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KINETICS OF THE OXIDATION OF HYDRAZINE BY HYDROGEN
PEROXIDE, CATALYZED BY COPPER (II)

Carl R. Wellman, et al

Ballistic Research Laboratories
Aberdeen Proving Ground, Maryland

August 1975

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Carl R. Wellman
J. Richard Ward
Lester P. Kuhn

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (1pk) Hydrazine is oxidized by hydrogen peroxide in the presence of copper(II) to form nitrogen and water. The rate of reaction between stoichiometric amounts of hydrazine and hydrogen peroxide in the presence of copper(II) was followed by monitoring the rate of evolved nitrogen. The rate was first order with respect to concentrations of hydrogen peroxide and copper(II), but was independent of the concentration of hydrazine. The most likely mechanism involves formation of a copper(II) - hydrazine complex that reacts with the		

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hydrogen peroxide. The enthalpy of activation and entropy of activation turned out to be 5.8 ± 0.2 kcal/mole and -28 ± 1 cal/mole-K

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I. INTRODUCTION

Hydrazine, a common ingredient in liquid propellants, has been extensively investigated over the past seventy years.¹ The kinetics and mechanism of reactions involving hydrazine are of interest in understanding the ignition and combustion of such propellants and also in understanding reactions that might lead to reduced shelf life.

In 1949 Gordon² measured the kinetics of the reaction between hydrogen peroxide and hydrazine in aqueous solution. The reaction rate was first-order in both hydrazine and hydrogen peroxide, and the rate of the reaction at 25°C was relatively slow. For nearly equal molar solutions of hydrazine and hydrogen peroxide the rate coefficient was reported as $4.1 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$.

In 1961 Corey³ reported that the *cis*-hydrogenation of olefins was possible in the presence of hydrazine, hydrogen peroxide, and trace amounts of copper(II). Interestingly, he reported that the reaction occurred "instantaneously." Thus the rate of reaction in the presence of copper(II) would have to be much faster than the one studied by Gordon in 1949. In addition Corey argued that the reactive species involved in the olefin hydrogenation was diimide, N_2H_2 . This was confirmed and further studies on N_2H_2 ensued.⁴⁻⁹

¹W. C. E. Higginson, "Recent Aspects of the Inorganic Chemistry of Nitrogen", Special Publication No. 10 of the Chemical Society, London (1957).

²A. S. Gordon, "The Reaction Between Hydrazine and Hydrogen Peroxide in the Liquid Phase," Third Combustion Symposium, Williams and Wilkins Co., Baltimore, MD, 1949.

³E. J. Corey, W. L. Mock, and D. J. Pasto, "Chemistry of Diimide. Some New Systems for the Hydrogenation of Multiple Bonds," *Tetrahedron Letters*, 11, 347 (1961).

⁴E. J. Corey, D. L. Pasto, and W. L. Mock, "Chemistry of Diimide II. Stereochemistry of Hydrogen Transfer to Carbon-Carbon Multiple Bonds," *J. Am. Chem. Soc.*, 83, 2957 (1961).

⁵E. E. van Tamelen, R. S. Doney, M. F. Lease, and W. H. Pirkle, "Selectivity and Mechanism of Diimide Reductions," *J. Am. Chem. Soc.*, 83, 4302 (1961).

⁶S. Hunig, H. R. Keller, and W. Thier, "The Chemistry of Diimine," *Angewandte Chemie (Int'l Ed.)*, 4, 271 (1965).

⁷C. Willis and R. A. Back, "Diimide: Some Physical and Chemical Properties, and the Kinetics and Stoichiometry of the Gas-Phase Decomposition," *Can J. Chem.*, 51, 3605 (1973).

⁸S. K. Vidyarthi, C. Willis, R. A. Back, and R. M. McKittrick, "The Reaction of Diimide with Olefins in the Gas Phase," *J. Am. Chem. Soc.*, 96, 7674 (1974).

⁹D. B. Paul, "The Apparent Intervention of Diimide during a Pyredazine Synthesis. A Re-examination of the Reaction Between Hydrazine and Pyrazine-2,3-Dicarboxylic Acid Derivatives," *Aust. J. Chem.*, 27, 1331 (1974).

¹⁰H. Erlenmeyer, C. Flierl, and H. Sigel, "Zur Cu^{2+} katalysierten Reaktion zwischen Wasserstoffperoxide und Hydrazin bzw. Hydroxylamin," *Chimia*, 22, 433 (1968).

Despite this attention to N_2H_2 as a hydrogenating agent, the kinetics and mechanism of the copper(II)-hydrazine-hydrogen peroxide reaction has not been elucidated. Siegel and co-workers^{10,11} examined the kinetics of the oxidation of hydrazine by hydrogen peroxide in the presence of copper(II)-2, 2'-dipyridyl complex, but were not able to measure the kinetics in the presence of hydrated copper(II) because copper oxide precipitated. In this report the kinetics have been successfully measured by using sufficiently small quantities of copper(II) to avoid precipitation of oxide.

II. EXPERIMENTAL

A. Reagents

Anhydrous hydrazine, 97% solution, was obtained from Matheson, Coleman, and Bell, Norwood, OH. Hydrogen peroxide, 90% solution, was obtained from the Becco Chemical Division, FMC Corp., Buffalo, NY. A 4-molar stock solution of each reagent was prepared with cold double distilled water. The stock solutions were stored in a refrigerator when not in use. All metal salts used in these experiments were reagent grade.

B. Procedure

The experiments were initially conducted in a 125 ml Erlenmeyer flask equipped with a side-arm that led to a gas bubbler and gas buret for measuring and collecting the evolved gas over mercury. The neck of the 125 ml reaction flask was firmly fitted with a silicone rubber stopper that contained a 15 ml buret for the addition of 4-molar hydrazine and an inlet tube for the introduction of helium or argon to deaerate the reaction mixture. The reaction flask temperature was controlled by immersing in a thermostatted water bath at the desired reaction temperature. Vigorous stirring was maintained with a teflon coated magnetic stirring bar. After adding the desired amount of copper(II), hydrogen peroxide, and double distilled water, the reaction flask was placed in the constant temperature water bath. The reaction flask's contents were deaerated for at least 15 minutes by bubbling helium or argon through the solution

¹⁰H. Erlenmeyer, C. Flierl, and H. Sigel, "Zur Cu^{2+} katalysierten Reaktion zwischen Wasserstoffperoxide und Hydrazin bzw. Hydroxylamin," Chimia, **22**, 133 (1968).

¹¹H. Erlenmeyer, C. Flierl, and H. Sigel, "On the Kinetics and Mechanism of the Reactions of Hydrogen Peroxide with Hydrazine or Hydroxylamine, Catalyzed by Cu^{2+} -2,2'-Bipyridyl Complex", J. Am. Chem. Soc., **91**, 1065 (1969).

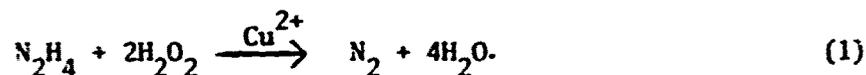
while stirring vigorously. The flow of inert gas was stopped and the desired amount of 4-molar hydrazine introduced as a "slug" through the altered buret tip. The timer was started and the reaction product gas collected in the 100 ml gas buret. The gas was maintained at atmospheric pressure with the leveling bulb of the gas buret. The time elapsed for the collection of every 10 mls of gas was recorded.

A number of experiments were conducted in the 125 ml reaction flask using a total constant volume of 50 mls. From these runs the order of reaction with respect to the total concentration of copper(II) increased as the concentration of copper(II) increased. This was found to be caused by the high enthalpy of reaction (196 Kcal/mole) which raised the temperature of the reaction during the course of a run. In all subsequent experiments the reaction flask contents were monitored with a 10 mil copper-constantan thermocouple enclosed in a thin-wall pyrex tube inserted through the silicone rubber stopper and immersed in the reaction solution. The analog signal received was displayed on a strip-chart potentiometric recorder. In this manner it was possible to determine the experimental conditions required to minimize the effect of the heat of reaction on the rate. In order to keep the temperature constant throughout the kinetic run, the reaction solution was increased to 300 mls and the concentrations of hydrogen peroxide and of hydrazine were halved.

The stock solutions of hydrazine, hydrogen peroxide, and copper(II) were analyzed by standard iodimetric procedures.^{12,13}

III. RESULTS

The stoichiometry of the reaction was reported by Graham¹⁴ as



The stoichiometry was confirmed by measuring the total amount of gas produced.

The rate law was determined by measuring the initial rate of

¹²H. H. Willard, H. H. Furman, and C. E. Bricker, Elements of Quantitative Analysis-Theory and Practice, 4th edition. D. Van Nostrand Co., Inc., New York, 1956, pp 255-276.

¹³H. H. Furman, ed., Standard Methods of Chemical Analysis, Vol. 1 The Elements, 6th edition, D. Van Nostrand Co., Inc., New York, 1962 p 404.

¹⁴D. P. Graham, "Promoter Action in Reactions of Oxidation Concomitant with the Catalytic Decomposition of Hydrogen Peroxide. I. The Oxidation of Hydrazine," J. Am. Chem. Soc., 52, 3035 (1930).

reaction.¹⁵ The pH of the reaction solution was estimated from equation (2)

$$[H^+] = \left(\frac{K_1 K_2 [H_2O_2]}{K_2 + [N_2H_4]} \right)^{\frac{1}{2}}, \quad (2)$$

where K_1 and K_2 are the acid dissociation constants for H_2O_2 and $N_2H_5^+$, respectively. A derivation of equation (2) is included in the Appendix. The pK_a 's for K_1 and K_2 are 11.6¹⁶ and 8.07.¹⁰

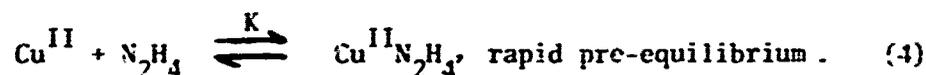
The results for the runs in which the concentration of copper(II) was kept the same is shown in Table I. In Table II the results with varying copper(II) concentrations are shown. In Table III some selected runs were made with copper(II) acetate and copper(II) perchlorate instead of copper(II) sulphate to demonstrate that the rate is independent of the anion. From these results it is clear that the rate law may be represented as

$$\frac{d(N_2)}{dt} = k_{obs} (H_2O_2)_T (Cu(II))_T, \quad (3)$$

where $(H_2O_2)_T$ and $(Cu(II))_T$ stand for the total concentrations of hydrogen peroxide and copper(II). In addition the rate is independent of pH within the limited range examined here.

IV. DISCUSSION

The rate law indicates that the rate-determining step for the reaction involves copper ion and hydrogen peroxide. Since copper(II) has been shown to react slowly with hydrogen peroxide,^{5,10} the more likely mechanism consists of a copper-hydrazine complex reacting with hydrogen peroxide. Such a scheme is shown below



¹⁵I. Amdur and G. G. Hammes, *Chemical Kinetics-Principles and Selected Topics*, McGraw-Hill Book Co., Inc., New York, 1966, pp 9-10.

¹⁶J. Schubert, V. S. Sharma, E. R. White, L. S. Bergelson, "Catalytic Decomposition of Hydrogen Peroxide by Copper Chelates and Mixed Ligand Complexes of Histamine in the Presence of Phosphate Buffer in the Neutral pH Region", *J. Am. Chem. Soc.*, 90, 4476 (1968).

TABLE I.
 Determination of the Reaction Order of
 Hydrazine and Hydrogen Peroxide^{a,b}

$N_2H_4, M \times 10^2$	$H_2O_2, M \times 10^2$	Rate, mls N_2 /min	pH ^c
1.64	6.54	7.3	9.5
3.27	6.54	7.4	9.7
6.54	6.54	7.4	9.8
13.1	6.54	7.4	10.
3.27	3.27	3.6	9.8
3.27	6.54	7.4	9.7
3.27	13.1	15	9.5
1.64	3.27	3.6	9.7
3.27	6.54	7.4	9.7
6.54	13.1	15	9.7

^aTotal volume equal to 300 mls, T = 298K

^bCopper(II) sulphate concentration $1.23 \times 10^{-6}M$

^cCalculated from equation (2).

TABLE II.
Determination of Reaction Order of
Copper(II) Sulphate^{a,b}

Copper(II), M x 10 ⁷	Rate, mls N ₂ /min
3.29	1.95
6.57	4.1
9.86	6.2
13.2	8.3
16.4	10.4
24.6	16.2

^aTotal volume of solution is 300 ml, T = 298 K

^b[N₂H₄] = 0.033M, [H₂O₂] = 0.0654M, pH = 9.7

TABLE III.
Comparison of Reaction Rate for
Different Copper(II) Salts^{a,b}

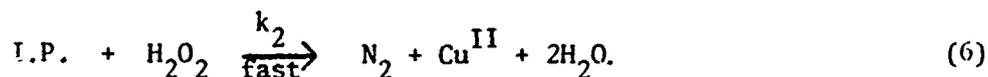
Copper(II) x 10 ⁵ , millimoles	Rate, mls/min ^c	Rate, mls/min ^d
5	---	0.5
10	---	1.0
12.5	1.3	---
15	---	1.5
20	---	2.1
25	2.6	---
30	---	3.1
40	---	4.1
50	5.1	5.1

^aTotal volume solution equal to 300 mls, T = 298K

^b[N₂H₄] = 0.017M, [H₂O₂] = 0.033M, pH = 9.7

^ccopper(II) perchlorate

^dcopper(II) acetate



The rate law for this mechanism is then

$$\frac{d(\text{N}_2)}{dt} = \frac{k_1 K(\text{N}_2\text{H}_4) (\text{H}_2\text{O}_2) (\text{Cu}^{\text{II}})_T}{1 + K(\text{N}_2\text{H}_4)}, \quad (7)$$

where $(\text{Cu}^{\text{II}})_T$ represents the total concentration of copper(II) in solution. If $K \times (\text{N}_2\text{H}_4)$ is greater than unity, then (7) reduces to the experimentally observed rate law, equation (3). For Cu^{2+} and N_2H_4 , $\log K$ was reported as 4.2.¹⁰ Even if the reactive copper(II) complex is $\text{Cu}^{\text{II}}(\text{OH})(\text{N}_2\text{H}_4)$ which should have a somewhat smaller value of K , the product $K \times (\text{N}_2\text{H}_4)$ is most certainly greater than unity. At the pH of these kinetic runs, the predominate form of the copper(II) is CuOH^+ since the pK_a for hydrated copper(II) is 8.0.¹⁷ The intermediate products in equation (5) are not required by the rate law, but are put into the mechanistic scheme, since N_2H_2 has been inferred to be present by Corey and others.

To obtain enthalpy and entropy of activation for this reaction, additional runs were made at 15°C and 35°C. The rate of reaction was recast into $\text{M}^{-1} \text{sec}^{-1}$ by converting the volume of nitrogen evolved into moles of nitrogen evolved. The results of these runs are shown in Table IV.

The activation parameters were computed from a non-linear least-squares fit of equation (8)

$$k_1 = \frac{kT}{h} e^{-\Delta H^*/RT} e^{\Delta S^*/R}, \quad (8)$$

¹⁷F. Basolo and R. G. Pearson, *Mechanism of Inorganic Reactions*, Wiley and Sons, Inc., NY, 1958, p 387.

TABLE IV.
Rate Coefficients Used To Compute Activation Parameters^a

Cu(II), M x 10 ⁷	H ₂ O ₂ , M	Rate, mls N ₂ /min	k ₁ , M ⁻¹ sec ⁻¹ x 10 ⁻²	T, K
8.22	0.067	3.2	1.4	288
12.3	.067	4.7	1.3	288
16.4	.067	6.8	1.5	288
8.22	.065	4.9	2.1	298
12.3	.065	7.3	2.1	298
16.4	.065	10.2	2.2	298
8.22	.065	7.3	3.0	308
12.3	.065	10.4	2.8	308
16.4	.065	14.3	2.9	308

^a[N₂H₄] = 0.033 Min all runs.

where

- k_1 = rate coefficient,
- k = Boltzmann's constant,
- h = Planck's constant,
- T = temperature,
- ΔH^* = enthalpy of activation,
- ΔS^* = entropy of activation,
- R = gas constant.

The non-linear least squares fit was performed with a Los Alamos program¹⁸ in which temperature was the independent variable, the rate coefficient was the dependent variable, and the ΔH^* and ΔS^* were the two parameters to be fit. The results of the calculation are shown below including the standard deviation of each activation parameter

$$\Delta H^* = 5.8 \pm 0.2 \text{ Kcal/mole,}$$

$$\Delta S^* = 28 \pm 1 \text{ cal/mole-K.}$$

The rate coefficients at 288, 298, and 308 computed from the best-fit values are 142, 206, and 293 $M^{-1}sec^{-1}$, respectively.

A comparison among the rate coefficients at 25°C for the uncatalyzed oxidation of hydrazine and hydrogen peroxide, and this reaction catalyzed by hydrated copper(II) and the copper(II)-2, 2'-dipyridyl complex is shown below which demonstrates the efficacy of the copper catalyst.

catalyst	$k_1 M^{-1} sec^{-1}$	Reference
none	1.8×10^{-5}	2
copper(II)	210	This work
Cu^{2+} -2,2'-dipyridyl	127	11

¹⁸R. H. Moore and R. K. Ziegler, "The Solution of the General Least Squares Problem with Special Reference to High-Speed Computers," Los Alamos Scientific Laboratory Report LA-2367, March 1960.

A glance at the first two rate coefficients shows why Corey and co-workers needed a trace of copper(II) in order to hydrogenate olefins at room temperature. Presumably the increased reactivity of hydrazine coordinated to copper ion arises from a shift in electron density from hydrazine toward the positively-charged copper(II) that facilitates removal of a hydrogen atom from each nitrogen.

V. CONCLUSION

Copper(II) accelerates the rate of the oxidation of hydrazine by hydrogen peroxide through formation of a copper(II) - hydrazine complex.

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APPENDIX A
CALCULATION OF THE PH OF AN AQUEOUS SOLUTION
OF HYDRAZINE AND HYDROGEN PEROXIDE

APPENDIX A.
 CALCULATION OF THE pH OF AN AQUEOUS SOLUTION
 HYDRAZINE AND HYDROGEN PEROXIDE.

The appropriate equations are

$$K_1 = \frac{[H^+][HO_2^-]}{[H_2O_2]} \quad A - (1)$$

$$K_2 = \frac{[H^+][N_2H_4]}{[N_2H_5^+]} \quad A - (2)$$

$$[H^+] + [N_2H_5^+] = [HO_2^-] \quad A - (3)$$

from (1) and (3)

$$K_1 (H_2O_2) = (H^+) \left((H^+) + [N_2H_5^+] \right) \quad A - (4)$$

from (2) and (4)

$$K_1 (H_2O_2) = (H^+) \left((H^+) + \frac{(H^+) (N_2H_4)}{K_2} \right) \quad A - (5)$$

$$K_1 K_2 (H_2O_2) = K_2 (H^+)^2 + (H^+)^2 (N_2H_4) \quad A - (6)$$

$$(H^+)^2 = \frac{K_1 K_2 (H_2O_2)}{K_2 + (N_2H_4)}, \quad A - (7)$$

$$(H^+) = \left(\frac{K_1 K_2 (H_2O_2)}{K_2 + (N_2H_4)} \right)^{\frac{1}{2}}. \quad A - (8)$$