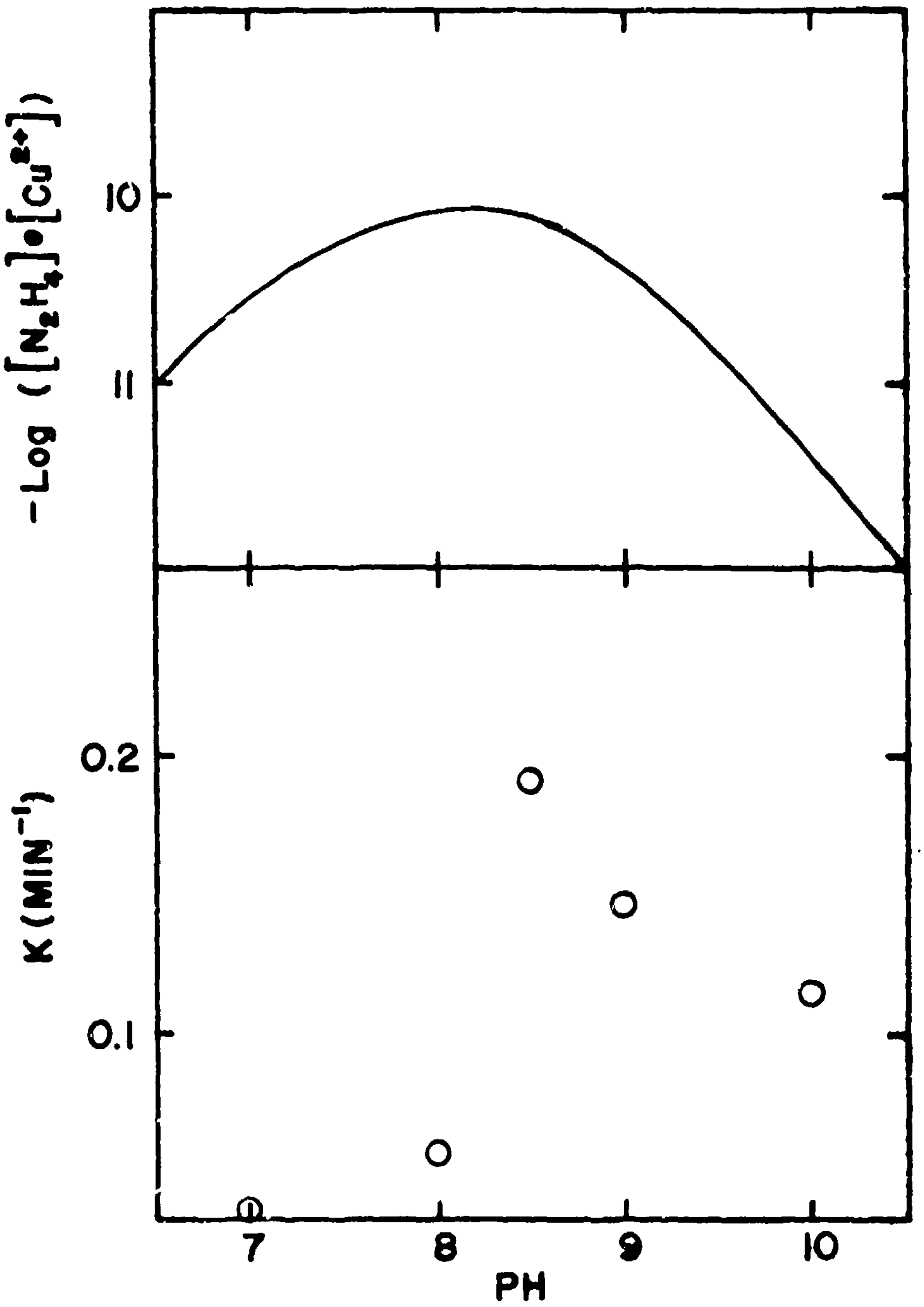

Figure 10. (A) Calculated Log Product of the Free Copper Concentration and Unhydrolyzed Hydrazine Concentration Versus pH

(B) Influence of pH on the Oxidation Rate Constant. Initial Hydrazine 1 x 15^{0-4} Moles/ℓ, 20°C, 10 mg/ℓ Dissolved Oxygen

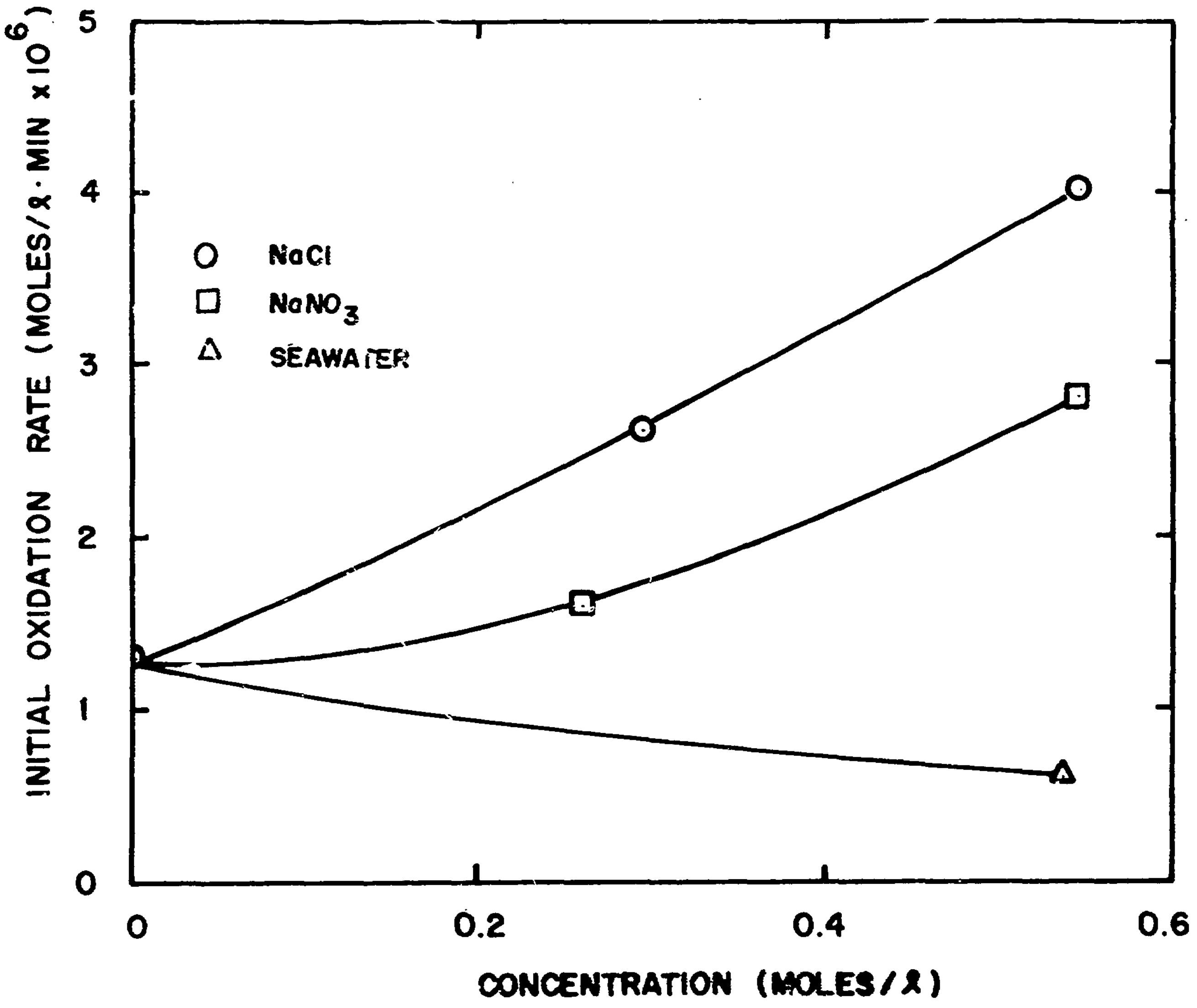

Figure 11. Influence of Electrolyte Composition on the Initial Oxidation Rate: Initial Hydrazine 1 x 10^{0-4} Moles/ℓ, pH 8, $20^{\circ}C$, 10 mg/ℓ Dissolved Oxygen

This increase is not observed in seawater collected from the Gulf of Mexico of approximately the same salinity. This discrepancy may be due to the complexing or precipitation of free copper with organic or inorganic ligands such as carbonate in the seawater. Hydrazine is also known to form a weak compound with carbon dioxide "carbazic acid" $(N_2H_4)_2CO_2$, which would inhibit the reaction. The effect of added bicarbonate on the degradation of hydrazine is illustrated in Figure 12 which shows a semi-log plot of hydrazine concentration versus time for varying concentrations of added bicarbonate. It follows from Figure 11 that the high concentration ($\sim 2 \times 10^3$ moles/ℓ) of bicarbonate found in seawater would decrease the reaction velocity more than the expected increase due to an ionic strength of 0.55 moles/ℓ. This observed increase in reaction velocity with ionic strength is unexpected from activity rate theory [Capellos and Bielski (Reference 20)]. The charge product of the two reacting species, N_2H_4 and Cu^{2+}, is zero and the reaction constant should be independent of ionic strength.

EFFECT OF TEMPERATURE

Figure 13 illustrates the influence of temperature on the oxidation of hydrazine over the temperature range 5 - 30°C. There is a 40-fold increase in the reaction rate. An Arrhenius plot of ln K versus the reciprocal of the absolute temperature in Figure 14 shows a change in slope at temperatures below 10°C. The shape of this plot indicates a multi-step reaction series as shown in Equations (5) and (8) and that the controlling mechanism is different in the two different temperature regions [Levenspiel (Reference 21)]. Lurker (Reference 7) also observed that at 6°C a kinetic model developed by Gramley (Reference 8) was not applicable although it was consistent at 24°C and 37°C.

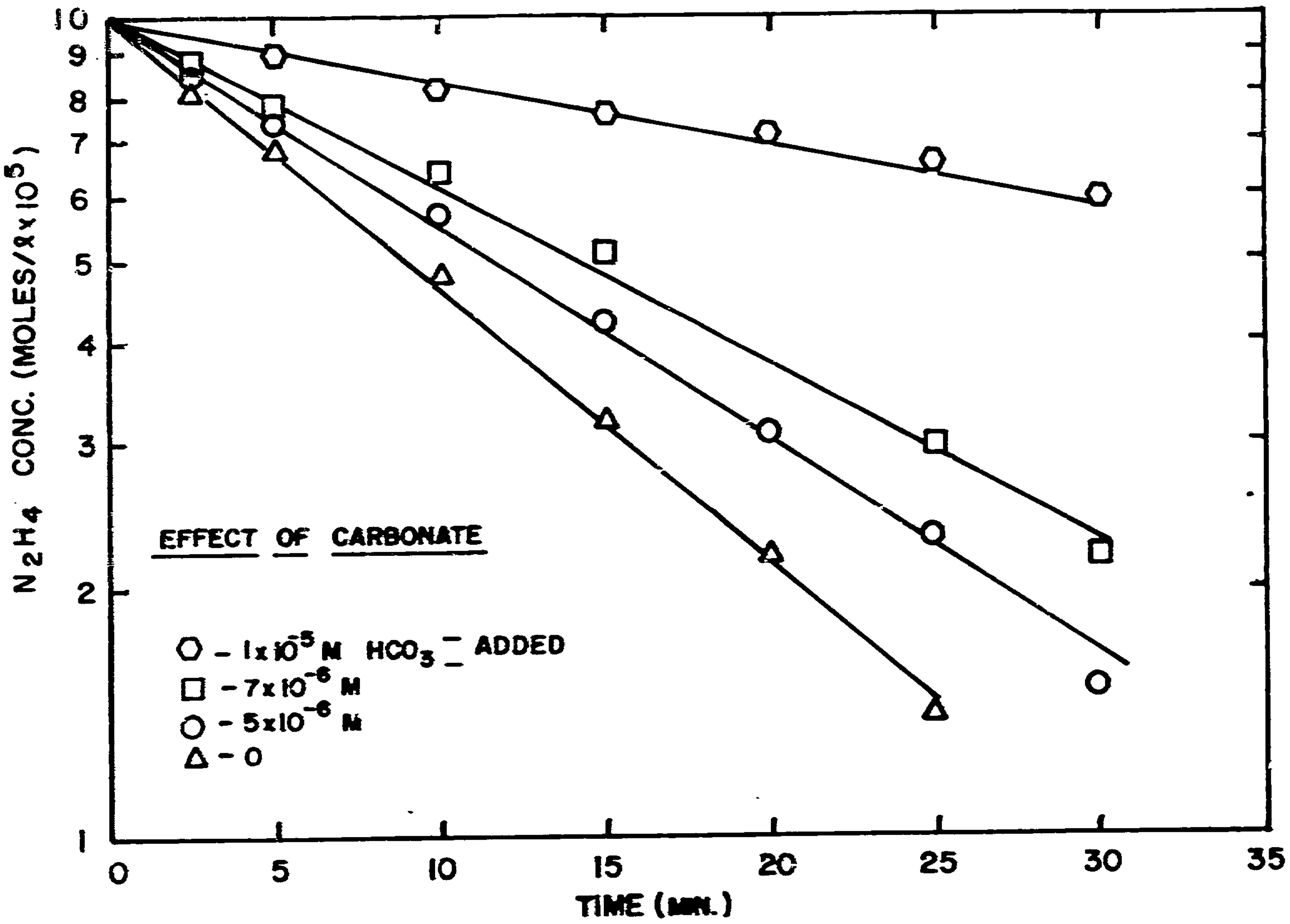

Figure 12. Influence of Bicarbonate on the Concentration of Hydrazine as a Function of Time: 1×10^{-6} Moles/ℓ Cu, pH 8, 20°C 10 mg/ℓ Dissolved Oxygen

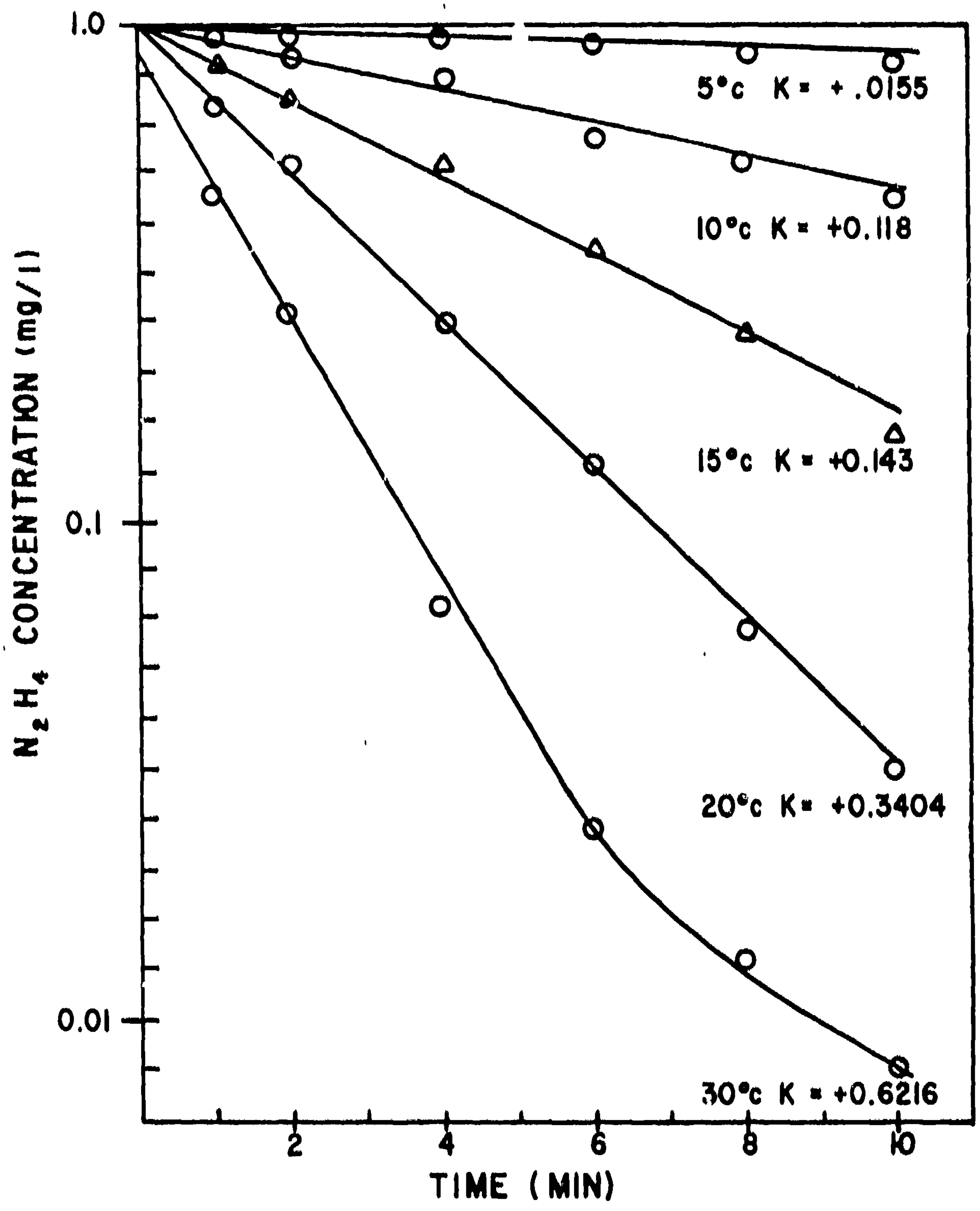

Figure 13. Influence of Temperature on the Concentration of Hydrazine as a Function of Time: 1 x 10^{-6} Moles/ℓ, Cu, pH 8, 10 mg/ℓ Dissolved Oxygen

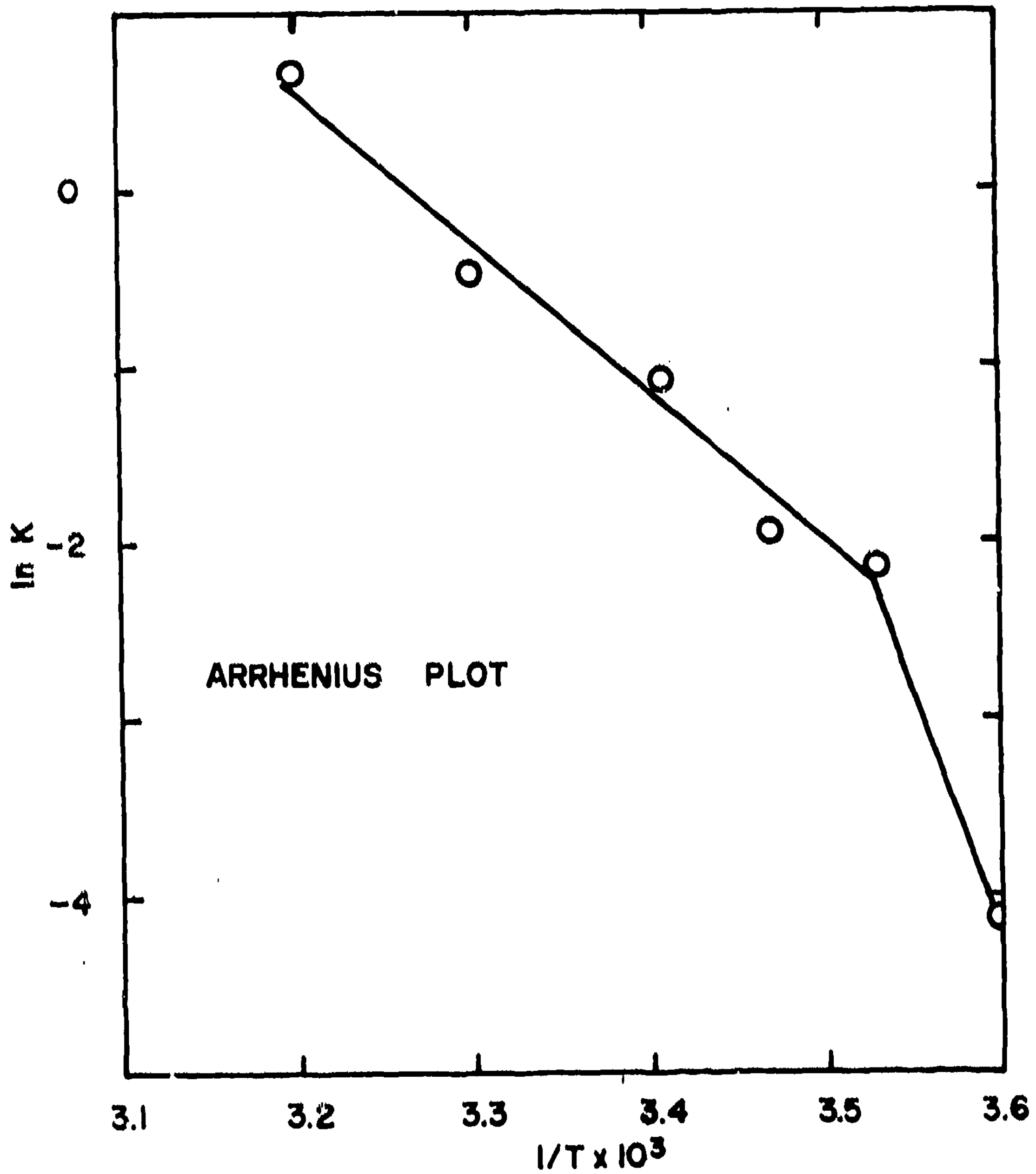

Figure 14. Plot of ln Rate Constant Versus 1/T for the Oxidation of Hydrazine: Initial Hydrazine 1×10^{-4} Moles/ℓ, 1×10^{-6} Moles/ℓ, Cu, pH 8, 10 mg/ℓ Dissolved Oxygen

SECTION V

SUMMARY

The degradation of hydrazine in natural waters, in the absence and presence of suspended solids, is a slow process without an added metal catalyst such as copper. In five days, reductions of less than 25 percent were measured in pond water and 40 percent in seawater. In distilled water, reductions of less than 2 percent were observed. Copper exhibits a catalytic effect on the oxygen oxidation of hydrazine which is measurable at concentrations as low as 10^{-7} moles/ℓ, and further increases the oxidation rate for increasing copper concentrations up to 10^{-4} moles/ℓ copper. In oxygen-free atmospheres there is a stoichiometic oxidation of hydrazine by copper. Any change in oxidation rate with increasing oxygen concentration was not measurable at oxygen concentrations measured with the dissolved oxygen probe used in these studies. The oxidation rate is influenced by pH with the maximum rate occurring between pH 8 and 9. This can be explained by the hydrolysis chemistry of hydrazine and copper.

The oxidation rate exhibits an unexplained increase with increasing ionic strength; however, this increase is not observed in seawater. This is probably the result of other inorganic and organic copper complexing compounds in seawater. Finally, there is a significant decrease in the oxidation rate with decreasing temperature, and a change in the slope of the 1/T versus ln K plot confirms the multi-step reaction mechanisms proposed.

The slow degradation rates found in the absence of added catalysts indicates that hydrazine should be assumed to be conservative in modeling aqueous spills. Any significant reductions in solution concentration will occur from dispersion and dilution rather than oxidation. This does not take into account biological breakdown of hydrazine; however, the toxicity of hydrazine to lower organisms such as bacteria

[MacNaughton, Farmwald, McDaniels and Urda (Reference 22)] and phytoplankton [Harrah (Reference 23)] would diminish the importance of this mechanism.

REFERENCES

1. Browne, A. W. and Shatterly, F. F., "On the Oxidation of Hydrazine," I, Jor. Amer. Chem. Soc. 29 1305 (1907); II, 30 53 (1908); III, 31 221 (1909a); IV, 31 783 (1909b).

2. Bray, W. C. and Cuy, E. J., "The Oxidation of Hydrazine 1. The Volumetric Analysis of Hydrazine by the Iodic Acid, Iodine, Bromine and Hypochlorous Acid Methods." Jor. Amer. Chem. Soc. 46 858 (1924).

3. Gilbert, E. C., "Studies on Hydrazine. The Autooxidation," Jor. Amer. Chem. Soc. 51 2744 (1929).

4. Ellis, S. R. M. and Moreland, C., "The Reaction Between Hydrazine and Oxygen," Proceedings of the International Conference on Hydrazine and Water Treatment. Bournemouth, England (1957).

5. Ellis, S. R. M., Jeffreys, G. V. and Hill, P., "Oxidation of Hydrazine in Aqueous Solution," Jor. Appl. Chem. 10 347 (1960).

6. Gaunt, H. and Wetton, E. A. M., "The Reaction Between Hydrazine and Oxygen in Water," Jor. Appl. Chem. 16 171 (1966).

7. Lurker, P. A., "Catalytic Deoxygenation of Aqueous Solutions by Hydrazine," AMRL Technical Report 76-23, Wright-Patterson AFB, Ohio (1976).

8. Gramley, W. and Ford, R. E., "Deoxygenation of Environmental Waters by Hydrazine-Type Fuels," AMRL Technical Report 73-125, Wright-Patterson AFB, Ohio (1973).

9. Sillen, L. G. and Martell, A., Stability Constants of Metal-Ion Complexes, Special Publication No. 17, The Chemical Society London (1964); Supplement 1, Special Publication No. 25 (1971).

10. Audrieth, L. F. and Ogg, B. A., The Chemistry of Hydrazines, Wiley and Sons, New York (1951).

11. Bannerja, D. and Singh, I. P., "Studies on the Hydrazine Complexes of Some Bivalent Metal Ions in Aqueous Solutions," Z. Anorg. Chem. 349 213 (1967).

12. Cotton, F. A. and Wilkinson, G., Advanced Inorganic Chemistry, Interscience, New York (1972).

13. Latimer, W. M., The Oxidation States of the Elements and their Potentials in Aqueous Solution, 2nd Ed. Prentice Hall Inc, New Jersey (1952).

14. Feitknecht, W. and Schindler, P., "Solubility Constants of Metal Oxides, Hydroxides and Metal Hydroxide Salts in Aqueous Solution," Pure and Applied Chem. 6 130 (1963).

15. Arnek, R., "On the Thermochemistry of Some Hydrolytic Species," Arkiv for Kemi, 32, 55 (1970).

16. Schiendler, P., Reinert, M. and Gamsjager, H., "Loslichbeitkonstanten Und Freie Bildungsenthalpien Von $Cu_2(OH)_2 CO_3$ (Malachit) and $Cu_3(OH)_2$ (Azurit) bei 25°C," Helv. Chim. Acta 51 1845 (1968).

17. Watt, G. W. and Chrisp, J. D., "A Spectrophotometric Method for the Determination of Hydrazine," Anal. Chem. 24 2006 (1972).

18. Eyl, A. W., Stauffer, T. B., Urda, G. A. and MacNaughton, M. G., "Control and Treatment of Small Hydrazine Spills," CEEDO TR-78-12, Tyndall AFB, Florida (1978).

19. Stumm, W. and Lee, G. F., "Oxygenation of Ferrous Iron," Ind. and Eng. Chem. 53 143 (1961).

20. Capellos, C. and Bielski, B., Kinetic Systems: Mathematical Descriptions of Chemical Kinetics in Solution, Wiley Interscience, New York (1972).

21. Levenspiel, O., "Chemical Reaction Engineering," John Wiley and Sons, New York (1972).

22. MacNaughton, M. G., Farmwald, J., MacDaniels, L. and Urda, G., "Biological Degradation of Hydrazine," CEEDO Technical Report 78-13, Tyndall AFB, Florida (1978).

23. Harrah, C. B., "Biological Efforts of Aqueous Hydrazine Solutions," Paper 14, Proceedings of the Conference on Environmental Chemistry of Hydrazines, CEEDO TR-78-14, Tyndall AFB, Florida (1978).

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