(Figure 7) all the phosphorus ligands collapses the resonance at −14.20 ppm to a doublet ($J_{\text{H-Rh}} = 31$ Hz), the resonance at −9.80 ppm remains unaltered as a doublet ($J_{\text{H-Rh}} = 38$ Hz), and the signal at −13.20 ppm becomes a singlet with no rhodium coupling. The magnitude of these couplings, along with the fact that the hydride signal at −9.80 ppm shows the smallest (<2 Hz) coupling to phosphorus, indicates that this hydride is terminal on rhodium ($H_A$). The hydride resonance at −14.20 ppm, which shows strong coupling to both Rh and all phosphines on Ru must be bridging the Ru–Rh bond ($H_C$). The remaining hydride (−13.20 ppm), which lacks rhodium coupling and couples strongly to the phosphine ligands, is thus terminal on ruthenium ($H_B$).

Since attempts to obtain crystals suitable for X-ray diffraction were unsuccessful, the *stereochemistry* of this complex was also deduced from the NMR data. The magnitudes of the $J_{\text{H-P}}$ couplings for the hydride ligands indicate that no hydrides are trans to phosphine ligands. The $^1$H NMR also reveals that a plane of symmetry is present that produces only six chemical shifts for the 12 cyclooctadiene protons. Assuming the presence of a Rh–Ru bond and an octahedral d$^6$ Ru center, which is consistent with the complex being rigid on the NMR time scale, the structure in eq 10 is proposed.

This structure is further supported by the $^{31}$P NMR, which reveals that only the phosphine trans to the proposed Ru–Rh bond shows Rh coupling ($J_{\text{P-Rh}} = 10$ Hz). The mutually trans phosphines show no coupling to rhodium. The formation of this thermodynamic product represents a novel case where hydride transfer (intramolecular migration) is a kinetically slow process. Moreover, no rapid hydride migration occurs in the thermodynamic product **3**.

## Conclusions

Deprotonation of neutral transition-metal polyhydrides with KH in THF serves as a high yield and convenient route to potassium salts of polyhydride anions. The accumulated evidence is that such "salts" are actually intimate ion pairs, with hydride ligands being sufficiently basic to compete effectively with THF for coordination sites on $K^+$. Conventional coordination geometries (octahedral, dodecahedral, etc.) are retained at the transition metal even in the presence of such hydride bridging. Although the above polyhydride anions can result from abstraction of terminal hydride ligands as $H^+$, there is evidence[24] that coordinated $H_2$ (as in $Re(H_2)(H)_5L_2$) may be deprotonated more rapidly. Polyhydride anions are sufficiently nucleophilic to react cleanly with transition-metal halogen bonds at temperatures low enough to allow detection of kinetic products before they rearrange to the thermodynamic product. Given the common occurrence of rapid hydride migration in mononuclear and polynuclear transition-metal complexes, the rearrangement of $(COD)Rh(\mu\text{-}H)_3Ru(PPh_3)_3$ to $(COD)Rh(H)(\mu\text{-}H)RuH(PPh_3)_3$ is unexpectedly slow. Moreover, since the kinetic product has three Ru–H bonds while the thermodynamic product has only two, the reaction clearly does not occur by a least motion mechanism.

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**Supplementary Material Available:** Tables of atomic positional parameters and anisotropic thermal parameters (4 pages); listing of observed and calculated structure factors for $\{K(THF)_2ReH_6(PPh_3)_2\}_2$ (18 pages). Ordering information is given on any current masthead page.

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# The Copper-Catalyzed Redox Reaction between Aqueous Hydrogen Peroxide and Hydrazine. 1. New Experimental Results and Observations

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**Abstract:** Important new data are reported which make it possible to deduce the most probable mechanism of the copper-catalyzed redox reaction between aqueous hydrogen peroxide and hydrazine: $2H_2O_2 + N_2H_4 \rightarrow 4H_2O + N_2$. The reaction is marked by an induction period $\tau_e$ which varies inversely with the catalyst concentration but essentially independently with the peroxide and hydrazine concentrations. Trace amounts of cerium ion, hydroquinone, quinone, and *o*-phenylenediamine promote the reaction markedly. Ultrasonication accelerates the reaction, whereas a viscosity increase in the reaction solution has the opposite effect. Maleate ion produces a quantitative increase in nitrogen output above the stoichiometric equivalent of peroxide. The reaction shows no wall effect. The nitrogen and peroxide profiles and the rate are described, respectively, by

$$\frac{N_{N_2}}{V} = \frac{1}{2}([H_2O_2]_0 - [H_2O_2]) = \frac{[H_2O_2]_0}{2}\left[1 - \left(\frac{b+1}{b+e^{t/\tau_e}}\right)^c\right]$$

$$\frac{1}{V}\frac{dN_{N_2}}{dt} = \frac{k_e[Cu]_T[H_2O_2]e^{t/\tau_e}}{b+e^{t/\tau_e}}$$

$$\tau_e = m\frac{1}{[Cu]_T}$$

where $b$, $c$, $k_e$, and $m$ are parameters whose empirical values at 25 °C are reported. The fundamental significance of the parameters and their interrelationships are given in the following paper.

## I. Introduction

Hydrazine and its substituted cousins have attracted a long and sustaining interest among chemists and chemical engineers on account of their importance as a fuel and chemical reagents.[1-9] Several books and review articles[1-9] and numerous papers[10-21] have

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(1) Schmidt, E. W. Hydrazine and Its Derivatives—Preparation, Properties, Applications; Wiley: New York, 1984.

been written about their chemistry.

The peroxide oxidation of hydrazine, in particular, has been studied by several groups of investigators.[10-13] The reaction is a constituent feature of hydrazine autoxidation reaction,[14-16] and, as such, its understanding is essential to the understanding of the latter. The reaction appears simple, but, actually, it is quite complex. For example, the reaction catalyzed by copper has been determined by Wellman et al.[10] (and confirmed in this study) to obey the apparently simple rate law (after an induction period, $\tau_e$),

$$\frac{d[N_2H_4]}{dt} = -k[Cu]_T[H_2O_2] \qquad \text{at } t > \tau_e \qquad (1)$$

but the reaction mechanism remains a perplexing riddle. Until now, there has been no report of a mechanistic study which could reconcile the involvement of free-radical intermediates on one hand and, on the other hand, an integer-order kinetics that is more characteristic of a nonradical reaction. In reporting their data, Wellman et al., other than mentioning the likely possibility of the intermediary of diimide ($N_2H_2$) and copper–hydrazine complex, were carefully noncommittal about the radical or nonradical nature of the reaction.

A nonradical, two-electron mechanism has been proposed by Erlenmeyer et al.[11] in connection with the study of the peroxide decomposition reaction in the presence of a limited amount of hydrazine. The experimental rate law which was reported

$$\frac{d[H_2O_2]}{dt} = -k[Cu]_T[H_2O_2][N_2H_4] \qquad (2)$$

differs from eq 1 because Erlenmeyer et al. used a combination of 2,2′-bipyridyl and a low hydrazine concentration ($<10^{-2}$ M) to run the reaction at a high copper concentration ($>10^{-4}$ M). The peroxide reaction included contributions from hydrazine reaction and oxygen formation reaction.

The nonradical mechanism gives a theoretical rate expression in apparent agreement with eq 2, but, in fact, it is fundamentally flawed because we now have definitive evidence of free-radical intermediary (see later). Although there has been a strong suspicion—based in large part on the one-electron chemistry of hydrazine[17-21]—that the reaction most probably involves free-radical intermediates, there has, until now, been no direct evidence to substantiate the suspicion. In the absence of hard evidence, it is quite understandable how the possibility of radical intermediary might be dismissed, since free-radical reactions are often characterized by half- and three-half-order kinetics, rarely integer-order kinetics.

In this paper, we report the first conclusive evidence of radical intermediary, along with other new data which cast new light on the mechanism of the copper-catalyzed reaction. In the following paper, we show that the experimental findings and results of a model study collectively point to a composite radical–nonradical mechanism that involves the well-established intermediates, hydrazyl radical ($N_2H_3^\bullet$) and diimide.

## II. Strategy and Precaution and Apparatus and Procedure

The copper-catalyzed redox reaction was studied under conditions which were chosen to avoid the possibilities of copper precipitation and peroxide decomposition to oxygen. One or both of the complications were encountered in the earlier studies by Graham[12] and Erlenmeyer et al.[11]

Copper precipitation was avoided by keeping the catalyst concentration below $1.0 \times 10^{-5}$ M. The potency of the copper catalyst was such that, even at the low catalyst concentration, the reaction generally went to completion in less than 1 h at 25 °C. Peroxide decomposition was avoided in part by keeping the catalyst concentration low and in part by using hydrazine in stoichiometric excess over peroxide. The reactor solution was monitored for dissolved oxygen to ensure little or no peroxide decomposition during the reaction. At the end of the reaction the solution was visually inspected to confirm the absence of any metal precipitate.

The reaction was studied in a thermostated, three-necked, Morton-flask reactor that was hooked up to a constant-pressure manometric apparatus. The reactor system and the procedure were similar to that which had been described elsewhere.[22] The middle neck of the reactor carried a replaceable rubber septum and a screw cap and a side pout that led to the manometric unit. The rubber septum allowed the injection of catalyst, peroxide, or some other additive into the reaction solution. A second neck carried a sampling stem through which samples might be withdrawn for analysis. The third neck carried either a pH or dissolved oxygen electrode that allowed a continuous monitoring of the desired solution property during the reaction. Measurements of pH and dissolved oxygen concentration were made, respectively, with the aid of a Fisher Accumet (Model 610A) pH meter and a YSI (Model 57) dissolved oxygen meter.

In all runs except the ultrasonication runs, the reactor was placed in a waterbath sitting on top of a magnetic stirrer. Stirring was provided by a magnetic stir bar in the reactor. In studying the effect of ultrasonication on the reaction, the reactor was placed in an ultrasonic bath (Cole–Parmer Model 8845-4, 40 kHz). Temperature control in the ultrasonic bath was achieved by the periodic additions of ice cubes.

The reaction was initiated by injecting sequentially measured volumes of catalyst and peroxide (50 wt %) solutions to a deoxygenated hydrazine solution. Precaution should be taken to exclude trace oxygen from the hydrazine solution; otherwise erratic data (especially on the induction period) might result.

The reaction was followed by monitoring the nitrogen evolution. In some runs the peroxide and hydrazine concentrations were also monitored to provide a check on the stoichiometry. Peroxide was determined spectrophotometrically as a titanium–peroxide complex;[23] the molar ex-

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(2) Audrieth, L. F.; Ogg, B. A. *The Chemistry of Hydrazine*; Wiley: New York, 1951.

(3) Clark, C. C. *Hydrazine*; Mathieson Chemical Corp.; Baltimore, MD, 1953.

(4) Korovin, N. V. *Hydrazine* (in Russian); Khimiya: Moscow, USSR, 1980; *Chem. Abstr. 94*, 105806.

(5) Grekov, A. P.; Veselov, V. Ya. *Physical Chemistry of Hydrazine* (in Russian); Naukova Dumka: Kiev, USSR, 1979; *Chem. Abstr. 92*, 169679.

(6) Schiessl, H. W. Hydrazine—Rocket Fuel to Synthetic Tool. *Aldrich. Acta* **1980**, *13*(2), 33–40.

(7) Hudson, G. H.; Spencer, R. C. H.; Stern, J. P. Hydrazine. *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*; Longmans, Green and Co.: London, 1967; Vol. VIII, Supplement II, Nitrogen (Part II), pp 69–114.

(8) Raphaelian, L. A. Hydrazine. *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed.; Wiley: New York, 1966; Vol. 11, pp 164–196.

(9) Smith, P. A. S. *The Chemistry of Open-Chain Nitrogen Compounds*; W. A. Benjamin, Inc.: New York, 1966; Vol. II.

(10) Wellman, C. R.; Ward, J. R.; Kuhn, L. P. Kinetics of the Oxidation of Hydrazine by Hydrogen Peroxide, Catalyzed by Hydrated Copper(II). *J. Am. Chem. Soc.* **1976**, *98*, 1683–1684.

(11) Erlenmeyer, H.; Flierl, C.; Sigel, H. On the Kinetics and Mechanism of the Reactions of Hydrogen Peroxide with Hydrazine or Hydroxylamine, Catalyzed by $Cu^{2+}$ and by $Cu^{2+}$-2,2′-Bipyridyl Complex. *J. Am. Chem. Soc.* **1969**, *91*, 1065–1071.

(12) Graham, D. P. Promoter Action in Reactions of Oxidation Concomitant with the Catalytic Decomposition of Hydrogen Peroxide. I. The Oxidation of Hydrazine. *J. Am. Chem. Soc.* **1930**, *52*, 3035–3045.

(13) Gordon, A. S. The Reaction between Hydrazine and Hydrogen Peroxide in the Liquid Phase. *Third Symposium on Combustion and Flame and Explosion Phenomena*; Williams & Wilkins Co.: Baltimore, MD, 1949; pp 493–497.

(14) Gilbert, E. C. Studies on Hydrazine. The Auto-oxidation. *J. Am. Chem. Soc.* **1929**, *51*, 2744–2751.

(15) Audrieth, L. F.; Mohr, P. H. Autoxidation of Hydrazine: Effect of Dissolved Metals and Deactivators. *Ind. Eng. Chem.* **1951**, *43*, 1774–1779.

(16) Ellis, R. M.; Jeffreys, G. V.; Hill, P. Oxidation of Hydrazine in Aqueous Solution. *J. Appl. Chem.* **1960**, 347–352.

(17) Higginson, W. C. E. The Oxidation of Hydrazine in Aqueous Solution. *Special Publication No. 10*; The Chemical Society: London, 1957; pp 95–112.

(18) Hayon, E.; Simic, M. Intermediates Produced from the One-Electron Oxidation of Hydrazine. Evidence for the Formation and Decay of Tetrazane and Triazene. *J. Am. Chem. Soc.* **1972**, *94*, 42–47.

(19) Belloni, J.; Haissinsky, M. Radiolyse $\gamma$ de Solutions Aqueuses d'-Hydrazine. *Int. J. Radiat. Phys. Chem.* **1969**, *1*, 519–527.

(20) Bottomley, F. The Reactions of Hydrazine with Transition-Metal Complexes. *Quart. Rev. Chem. Soc.* **1970**, *24*, 617–638.

(21) Adams, J. Q.; Thomas, J. R. Electron Paramagnetic Resonance of a Hydrazine Radical Ion. *J. Chem. Phys.* **1963**, *39*, 1904–1906.

(22) Giles, D. W.; Cha, J. A.; Lim, P. K. The Aerobic and Peroxide Coupling of Aqueous Thiols—I. Kinetic Results and Engineering Significance. *Chem. Eng. Sci.* **1986**, *41*, 3129–3140.

(23) Weissler, A. Simultaneous Spectrophotometric Determination of Titanium, Vanadium, and Molybdenum. *Anal. Chem.* **1945**, *17*, 695–698.

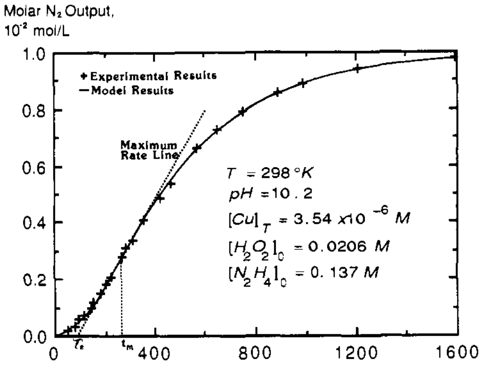


**Figure 1.** A representative reaction profile.

tinction coefficient of the complex (in a 5 M HCl solution) was found to be 585 $M^{-1}$ $cm^{-1}$ at 430 nm. Hydrazine was determined titrimetrically as the hydrazinium ion; the $pK_a$ values of the latter was found to be 8.05 at 25 °C.

ESR evidence of radical intermediary in the reaction was sought by flowing reaction solutions through an aqueous flat cell that is placed in the cavity of an IBM-Bruker ER 200 ESR spectrometer. The spectrometer has a radical detection sensitivity of about $10^{-6}$ $M^{-1}$ for aqueous solutions.

## III. Observations, Results, and Discussion

**(A) Reaction Stoichiometry.** The redox reaction between aqueous hydrogen peroxide and hydrazine is catalyzed by trace copper ions down to the level of $10^{-7}$ M. In the absence of the trace metal, the reaction is exceedingly slow. The reaction produces water and dinitrogen according to the stoichiometry

$$H_2O_2 + N_2H_4 \rightarrow 2H_2O + N_2 \qquad \text{(A)}$$

As closely as can be determined, nitrogen formation accounts for all of the hydrazine consumed. Any ammonia or other nitrogeneous product which may be formed is present in a neglibly low concentration.

The reaction profile of a representative run is shown in Figure 1. The solid line which fits the experimental data point are model results based on a reaction mechanism which will be presented in the following paper. The model results are described by the following equation:

$$\frac{N_{N_2}}{V} = \frac{1}{2}([H_2O_2]_0 - [H_2O_2]) = \frac{[H_2O_2]_0}{2}\left[1 - \left(\frac{b+1}{b+e^{t/\tau_e}}\right)^c\right] \qquad (3)$$

where $N_{N_2}/V$ is the molar nitrogen output per unit volume of reaction solution, $[H_2O_2]_0$ and $[H_2O_2]$ are the peroxide concentrations initially and at time $t$, $b$ and $c$ are constants at a given temperature, and $\tau_e$ is the induction period and is a function of the catalyst concentration (see next section). The values and significance of the various parameters are presented later.

**(B) Induction Data and Evidence of Cage Effect.** As evident in Figure 1, the reaction is marked by an induction period $\tau_e$, which is defined as the time intercept obtained by extrapolating the maximum rate tangent line to the time axis (see Figure 1). Despite its prominence as a characteristic feature of the reaction, the induction period has, surprisingly, received little attention. As nearly as can be determined, there has been no previous report of induction data in the literature. As it turns out, the induction data provide an essential key to resolving the mechanistic puzzle.

The dependence of $\tau_e$ on the concentrations of hydrazine, peroxide, and catalyst is shown in Table I and Figure 2. It is seen that $\tau_e$ is independent of the hydrazine concentration. The dependence on the peroxide concentration is sufficiently weak to be considered as essentially zeroth-order. On the other hand, the dependence on the catalyst concentration is pronounced, and the data suggest an approximately inverse correlation:

$$\tau_e = m\frac{1}{[Cu]_T} \qquad (4)$$

**Table I.** Zeroth-Order Dependence of Rate and Induction Period on the Hydrazine Concentration[a]

| hydrazine concentration, M | rate, M/h | induction, period, s |
|---|---|---|
| 0.501 | 0.065 | 102.3 |
| 0.137 | 0.060 | 110.0 |
| 0.068 | 0.059 | 106.0 |

[a] T = 298 K, pH = 10.9, $[Cu]_T = 3.33 \times 10^{-6}$ M, $[H_2O_2]_0 = 0.0255$ M.

**Table II.** Dependence of the Reaction Rate and Induction Period on Ultrasonication and Solution Viscosity[a]

| set | glycerol, M | rate, M/h | induction period, s |
|---|---|---|---|
| standard run | 0.0 | 0.0226 | 201.0 |
| viscostiy run | 5.45 | 0.0181 | 252.0 |
| ultrasonication run | 0.0 | 0.0345 | 70.1 |

[a] $T = 298$ K, pH = 10.2, $[Cu]_T = 1.40 \times 10^{-6}$, $[H_2O_2]_0 = 0.0255$ M, $[N_2H_4]_0 = 0.137$ M.

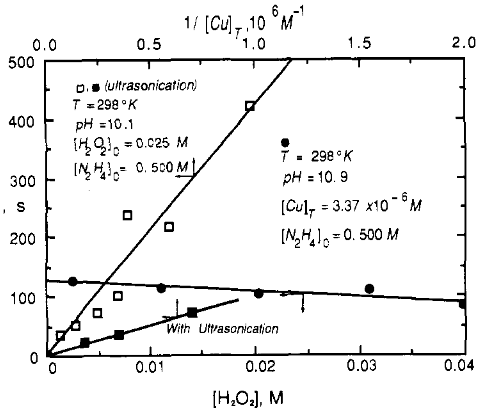


**Figure 2.** Variation of induction period with the concentrations of peroxide and copper catalyst.

It should be noted that the slope $m$ in eq 4 is sensitive to ultrasonication.

A zeroth-order dependence of $\tau_e$ on hydrazine concentration may be explained in terms of a Michaelis–Menten feature, i.e., the formation of a complex between the catalyst and hydrazine in the presence of an overwhelming excess of the latter. A zeroth-order dependence on peroxide concentration may suggest either a noninvolvement of peroxide in the initiation reaction or, in the event of a peroxide involvement, an equal peroxide dependence—possibly, first order—by the "steady-state" concentration of the intermediate and the initiation rate (so that the peroxide dependence cancels out in the time expression).

An inverse dependence of $\tau_e$ on copper concentration, on the other hand, is unexpected because it implies an initiation rate that is an order higher in copper than the "steady-state" concentration of the intermediate. Since the "steady-state" or maximum rate is first order with respect to copper (see section III-E), the result may be taken to mean an initiation step that is second-order in copper. Considering the low concentration ($\cong 10^{-6}$ M) of the catalyst (of which essentially all is tied up by hydrazine), a bimolecular copper interaction involving peroxide and hydrazine would seem rather improbable. A unimolecular copper initiation is more likely, but it seems incompatible with the required second-order copper dependence. A unimolecular copper initiation might be expected to give $\tau_e$ a zeroth-order copper dependence.

The foregoing analysis, however, misses a crucial point. It turns out that a unimolecular-copper initiation can give rise to an apparent second-order copper dependence, provided it contains an autocatalysis feature. As will be shown in the following paper, the induction data may be construed as evidence for autocatalysis.

The sensitivity of the reaction to ultrasonication (see Figure 2 and Table II) is also unusual, and it might not have been expected except for the results of a radical probe experiment that

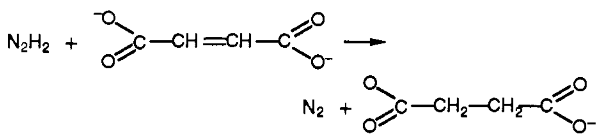
**Table III.** Confirmation of the Intermediary Role of Diimide in the Reaction: Effect of Sodium Maleate on the Reaction Stoichiometry of Nitrogen[a]

| $[(CHCOONa)_2]$, M | $[N_2]_\infty$, mol/L | increase relative to $[(CHCOONa)_2]$ |
|---|---|---|
| 0.0 | 0.0150 | 0 |
| 0.0045 | 0.0172 | 0.5 |

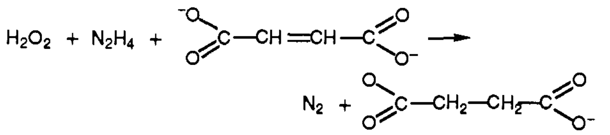
[a] $T = 298$ K, pH = 10.9, $[Cu]_T = 3.3 \times 10^{-6}$ M, $[H_2O_2]_0 = 0.030$ M, $[N_2H_4]_0 = 0.500$ M.

suggest the possibility of a cage effect (see section III-D-1). The results of the ultrasonication study as well as the result of a viscosity-variation run which is also presented in Table II confirm the cage effect. As will be shown in the following paper, the cage effect is fully consistent with the notion of autocatalysis.

**(C) Evidence in Support of the Intermediary of Diimide.** Diimide, $N_2H_2$, has widely been assumed to play an intermediary role in hydrazine oxidation reactions.[1,17-20,23-25] Confirmation of the intermediary role was sought using maleate ion as a probe. Sodium maleate was added to the reaction solution to scavenge diimide by means of the hydrogenation reaction.[24-26]


(B)

If diimide was present in the solution, the hydrogenation reaction should increase nitrogen formation by an amount equal to the amount of diimide consumed by the maleate ion. The result of the diimide-scavenging experiment is presented in Table III, and it confirms the expectation of a higher nitrogen output. The increase in the nitrogen formation, in fact, corresponds to the stoichiometric equivalent of the sodium maleate added ($[^{-}OOCCH{=}CHCOO^{-}] = [H_2O_2] = [N_2]/2$).


(C)

**(D) Evidence in Support of the Intermediary of Free Radicals.** Along with diimide, hydrazyl radical, $N_2H_3^{\bullet}$, has also been widely assumed to play an intermediary role in hydrazine oxidation reactions.[1,2,17-21] Evidence based on a spin-trapping study has been claimed for the intermediary of $N_2H_3^{\bullet}$ in the copper-catalyzed peroxide–hydrazine reaction,[27] but the evidence is less than definitive because the radical in question could have been derived from peroxide decomposition through the intermediary of hydroxy and peroxy radicals. In view of the integer-order kinetics which seems hard to reconcile with a free-radical mechanism (particularly in light of the nonradical mechanism proposed by Erlenmeyer et al.[11]), it was decided that confirmatory evidence of radical intermediary was needed to settle the issue.

**(1) Radical-Probe Experiments.** Evidence of radical intermediary in the copper-catalyzed reaction was sought by studying the effects, on the reaction, of substances which may affect radical intermediates. The results of experiments with various additive probes are presented in Table IV.

As may be expected on the basis of its ability to produce hydrazyl radical,[21] cerium(IV) increased the rate of the reaction markedly. It turns out that cerium promotes the peroxide–hydrazine reaction even in the absence of copper, and cerium(III) produces essentially the same rate increase as cerium(IV). As a catalyst for the reaction, cerium ion is almost as potent as copper ion.

**Table IV.** Effects of Additives on the Reaction Rate and Induction Period[a]

| additive | concentration of additive, M | copper concentration, $10^{-6}$ M | rate, M/h | relative increase, % | induction period, s |
|---|---|---|---|---|---|
| standard run | 0.0 | 3.33 | 0.0690 | 0.0000 | 113.4 |
| cerium | 6.03E-6 | 3.33 | 0.1805 | 161.6 | 36.2 |
| hydroquinone | 4.0E-4 | 3.33 | 0.0830 | 20.2 | 97.9 |
| *o*-phenylene-diamine | 1.02E-4 | 3.33 | 0.0808 | 17.1 | 118.5 |
| *p*-quinone | 1.02E-4 | 3.33 | 0.1007 | 45.9 | 52.9 |
| *p*-quinone | 1.02E-4 | 0.0 | 0.003 |  | 224.6 |
| cerium | 5.93E-6 | 0.0 | 0.0456 |  | 280.0 |

[a] $T = 298$ K, pH = 10.9, $[H_2O_2]_0 = 0.030$ M, $[N_2H_4]_0 = 0.500$ M.

The results of the experiments with *o*-phenylenediamine, hydroquinone, and quinone were most unexpected but, at the same time, very revealing. Instead of rate reductions which might be expected on the basis of their known radical-scavenging activities, the organic additives produced significant rate increases. The results imply that the organic additives were engaged in radical-generation activities that more than offset their radical-annihilation activities. Moreover, considering the low concentrations of the additives which produced the rate increases, one may surmise that the additives must have exerted their influence through a radical-chain mechanism. The results thus confirm the intermediary role of free radicals in the reaction and invalidate the nonradical mechanism of Erlenmeyer et al.[11]

The promoting effect of hydroquinone and quinone might be ascribed to the following reactions:

$$C_6H_4OH(O^-) + H_2O_2 \rightarrow C_6H_4OH(O^{\bullet}) + OH^- + OH^{\bullet} \quad (D)$$

$$C_6H_4OH(O^{\bullet}) + H_2O_2 \rightarrow C_6H_4O_2 + H_2O + OH^{\bullet} \quad (E)$$

$$C_6H_4O_2 + N_2H_4 \rightarrow C_6H_4OH(O^{\bullet}) + N_2H_3^{\bullet} \rightarrow C_6H_4(OH)_2 + N_2H_2 \quad (F)$$

$$C_6H_4OH(O^{\bullet}) + N_2H_4 \rightleftarrows C_6H_4(OH)_2 + N_2H_3^{\bullet} \quad (G)$$

An analogous set of reactions might likewise be proposed to account for the promoting effect of *o*-phenylenediamine. The reactions would presumably involve the counterparts of quinone and semiquinone, namely 1,2-benzoquinonediimine and 1,2-semiquinonediimine.

Evidence for the above reactions was provided by control experiments. Addition of hydroquinone to an alkaline peroxide solution produced a darkening of solution which marked the formation of semiquinone radical and quinone. The presence of the two product species was detected, respectively, by their characteristic ESR and UV spectra. Addition of hydrazine to a quinone solution produced a rapid decoloration of solution that was followed immediately by the evolution of nitrogen gas. Addition of hydrazine to a semiquinone solution eliminated the ESR signal of the radical.

Reactions D through G may, at first sight, provide a seemingly reasonable explanation for the promoting effect of hydroquinone and quinone. However, further reflection raises more serious doubts. Considering the high reactivity of hydrazyl radical (see the following paper), one may expect the radical to be reactive toward hydroquinone, quinone, and semiquinone. Reaction G, therefore, is most probably reversible. The question, then, is whether reactions D through G could generate a net gain of radical-chain carriers over that which are consumed by the radical scavengers and their semiquinone intermediates.

The disappearance of the promoting effect of the organic additives in the absence of copper is significant in this context (see Table IV). The results suggest that the promoting effect of the radical scavengers is tied to the catalyst and that reactions D through G are unlikely to produce a net gain of chain carriers over that which are consumed by the scavengers.

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(24) Hunig, S.; Muller, H. R.; Thier, W. The Chemistry of Diimine. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 271–382.

(25) Back, R. A. The Preparation, Properties and Reactions of Diimide. *Rev. Chem. Intermed.* **1984**, *5*, 293–323.

(26) Corey, E. J.; Pasto, D. J.; Mock, W. L. Chemistry of Diimide. II. Stereochemistry of Hydrogen Transfer to Carbon–Carbon Multiple Bonds. *J. Am. Chem. Soc.* **1961**, *83*, 2957–2958.

(27) Noda, A.; Noda, H.; Ohno, K.; Sendo, T.; Hirata, M. Spin Trapping of a Free Radical Intermediate Formed During Microsomal Metabolism of Hydrazine. *Biochem. Biophys. Res. Commun.* **1985**, *133*, 1086–1091.

The results of the ultrasonication study support the foregoing conclusion. They establish that the promoting effect of the radical scavengers arises from the breaking of solvent cage that traps reactive chain carriers. Specifically, the radical scavengers and ultrasonification may be thought to affect the equilibrium of solvent cage in the following reaction:

$$CuN_2H_4 + N_2H_2 \rightleftarrows \underset{\text{(cage)}}{Cu(N_2H_3^\bullet)_2} \rightarrow Cu + 2N_2H_3^\bullet \quad \text{(H)}$$

As will be shown in the following paper, reaction H is also fully in accord with induction data that implicate an autocatalysis feature (see section III-B).

The rate increases produced by the radical scavengers may be ascribed to the following cage-release reactions:

$$\underset{\text{(cage)}}{Cu(N_2H_3^\bullet)_2} + C_6H_4OH(O^-) \rightarrow Cu + C_6H_4OH(O^\bullet) + N_2H_4 + N_2H_3^\bullet \quad \text{(I)}$$

$$\underset{\text{(cage)}}{Cu(N_2H_3^\bullet)_2} + C_6H_4O_2 \rightarrow Cu + C_6H_4OH(O^\bullet) + N_2H_2 + N_2H_3^\bullet \quad \text{(J)}$$

Presumably, by converting one of the two reactive hydrazyl radicals into a much less reactive semiquinone radical, hydroquinone and quinone allow the other caged hydrazyl radical more time and opportunity to diffuse into the aqueous bulk. The semiquinone radical which is formed in the solvent cage may react with the other caged hydrazyl radical according to reaction F, but the rate constant would be orders of magnitude lower than that between hydrazyl radicals.

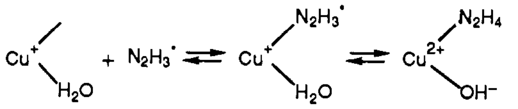
Once released from the solvent cage, the semiquinone radical can participate in reaction E or G to form another hydrazyl radical and to regenerate quinone or hydroquinone. The chain reactions can continue indefinitively, so long as there is an excess of peroxide and hydrazine to keep the chain going. The chain feature may explain the pronounced enhancement effect of the organic additives on the copper-catalyzed redox reaction between peroxide and hydrazine.

**(2) ESR Experiments.** Additional evidence of free-radical intermediary was sought by using an ESR flow technique, but the results, unfortunately, were inconclusive. No ESR signal could be detected when reaction solutions were allowed to flow through the cavity of an IBM-Bruker ER-200 ESR spectrometer. Nitrogen formation in the reaction was a complicating factor which could have reduced the already low sensitivity of ESR spectrometer toward aqueous systems, but the main reason for the failure to detect radical intermediates is their high reactivities. The results of a model analysis (see the following paper) later suggest a hydrazyl radical concentration of the order of $10^{-9}$ M.

Evidence of the hydrazyl radical was then sought in aqueous mixtures of copper(II) and hydrazine. By analogy with cerium(IV)–hydrazine mixtures which are known to produce nitrogen gas through the one-electron intermediary of hydrazyl radical,[21] copper–hydrazine mixtures might be expected to behave likewise. Nitrogen formation was confirmed, but, unlike cerium–hydrazine mixtures, the copper–hydrazine mixtures did not produce a definitive free-radical signal. Instead, the mixtures produced time-dependent ESR spectra that were similar, but not identical, with that of aqueous copper(II).

The copper-like ESR spectra may be assigned simply to a copper(II)–hydrazine complex, but this interpretation would require one to invoke, if one were to avoid free-radical intermediary, a bimolecular reaction between two copper(II) complexes to account for nitrogen formation. The fact that reactions between hydrazine and metal oxidants[28-35] are all known to follow first-, rather than second-, order kinetics (with respect to the metal oxidant) would seem to rule out this possibility.

A more plausible explanation for the copper(II)-like spectra is the following inter- and intramolecular exchange interactions:



$$Cu^+\!\begin{smallmatrix}/\\ \backslash H_2O\end{smallmatrix} + N_2H_3^\bullet \rightleftarrows Cu^+\!\begin{smallmatrix}/N_2H_3^\bullet\\ \backslash H_2O\end{smallmatrix} \rightleftarrows Cu^{2+}\!\begin{smallmatrix}/N_2H_4\\ \backslash OH^-\end{smallmatrix} \quad \text{(K)}$$

If the proposed interactions occur reversibly and rapidly, as seems likely, the hydrazyl radical will be coupled magnetically to copper(II), and, as a result, it will give a copper(II)-like spectrum that will mask its very existence. The results of a computer simulation study verify that fast-exchange interactions may, in fact, give rise to the copper(II)-like spectra.

**Table V.** Absence of Wall Effect on the Reaction Rate and Induction Period[a]

| reactor | $[Cu]_T$, $10^{-6}$ M | rate, M/h | induction period, s |
|---|---|---|---|
| glass | 1.40 | 0.0224 | 169 |
| PTFE | 1.40 | 0.0215 | 167 |
| glass | 5.60 | 0.0740 | 82 |
| PTFE | 5.60 | 0.0808 | 83 |

[a] $T = 298$ K, pH = 10.2, $[H_2O_2]_0 = 0.0225$ M, $[N_2H_4]_0 = 0.137$ M.

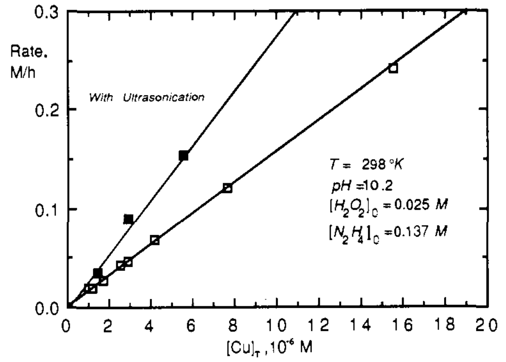


**Figure 3.** Rate dependence on the copper catalyst concentrations.

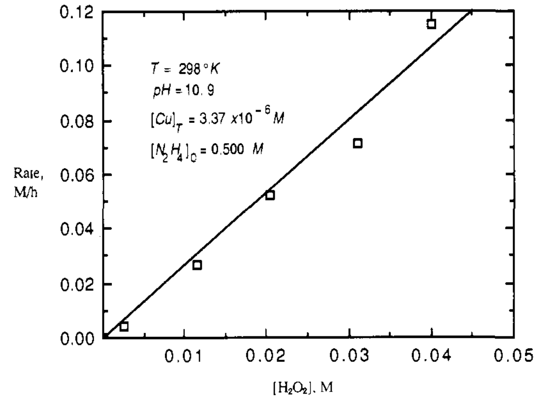


**Figure 4.** Rate dependence on the hydrogen peroxide concentrations.

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(28) Davies, G.; Kustin, K. The Stoichiometry and Kinetics of Manganese(III) Reactions with Hydrazine and Methylhydrazines in Acid Perchlorate Solution. *J. Phys. Chem.* **1969**, *73*, 2248–2253.

(29) Frank, M. S.; Ramaiah, A. K.; Rao, P. V. K. Kinetics and Mechanism of Oxidation of Hydrazine by Iron(III) in Presence of 1,10-Phenanthroline. *Ind. J. Chem.* **1979**, *18A*, 369–370.

(30) Cahn, J. W.; Powell, R. E. Oxidation of Hydrazine in Solution. *J. Am. Chem. Soc.* **1954**, *76*, 2568–2571.

(31) Brown, A.; Higginson, W. C. E. The Oxidation of Hydrazine in Aqueous Solution by Complex Ions. *J. Chem. Soc., Dalton Trans.* **1972**, 166–170.

(32) Gupta, K. K. S.; Gupta, S. S.; Chatterjee, H. R. Kinetics of the Oxidation of Hydrazine by Chromium(VI). *J. Inorg. Nucl. Chem.* **1976**, *38*, 549–552.

(33) Morris, D. F. C.; Ritter, T. J. Oxidation of Hydrazine by Halogeno-Complexes of Iridium(IV) in Acidic Perchlorate Solutions. *J. Chem. Soc. Dalton Trans.* **1980**, 216–219.

(34) Morrow, J. I.; Scheeres, G. W. Stoichiometry and Kinetics of Ceric(IV) Oxidation of Hydrazine in Acid Media. *Inorg. Chem.* **1972**, *11*, 2606–2628.

(35) Tikhonov, M. F.; Koltunov, V. S. Kinetics of the Reduction of Molybdenum(VI) by Hydrazine in a Perchloric Acid Solution. *Russ. J. Phys. Chem.* **1979**, *53*, 1143–1145.

Table VI. Values of Parameters, $b$, $c$, $k_e$, and $m$ for Some Representive Runs[a]

| set | $[\mathrm{Cu}]_T$, $10^{-6}$ M | $c$ | $k_e$, $(\mathrm{Ms})^{-1}$ | $m$, M/s | $b$ |
|---|---|---|---|---|---|
| 1 | 15.58 | 0.205 | 193.1 | 0.00053 | 6.2 |
| 2 | 7.60 | 0.204 | 197.7 | 0.00052 | 6.8 |
| 3 | 4.14 | 0.181 | 201.0 | 0.00045 | 4.4 |
| 4 | 2.93 | 0.192 | 199.6 | 0.00048 | 4.3 |
| 5 | 1.69 | 0.180 | 201.1 | 0.00045 | 7.6 |

[a] $T = 298$ K, pH = 10.2, $[\mathrm{H_2O_2}]_0 = 0.0225$ M, $[\mathrm{N_2H_4}]_0 = 0.136$ M.

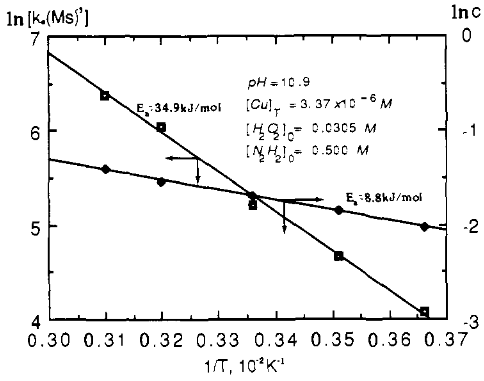

Figure 5. Temperature effect on the reaction.

(3) **Absence of Wall-Termination Effect.** The possibility that a wall-termination reaction may reconcile the intermediary of free radicals on one hand and a first-order rate dependence on catalyst on the other hand was investigated, and the results of the study, presented in Table V, indicate that the possibility may essentially be ruled out for the copper-catalyzed peroxide–hydrazine reaction. Had wall-termination reaction been important, its effect would have been revealed by the use of the reactors of different materials. The fact that essentially the same rate and induction period were obtained in the glass and polytetrafluoroethylene (Teflon) reactors suggests that wall termination is not an important factor.

(E) **Reaction Orders.** The "steady-state" rate which immediately follows the induction period varies linearly with the catalyst and peroxide concentrations, but essentially independently with the hydrazine concentration. The results, shown in Figures 3 and 4 and Table I, are in accord with the rate law reported previously by Wellman et al.:[10]

$$\left(\frac{\mathrm{d}[\mathrm{N_2H_4}]_s}{\mathrm{d}t}\right)_s = -k_e[\mathrm{Cu}]_T[\mathrm{H_2O_2}] \qquad (1)$$

At a given temperature, the empirical rate constant $k_e$ is sensitive to ultrasonication (Figure 3) and pH (section F).

A more complete analysis shows that over the full course of the reaction (including the induction period $\tau_e$), the rate is described more generally by

$$\frac{1}{V}\frac{\mathrm{d}N_{\mathrm{N_2}}}{\mathrm{d}t} = \frac{k_e[\mathrm{Cu}]_T[\mathrm{H_2O_2}]e^{t/\tau_e}}{b + e^{t/\tau_e}} \qquad (5)$$

where $b$ is a constant and $\tau_e$ is given by eq 4. Empirical values of parameters $b$, $c$, $k_e$, and $m$ are presented in Table VI for some representative runs. It is seen that at a given temperature and in the absence of an ultrasonication effect, the parameters are constants. The fundamental significance of the parameters are provided in the following paper.

(F) **Temperature and pH Effects.** The results of our temperature and pH studies are presented in Figures 5 and 6, respectively. The apparent activation energy of the reaction (based on $k_e$) is 34.9 kJ/mol. The activation energy for the dimensionless parameter $c$ is 8.8 kJ/mol.

Within the pH range 6–10.5, the reaction is essentially independent of pH. A pH less than 3 (where hydrazine exists as $\mathrm{N_2H_5^+}$) the reaction is stopped completely. At pH close to the p$K_a$ value of 11.8 for peroxide, the reaction rate decreases with increasing basicity. The rate reduction, however, is less than first order with respect to basicity. The results indicate that (i) $\mathrm{N_2H_5^+}$ is unreactive, (ii) peroxide is more reactive in its neutral $\mathrm{H_2O_2}$ form, and (iii) $\mathrm{HO_2^-}$, though much less reactive than $\mathrm{H_2O_2}$, nevertheless contributes appreciably to the reaction at pH above 12. The last two points suggest that, in this reaction as in other alkaline peroxide reactions,[22,36–40] peroxide reacts as an electrophile.

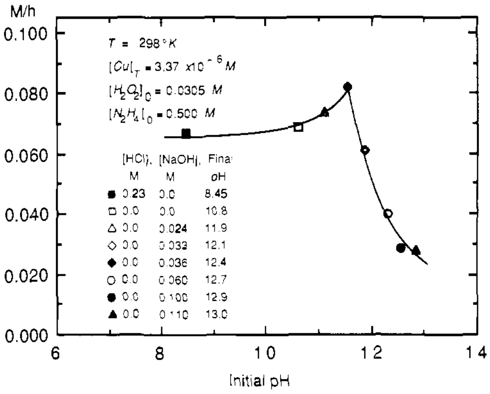

Figure 6. pH effect on the reaction.

The increases of rate with pH in the pH range of 11.0–11.5 are modest but experimentally significant. The results may be explained if diimide may be presumed to react as a nucleophile in neutral ($\mathrm{N_2H_2}$) and anionic ($\mathrm{N_2H^-}$) forms. As a nucleophile, diimide may be expected to be more reactive in the anionic form than in the neutral form. The step in the rate profile at pH 11.5 may thus be taken to reflect the relative distribution of the two diimide species, and the p$K_a$ value of diimide may be estimated to be about 11.5.

Evidence in support of the p$K_a$ value of diimide in the foregoing analysis may be found in the study of Hayon and Simic,[18] although it should be noted that the original investigators interpreted the same evidence in a different manner. The justifications and needs for reinterpreting the data in new light are provided in section II-C in the following paper.

## IV. Conclusion

The copper-catalyzed redox reaction between aqueous hydrogen peroxide and hydrazine is shown conclusively to involve radical intermediary and cage effect. The reaction is promoted by ultrasonication and by trace amounts of cerium ion, hydroquinone, quinone, and *o*-phenylenediamine. The nitrogen and peroxide profiles and the rate are given, respectively, by

$$\frac{N_{\mathrm{N_2}}}{V} = \frac{1}{2}([\mathrm{H_2O_2}]_0 - [\mathrm{H_2O_2}]) = \frac{[\mathrm{H_2O_2}]_0}{2}\left[1 - \left(\frac{b+1}{b+e^{t/\tau_e}}\right)^c\right]$$

$$\frac{1}{V}\frac{\mathrm{d}N_{\mathrm{N_2}}}{\mathrm{d}t} = \frac{k_e[\mathrm{Cu}]_T[\mathrm{H_2O_2}]e^{t/\tau_e}}{b + e^{t/\tau_e}}$$

where $\tau_e$, the induction period, is given by

$$\tau_e = m\frac{1}{[\mathrm{Cu}]_T}$$

The parameter values of $b$, $c$, $k_e$, and $m$ at 25 °C are reported.

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(36) Lee, Y.-N; Lind, J. A. Kinetics of Aqueous-Phase Oxidation of Nitrogen(III) by Hydrogen Peroxide. *J. Geophys. Res. D: Atmos.* **1986**, *91*-(D2), 2793–2800.

(37) Chin, F. Y.-C.; Lim, P. K. The Peroxide-Coupling Kinetics and Dissociation Constants of Aqueous Cysteine and Glutathione: Experimental and Model Results, and Implications. *Chem. Eng. Sci.* **1989**, *43*, 883–893.

(38) Walling, C.; Hodgdon, R. B., Jr. The Reaction of Acyl Peroxides with Phenols. *J. Am. Chem. Soc.* **1958**, *80*, 228–233.

(39) Temple, R. D. The Epoxidation and Cleavage of $\alpha,\beta$-Unsaturated Ketones with Alkaline Peroxide. *J. Org. Chem.* **1970**, *35*, 1275–1280.

(40) Mader, P. M. Kinetics of the Hydrogen Peroxide–Sulfite Reaction in Alkaline Solution. *J. Am. Chem. Soc.* **1958**, *80*, 2634–2639.

The fundamental significance of the parameters and their interrelationships are given in the following paper.

**Acknowledgment**. Financial support from the U.S. National Science Foundation (Grant CPE-8419211) is gratefully acknowledged.

**Registry No.** $H_2O_2$, 7722-84-1; $N_2H_4$, 302-01-2; Cu, 7440-50-8; (*Z*)-$O_2CCH{=}CHCO_2^{2-}$, 142-44-9; cerium, 7440-45-1; hydroquinone, 123-31-9; quinone, 106-51-4; *o*-phenylenediamine, 95-54-5.

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# The Copper-Catalyzed Redox Reaction between Aqueous Hydrogen Peroxide and Hydrazine. 2. Reaction Mechanism, Model Analysis, and a Comparison of Model and Experimental Results

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**Abstract**: The experimental findings presented in the preceding paper are shown to be fully explanable in terms of the following reaction mechanism:

Initiation

$$Cu^{I}N_2H_4 + H_2O_2 \xrightarrow{k_1} Cu(I) + N_2H_2 + 2H_2O \qquad \text{(slow)}$$

$$Cu^{I}N_2H_4 + N_2H_2 \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} \underset{\text{(cage)}}{Cu(N_2H_3^{\bullet})_2} \xrightarrow[\text{(slow)}]{k_3} Cu(I) + 2N_2H_3^{\bullet}$$

Propagation

$$N_2H_3^{\bullet} + H_2O_2 \xrightarrow{k_4} N_2H_2 + H_2O + OH^{\bullet}$$

$$OH^{\bullet} + N_2H_4 \xrightarrow{k_5} H_2O + N_2H_3^{\bullet}$$

Concerted $S_N2$ Reaction

$$N_2H_2 + H_2O_2 \xrightarrow{k_6} N_2 + 2H_2O$$

Termination

$$2N_2H_3^{\bullet} \xrightarrow{k_7} N_2H_2 + N_2H_4$$

The mechanism is shown given the following theoretical expressions in accord with the experimental results:

$$\frac{1}{V}\frac{dN_{N_2}}{dt} = \frac{k_3k_4^2K_2[Cu]_T[H_2O_2]e^{t/\tau}}{k_6k_7(b + e^{t/\tau})}$$

$$\frac{N_{N_2}}{V} = \frac{1}{2}([H_2O_2]_0 - [H_2O_2]) = \frac{[H_2O_2]_0}{2}\left[1 - \left(\frac{b+1}{b+e^{t/\tau}}\right)^{(k_4/k_7)}\right]$$

where

$$K_2 = \frac{k_{2f}}{k_{2r} + k_3}, \qquad \tau = \frac{k_6}{2k_3k_4K_2[Cu]_T}, \qquad b = \frac{[N_2H_3^{\bullet}]_s}{[N_2H_3^{\bullet}]^*} - 1$$

and $[N_2H_3^{\bullet}]^*$ and $[N_2H_3^{\bullet}]_s$ are, respectively, the hydrazyl radical concentrations at the beginning and at the end of the induction period. Parameter values are reported, and the model results are shown to agree closely with the experimental results.

In the preceding paper we report experimental results and observations for the copper-catalyzed redox reaction between aqueous hydrogen peroxide and hydrazine. In this paper we show that the kinetic findings lead logically to the most probable mechanism of the reaction. We use the experimental data to evaluate the kinetic parameters in the proposed mechanism and show that the resulting rate and integral expressions produce model results in close agreement with the experimental results.

## I. Proposed Reaction Mechanism and Justification

The reaction mechanism which is most probable for the copper-catalyzed redox reaction between aqueous hydrogen peroxide and hydrazine is shown in Scheme I. The proposed mechanism contains the following kinetic features which have been established

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