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

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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.

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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Scheme I. Proposed Mechanism for the Copper-Catalyzed Redox Reaction between Aqueous Hydrogen Peroxide and Hydrazine

Initiation

$$Cu^+ + N_2H_4 \overset{K_1}{\rightleftharpoons} Cu^+N_2H_4$$

$$Cu^+N_2H_4 + H_2O_2 \xrightarrow{k_1} Cu^+ + N_2H_2 + 2H_2O \qquad \text{(slow)} \qquad (1)$$

$$Cu^+N_2H_4 + N_2H_2 \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} \underset{\text{(cage)}}{Cu^+(N_2H_3^\bullet)_2} \qquad (2)$$

$$Cu^+(N_2H_3^\bullet)_2 \xrightarrow{k_3} Cu^+ + 2N_2H_3^\bullet \qquad \text{(slow)} \qquad (3)$$

Propagation

$$N_2H_3^\bullet + H_2O_2 \xrightarrow{k_4} N_2H_2 + H_2O + OH^\bullet \qquad (4)$$

$$OH^\bullet + N_2H_4 \xrightarrow{k_5} H_2O + N_2H_3^\bullet \qquad (5)$$

Concerted S_N2 Reaction

$$N_2H_2 + H_2O_2 \xrightarrow{k_6} N_2 + 2H_2O \qquad (6)$$

Termination

$$2N_2H_3^\bullet \xrightarrow{k_7} N_2H_2 + N_2H_4 \qquad (7)$$

in the preceding paper: (i) the involvement of the hydrazyl radical and diimide, (ii) autocatalysis, and (iii) solvent cage effect.

The three kinetic features are embodied in steps 2 and 3, which may be viewed as the heart of the mechanism. The two steps are based on the following considerations: (1) an induction period, (2) an inverse correlation of the induction period with the catalyst concentration, (3) sensitivity of reaction to ultrasonication and viscosity variation, and (4) sensitivity of reaction to radical scavengers acting as cage breakers.

The autocatalysis feature is similar to that which involves hydroperoxide in autoxidation reactions.[1-5] In the latter reactions, hydroperoxide plays a similar role as that which is being proposed for diimide, namely, as an intermediate product and a radical initiator. Like diimide, the formation and decomposition of hydroperoxide is also catalyzed by copper (as well as other transition metals).[1-5] Moreover, hydroperoxide decomposition is also known to exhibit a solvent cage effect.[5]

Additional examples of cage effect are provided by homolytic decomposition reactions, such as that of azo compounds[6] and of aqueous dithionite ion,[7] in which geminate radicals are formed. Thus, aside from the evidence presented in the preceding paper, there are ample precedents to support the notion of cage effect in radical-forming reactions. In common with these reactions, step 2 is proposed to be reversible.

Step 1 is believed to generate the first diimide molecules that first launch the propagation chain comprising of steps 4 and 5, but, immediately after the initiation of the reaction, it quickly becomes insignificant relative to step 4. The involvement of a copper(I)–hydrazine complex is presumed in steps 1 and 2 to account for the pseudo-zeroth-order kinetics with respect to hydrazine. Consistent with the zeroth-order hydrazine kinetics, the stability constant of the copper–hydrazine complex is known to be quite high—a value of $10^{6.67}$ M^{-1} has been reported at 30 °C.[8]

The reaction between peroxide and copper–hydrazine complex in step 1 involves the transfer of two electrons, which may occur in a single step or in two one-electron steps in rapid succession as follows:

$$Cu^+N_2H_4 + H_2O_2 \underset{\text{(slow)}}{\xrightarrow{k_1}} \underbrace{Cu^{2+}OH^- + N_2H_3^\bullet}_{\text{cage}} + H_2O \underset{\text{(fast)}}{\xrightarrow{k_1'}} Cu^+ + N_2H_2 + 2H_2O$$

In the event that k_1' is much greater than k_1, the two-step formulation becomes equivalent to the one-step formulation.

An alternative formulation to step 1 is the following two-step sequence:

$$Cu^+N_2H_4 + H_2O_2 \xrightarrow{k_a} Cu^{2+}OH^- + N_2H_3^\bullet + H_2O \qquad (a)$$

$$Cu^{2+}OH^- + N_2H_4 \xrightarrow{k_b} Cu^+ + N_2H_3^\bullet + H_2O \qquad (b)$$

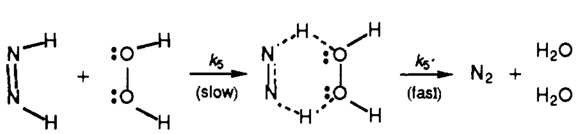
Whether the first or second formulation should be adopted depends on the relative magnitudes of k_1' and k_b. However, as far as the theoretical rate expression is concerned, both formulations are kinetically equivalent. In the interest of simplicity we choose the first formulation.

Step 6 is proposed as the countervailing reaction to step 4 to keep the diimide concentration in check. The reaction is formulated as an S_N2 reaction partly on the basis of our pH results (see section III-F, preceding paper). A possible alternative might be the diimide disproportionation reaction,

$$2N_2H_2 \rightarrow N_2 + N_2H_4^\bullet$$

However, that possibility may be discounted, in part because it would have resulted in an experimentally inconsistent rate expression that is two-thirds order with respect to copper and four-thirds order with respect to peroxide. Moreover, the disproportionation rate constant[9,10] is such that it would require a significant build-up of diimide, and this was not observed.

By analogy to hydrogenation reaction of diimide with unsaturated organics[9-11] step 6 may be presumed to proceed in a single concerted step via a cis configuration. Because of its ability to take up a cis planar structure,[12] diimide can undergo concerted reactions in which two or more bonds are made or broken simultaneously. Coupled with the ability of peroxide to rotate freely about the oxygen–oxygen bond, diimide may be presumed to react with peroxide through a cis planar transition state as follows:



Once the intermediary roles of hydrazyl radical and diimide are accepted, the other steps in the proposed mechanism—namely, steps 4, 5, and 7—become quite self-evident.

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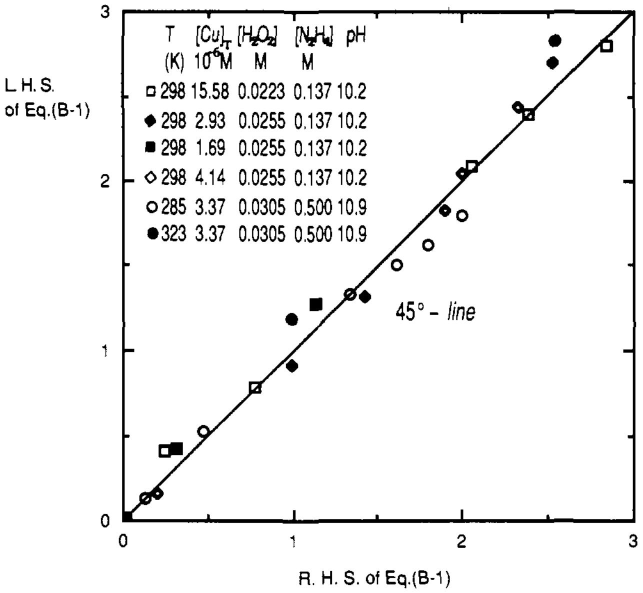

Figure 1. Results of Integral analysis: comparison of model and experimental results.

II. Model Analysis and a Comparison of Model and Experimental Results

(A) Theoretical Rate Equation and Integral Expressions. It is shown in the appendix that the mechanism presented in Scheme I leads to the following equations:

$$\frac{1}{V}\frac{\mathrm{d}N_{\mathrm{N_2}}}{\mathrm{d}t} = \frac{\dfrac{k_3k_4^2K_2}{k_6k_7}[\mathrm{Cu}]_T[\mathrm{H_2O_2}]\exp\left(\dfrac{t-t^*}{\tau}\right)}{b+\exp\left(\dfrac{t-t^*}{\tau}\right)} \cong \frac{k_3k_4^2K_2[\mathrm{Cu}]_T[\mathrm{H_2O_2}]e^{t/\tau}}{b+e^{t/\tau}} \tag{A}$$

$$\frac{N_{\mathrm{N_2}}}{V} = \frac{1}{2}([\mathrm{H_2O_2}]_0 - [\mathrm{H_2O_2}]) = \frac{[\mathrm{H_2O_2}]_0}{2}\left|1 - \left[\frac{b+1}{b+\exp\left(\dfrac{t-t^*}{\tau}\right)}\right]^{(k_4/k_7)}\right| \cong \frac{[\mathrm{H_2O_2}]_0}{2}\left[1-\left(\frac{b+1}{b+e^{t/\tau}}\right)^{(k_4/k_7)}\right] \tag{B}$$

$$\tau = \frac{1}{2k_7[\mathrm{N_2H_3^\bullet}]_s} = \frac{k_6}{2k_3k_4K_2[\mathrm{Cu}]_T} \tag{C}$$

$$b = \frac{[\mathrm{N_2H_3^\bullet}]_s}{[\mathrm{N_2H_3^\bullet}]^*} - 1 > 0 \tag{D}$$

$$K_2 = \frac{k_{2f}}{k_{2r}+k_3} \tag{E}$$

In the above equations, $N_{\mathrm{N_2}}$ is the cumulative nitrogen formation at time t, V is the volume of the reaction solution, $[\mathrm{N_2H_3^\bullet}]^*$ and $[\mathrm{N_2H_3^\bullet}]_s$ are, respectively, the concentrations of the hydrazyl radical at the beginning ($t = t^*$) and at the end of the introduction period τ_e.

Table I. Parameter Values of k_4/k_7, b, and $k_3k_4K_2/k_6$

T, K	$[\mathrm{Cu}]_T$, 10^{-6} M	$[\mathrm{H_2O_2}]_0$, M	k_4/k_7	b	$k_3k_4K_2/k_6$, $(\mathrm{M\ s})^{-1}$
298[a]	2.93	0.0255	0.193	4.3	1034.2
298[a]	15.58	0.0225	0.206	6.2	937.4
298[a]	4.14	0.0206	0.181	4.4	1110.5
298[b]	3.37	0.031	0.183	5.18	1144.3
285[b]	3.37	0.031	0.156	4.78	778.8
323[b]	3.37	0.031	0.244	6.05	2770.1

[a] $[\mathrm{N_2H_4}]_0 = 0.137$ M, pH = 10.2. [b] $[\mathrm{N_2H_4}]_0 = 0.500$ M, pH = 10.9.

Table II. Comparison of Model Results with Wellman's Data[a]

$[\mathrm{N_2H_4}]$, 10^{-2} M	$[\mathrm{H_2O_2}]$, 10^{-2} M	$[\mathrm{Cu}]_T$, 10^{-6} M	Wellman's results, M/h	model results, M/h	relative difference, %
1.64	6.45	1.23	0.0597	0.0585	2.0
3.27	6.54	1.23	0.0606	0.0585	3.5
13.1	6.54	1.23	0.0606	0.0585	3.5
3.27	3.27	1.23	0.0295	0.0292	1.0
1.64	3.27	1.23	0.0295	0.0292	1.0
3.30	6.54	0.329	0.0160	0.0156	2.5
3.30	6.54	1.32	0.068	0.0630	7.4
3.30	6.54	1.64	0.085	0.0782	8.0

[a] $T = 298$ K, pH = 9.5–10.0.

Time t^* corresponds to the time it takes diimide and hydrazyl radical to establish a pseudoequilibrium with each other while both are being built up to their respective "steady-state" concentrations during the induction period. Referring to steps 3 and 5 in the proposed mechanism, t^* is the time which elapses before what we will refer to as the long-chain approximation becomes applicable to diimide:

(rate of $\mathrm{N_2H_2}$ formation in the propagation chain sequence)
=(rate of $\mathrm{N_2H_2}$ consumption in the concerted $\mathrm{S_N2}$ reaction)

or

$$k_4[\mathrm{N_2H_3^\bullet}][\mathrm{H_2O_2}] = k_6[\mathrm{N_2H_2}][\mathrm{H_2O_2}]$$

or

$$k_4[\mathrm{N_2H_3^\bullet}] = k_6[\mathrm{N_2H_2}] \tag{F}$$

The results of a parameter analysis (see next section) suggest that t^* is small relative to τ_e. Accordingly, the exponential terms in the above equations may be replaced by $e^{t/\tau}$ for the sake of simplicity.

Note that the dimensionless parameter b is a constant for each run. It turns out (see later) that, at a given temperature, b is also a constant for different runs (with different catalyst and peroxide concentrations).

(B) Parameter Analysis and a Comparison of Model and Experimental Results. A comparison of the model equations with the corresponding experimental correlations (see the preceding paper) indicates a consistency in the functional form. Moreover, the comparison suggests the following relationships:

$$c = \frac{k_4}{k_7} \tag{G}$$

$$k_e = \frac{k_3k_4^2K_2}{k_6k_7} \tag{H}$$

$$\tau_e = \tau = \frac{k_6}{2k_3k_4K_2[\mathrm{Cu}]_T} \quad \text{(see Appendix)} \tag{I}$$

$$m = \frac{k_6}{2k_3k_4K_2} \tag{J}$$

In principle, only one complete set of data from one run is sufficient to determine the values of k_4/k_7, b, and $k_3k_4K_2/k_6$ at a given temperature. The parameter values may be most conveniently determined from the data using eq B and I. For the purpose on hand, eq B may be cast into the following more convenient form:

$$-\ln\left(1-\frac{2N_{N_2}}{V[H_2O_2]_0}\right) = \frac{k_4}{k_7}\ln\left[b+\exp\left(\frac{t}{\tau}\right)\right] - \frac{k_4}{k_7}\ln\,(b+1) \qquad \text{(B-1)}$$

$$= \frac{k_4 t}{k_7 \tau} - \frac{k_4}{k_7}\ln\,(b+1) \quad \text{for } t > \tau \qquad \text{(B-2)}$$

By plotting the data after the induction period in the manner prescribed by eq B-2, a straight line should be obtained which has a slope and an intercept equal to $k_4/k_7\tau$ and $-(k_4/k_7)\ln\,(b+1)$, respectively. Since the induction period τ is known from measurements, the values of k_4/k_7 and b may be determined. These values may then be used in eq B-1 to verify that the complete data, including the data taken during the induction period which have been left out in the first analysis, do, in fact, conform with eq B-1.

The value of k_4/k_7 may then be used in eq H and J to provide two independent estimates of the value of $k_3k_4K_2/k_6$. A close agreement between the two estimates is expected if the analysis is wholly consistent. This was, in fact, found to be the case.

Representative plots of the integral analysis are shown in Figure 1 for different runs, and, as expected, the data fall collectively along the universal, 45°-line. The fact that the linearity extends all the way down to the very first data points of each run suggests that t^* is, indeed, immeasurably small (as has been assumed) and may thus be neglected in the analysis.

The values of k_4/k_7, b, and $k_3k_4K_2/k_6$ which have been determined from the plots of different runs are presented in Table I. The results of the different runs at 25 °C indicate that the parameter groups are, within the experimental uncertainties, constants at a given temperature. The set of parameter values at each temperature may then be used with eq B and C to generate a model reaction profile for any combination of catalyst, peroxide, and hydrazine concentrations. An example of the model reaction profile is shown in Figure 1 of the preceding paper; good agreement with the experimental data is evident.

The model results may also be compared against the experimental data reported by Wellman et al.[13] As evident in Table II, the agreement between our model results and Wellman's data is good.

(C) Decoupling of Parameters and a Reexamination of the Hayon and Simic Study. Note that for the purpose of testing the reaction mechanism for consistency with the experimental data, it is not necessary that the individual kinetic parameters be known. In fact, the data obtained in this study alone do not permit a separate determination of the parameters. In order to decouple the parameters, one would need additional data or would have to make some extraneous assumptions. Clearly, the results of the analysis will depend critically on the additional data or assumptions.

The value of k_7, the self-termination rate constant of the hydrazyl radical, is important in this regard. If k_7 is known, one would be able to estimate k_4 from k_4/k_7 and k_3K_2/k_6 from $k_e = k_4(k_3K_2/k_6)(k_4/k_7)$. Moreover, one may then estimate the "steady-state" concentration of the hydrazyl radical ($[N_2H_3^\bullet]_s$) and the kinetic chain length of the reaction (υ) as follows:

$$[N_2H_3^\bullet]_s = \left(\frac{k_3K_2}{k_6}\right)\left(\frac{k_4}{k_7}\right)[Cu]_T \qquad \text{(K)}$$

$$\upsilon = \frac{k_4[N_2H_3^\bullet]_s[H_2O_2]}{k_3K_2[Cu]_T[N_2H_2]} = \left(\frac{k_6}{k_3K_2}\right)\frac{[H_2O_2]}{[Cu]_T} \qquad \text{(L)}$$

Hayon and Simic[14] have reported a $2k_t$ (= $2k_7$) value of 2.4×10^9 (M s)$^{-1}$ for hydrazyl radical at 25 °C. The case will be made shortly that the reported value may be several orders of magnitude too high. However, if one accepts, for the time being, the reported value for the sake of the argument, one would calculate k_4 to be 2.28×10^8 (M s)$^{-1}$ and k_3K_2/k_6 to be 1.5×10^{-5} at 25 °C. The last number leads to the order-of-magnitude estimates of 10^{-12} M and 10^9, respectively, for $[N_2H_3^\bullet]_s$ and υ. Compared to some known radical reactions, the above estimates seem way out of range. The longest chain reactions known to us are the autoxidation of aqueous sulfite, which has a chain length of 10^5–10^6,[15] and the polymerization of vinyl acetate, which has a chain length of 10^4–10^5 and a chain-carrier concentration of about 10^{-9} M.[16] Many radical reactions have chain lengths considerably shorter than 10^3.[17]

Considering the reversible and autocatalytic nature of the hydrazyl radical formation in the proposed mechanism, a case could perhaps be made for a kinetic chain length in the high limit of the longest chain reaction known. However, it seems unlikely that that limit could be as high as 10^9!

For a while, the unusually large estimate of the chain length caused us concern, notwithstanding the fact that the proposed mechanism provides a satisfactory explanation of all our findings. Attempts to modify the mechanism such that it would avoid the large estimate of the chain length on one hand and, on the other hand, provide a full accounting of our findings were unsuccessful. It was only after a fruitless self-examination that we turned to the study of Hayon and Simic for an answer.

A careful review of Hayon–Simic paper produces several points of contention which become evident only with today's hindsight. Of these, the most serious is the unsuspected need to take into account the effect of peroxide on the decay of the hydrazyl radical. By Hayon and Simic's own account, the radiolysis method which they used to generate the hydrazyl radical produced not only hydroxyl radical (for reaction with hydrazine) from the decomposition of water but also hydrogen peroxide and other side products. The peroxide formation relative to hydroxyl radical was 1:4, which is significant considering that the equivalence of peroxide is twice that of the radical. Without the benefit of our findings, the investigators have unwittingly overlooked the possibility that the hydrazyl radical can, in fact, react with peroxide with a rate constant comparable to its self-termination rate constant (k_4/k_7, according to our analysis, is about 0.19).

Judging from Hayon and Simic's data (Figure 3), the peroxide's contribution to the radical's decay must be quite substantial. If one were to accept the extinction coefficient they assigned to the hydrazyl radical (this is somewhat in doubt; see below), one would surmise that as much as 99% of the radical that could be generated (~20 mM) would have reacted by the time they started monitoring the radical's decay. It is not immediately obvious how the data obtained at the tail end of the reaction could be reliably treated, especially since there was evidence of product interference in the UV absorption spectra. However, if one nevertheless uses their data (Figure 3) and attempts a two-point integral analysis, one would arrive at the order-of-magnitude estimate of 100 cm/s for $2k_t/\epsilon$, which is well below 7×10^5 cm/s that is expected on the basis of their reported $2k_t$ and ϵ.

The radical's decay that escaped detection might be presumed to follow, exclusively, a bimolecular self-termination reaction. The presumption could account for the large $2k_t$ and ϵ reported by Hayon and Simic, but it is seriously in error because of the neglect of the peroxide reaction. The latter reaction might actually be the dominant reaction, if, as seems likely, the peroxide concentration was within one or two orders of magnitude higher than that of the hydrazyl radical.

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Indirect support for the foregoing analysis may be found in the unusually large value, namely $6.0 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, Hayon and Simic assigned to $2k_t$ of $N_2H_4^{\bullet+}$ (the protonated form of the hydrazyl radical). Considering the like-charge repulsion effect in $N_2H_4^{\bullet+}$, the reported $2k_t$ value seems rather high.

Moreover, the closeness of the apparent $2k_t$ value of $N_2H_4^{\bullet+}$ to that of $N_2H_3^\bullet$ may be taken to support the view that, the peroxide reaction, rather than the self-termination reaction, was the dominant decay reaction for the hydrazyl radical. Unlike the self-termination reaction, the peroxide reaction is not expected to show a charge effect at pH below the pK_a value of peroxide.

Additional justification for setting aside the results of Hayon and Simic's analysis may be found by comparing the reported $2k_t$ value for $N_2H_3^\bullet$ with the well-founded $2k_t$ value of $10^{6.4}\ (\mathrm{M\ s})^{-1}$ for peroxy ($HO_2^\bullet$) radical.[18] Considering the similarity between the two radicals, e.g., the presence of a free electron pair adjacent to the spin site (that could exert a repulsion effect on the self-termination reaction), an isoelectronic configuration, a comparable structure, a neutral charge and the presence of a dissociable proton, one should not expect a difference as large as three orders of magnitude between their $2k_t$ values. By itself, the comparison by molecular attributes may not be a sufficient basis to challenge Hayon and Simic's analysis, but, taken in conjunction with the other considerations, it reinforces the case for revising their results.

Finally, in the light of our findings and that of others, a more plausible explanation may be provided for the step observed at pH 11.5 in Hayon and Simic's UV absorbance curve (see the insert in their Figure 3). The step coincides squarely with the step in our rate-vs-pH curve (see Figure 6 of the preceding paper), and, as we have suggested in the preceding paper, it may be taken as evidence in support of the presence of diimide. According to this view, the pK_a value of diimide may be deduced to be 11.5.

In analyzing their UV absorbance data in connection with the hydrazyl decomposition reaction, Hayon and Simic were misled into thinking that diimide was not involved in the reaction. The misguided conclusion was based on the faulty premise that the intermediary of diimide would be indicated by the presence of hydrogen as a product of the decomposition reaction:

$$N_2H_2 \rightarrow N_2 + H_2 \tag{M}$$

However, it is now evident from the studies of Foner and Hudson[19] and Willis and Beck[9] that diimide can decompose by the disproportionation reaction

$$2N_2H_2 \rightarrow N_2 + N_2H_4 \tag{N}$$

without the formation of hydrogen. In a 1984 review,[10] Back surveyed the available evidence (much of which appeared after Hayon and Simic's study) and concluded that, in liquid phase, the disproportionation reaction N is the only important loss process under most conditions. Only at high pH would reaction M become significant. Evidently, diimide dissociation at high pH (above the presumed pK_a value of 11.5) introduces a like-charge repulsion effect that slows the disproportionation reaction.

Thus, in light of the new evidence, the important study of Hayon and Simic appears to need some major revisions. Specifically, the diimide intermediary may have to be reinstated, and, at the same time, the intermediary of triazene that had been postulated in its place may have to be discarded. The $2k_t$ (and ϵ) values of $N_2H_3^\bullet$ and $N_2H_4^{\bullet+}$ may have to be reduced substantially. Unfortunately, the paper does not provide sufficient information on peroxide to permit a reanalysis of the data.

Until k_7 is definitively determined, the values of k_4, $[N_2H_3^\bullet]_s$, and υ can only be estimated by using some presumed k_7 value. If one were to assume $k_7 \cong 10^6\ (\mathrm{M\ s})^{-1}$ (which corresponds to the k_t value of $HO_2^\bullet$ radical), then one would obtain the estimates of $2 \times 10^5\ (\mathrm{M\ s})^{-1}$, 10^{-9} M, and 10^6, respectively, for k_4, $[N_2H_3^\bullet]_s$, and υ. Compared to known radical reactions mentioned earlier, the new estimates appear reasonable.

III. Conclusion

The results of a kinetic study and a model analysis suggest that the copper-catalyzed redox reaction between aqueous peroxide and hydrazine may proceed by the mechanism shown in Scheme I. Values of the kinetic parameters in the mechanism are evaluated by using experimental data, and the model results are shown to agree closely with the experimental results.

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Appendix: Model Expressions for Reaction Rate and Concentration Profile

Referring to the postulated mechanism in Scheme I,

$$\frac{1}{V}\frac{\mathrm{d}N_{N_2}}{\mathrm{d}t} = \frac{\mathrm{d}(N_{N_2}/V)}{\mathrm{d}t} \equiv \frac{\mathrm{d}[N_2]}{\mathrm{d}t} = k_6[N_2H_2][H_2O_2] \tag{A1}$$

where V is the reaction-solution volume which is a constant for a given run, and $[N_2]$ is a hypothetical nitrogen concentration defined by

$$[N_2] \equiv \frac{N_{N_2}}{V} \tag{A2}$$

Let t^* be the time (assumed $\ll \tau_e$) which elapses before the long-chain approximation becomes applicable to diimide, i.e.,

(rate of diimide formation in propagation chain) ≅ (rate of diimide consumption in concerted reaction)

for $t > t^*$ or

$$k_4[N_2H_3^\bullet][H_2O_2] \cong k_6[N_2H_2][H_2O_2]$$

or

$$[N_2H_2] \cong \frac{k_4}{k_6}[N_2H_3^\bullet] \tag{A3}$$

for $t > t^*$. The long-chain approximation may be justified by the observation that, if one were to solve numerically the system of differential equations based on the proposed mechanism, one would obtain the empirical result that $[N_2H_2]$ and $[N_2H_3^\bullet]$ are in apparent equilibrium with each other over wide ranges of rate constants. The computer analysis (using an IMSL subroutine package) shows that the apparent equilibrium, which is embodied in eq A3, holds even for most of the induction period (except at its very beginning). The empirical result may be rationalized by noting that, except for a very short time t^* close to 0, $N_2H_3^\bullet$ is derived primarily from N_2H_2 that is formed in the propagation chain, rather than in reation 1 which is presumed slow. Thus, at $t > t^*$ reaction 1 ceases to be important relative to reaction 4.

Moreover, since $[H_2O_2]_0 \gg [Cu]_T$, the N_2H_2 that is formed in the propagation chain may be expected to react primarily with peroxide in reaction 6 (assuming $k_3 \ll k_{2r}$, which seems very likely). Thus, the validity of the long-chain approximation rests on the premise that, at any given time $t > t^*$, the N_2H_2 used in the autocatalytic formation of $N_2H_3^\bullet$ is derived primarily from, and is a small fraction of, the N_2H_2 which is formed in the propagation chain. The final justification for the long-chain assumption rests on a good agreement between the model and experimental results (see later).

$$\frac{\mathrm{d}[N_2H_3^\bullet]}{\mathrm{d}t} = 2k_3K_2[CuN_2H_4][N_2H_2] - 2k_7[N_2H_3^\bullet]^2 \qquad \text{where } K_2 = \frac{k_{2f}}{k_{2r} + k_3}$$

$$= 2k_7\left(\frac{k_3k_4K_2}{k_6k_7}[CuN_2H_4][N_2H_3^\bullet] - [N_2H_3^\bullet]^2\right) \qquad \text{(using eq A3)} \tag{A4}$$

At time $t > \tau_e$, the "steady-state" concentration of hydrazyl radical, $[N_2H_3^\bullet]_s$, is given by

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[18] Denisov, E. T. *Liquid-Phase Reaction Rate Constants*; Plenum Publishing Corp.: New York, 1974; p 413.

[19] Foner, S. N.; Hudson, R. L. Diimide: Identification and Study by Mass Spectrometry. *J. Chem. Phys.* **1958**, *28*, 719–720.

$$\frac{\mathrm{d}[\mathrm{N_2H_3^{\bullet}}]}{\mathrm{d}t} = 2k_7\left(\frac{k_3k_4K_2}{k_6k_7}[\mathrm{CuN_2H_4}][\mathrm{N_2H_3^{\bullet}}]_\mathrm{s} - [\mathrm{N_2H_3^{\bullet}}]_\mathrm{s}^2\right) = 0$$

or

$$[\mathrm{N_2H_3^{\bullet}}]_\mathrm{s} = \frac{k_3k_4K_2}{k_6k_7}[\mathrm{CuN_2H_4}] = \frac{k_3k_4K_1K_2[\mathrm{Cu}]_T[\mathrm{N_2H_4}]}{k_6k_7(1 + K_1[\mathrm{N_2H_4}])} \cong \frac{k_3k_4K_2}{k_6k_7}[\mathrm{Cu}]_T \quad (\mathrm{A5})$$

where $[\mathrm{Cu}]_T$ is the total concentration of catalyst added to the solution, and K_1 is the stability constant of copper–hydrazine complex which has reported to be $10^{6.67}$ $\mathrm{M^{-1}}$,[8] and $K_1[\mathrm{N_2H_4}]$ is very much greater than 1.

Equations A4 and A5 give

$$\frac{\mathrm{d}[\mathrm{N_2H_3^{\bullet}}]}{\mathrm{d}t} = 2k_7([\mathrm{N_2H_3^{\bullet}}]_\mathrm{s}[\mathrm{N_2H_3^{\bullet}}] - [\mathrm{N_2H_3^{\bullet}}]^2)$$

or

$$\frac{\mathrm{d}[\mathrm{N_2H_3^{\bullet}}]}{[\mathrm{N_2H_3^{\bullet}}]([\mathrm{N_2H_3^{\bullet}}]_\mathrm{s} - [\mathrm{N_2H_3^{\bullet}}])} = \left(\frac{1}{[\mathrm{N_2H_3^{\bullet}}]} + \frac{1}{[\mathrm{N_2H_3^{\bullet}}]_\mathrm{s} - [\mathrm{N_2H_3^{\bullet}}]}\right)\frac{\mathrm{d}[\mathrm{N_2H_3^{\bullet}}]}{[\mathrm{N_2H_3^{\bullet}}]_\mathrm{s}} = 2k_7\mathrm{d}t \quad (\mathrm{A6})$$

Integrating both sides of eq A6 implicitly between the time intervals t^* and t,

$$\ln\frac{[\mathrm{N_2H_3^{\bullet}}]}{[\mathrm{N_2H_3^{\bullet}}]^*} - \ln\left(\frac{[\mathrm{N_2H_3^{\bullet}}]_\mathrm{s} - [\mathrm{N_2H_3^{\bullet}}]}{[\mathrm{N_2H_3^{\bullet}}]_\mathrm{s} - [\mathrm{N_2H_3^{\bullet}}]^*}\right) = 2k_7[\mathrm{N_2H_3^{\bullet}}]_\mathrm{s}(t - t^*) \equiv \frac{(t - t^*)}{\tau} \quad (\mathrm{A7})$$

where $[\mathrm{N_2H_3^{\bullet}}]^*$ is the concentration of hydrazyl radical at time t^* and

$$\tau \equiv \frac{1}{2k_7[\mathrm{N_2H_3^{\bullet}}]_\mathrm{s}} = \frac{k_6}{2k_3k_4K_2[\mathrm{Cu}]_T} \quad (\mathrm{A8})$$

using eq A5. Equation A7 may be rearranged to give

$$[\mathrm{N_2H_3^{\bullet}}] = \frac{[\mathrm{N_2H_3^{\bullet}}]_\mathrm{s}\exp\left(\frac{t - t^*}{\tau}\right)}{\frac{[\mathrm{N_2H_3^{\bullet}}]_\mathrm{s}}{[\mathrm{N_2H_3^{\bullet}}]^*} - 1 + \exp\left(\frac{t - t^*}{\tau}\right)}$$

or using eq A5

$$= \frac{\frac{k_3k_4K_2}{k_6k_7}[\mathrm{Cu}]_T\exp\left(\frac{t - t^*}{\tau}\right)}{b + \exp\left(\frac{t - t^*}{\tau}\right)} \quad (\mathrm{A9})$$

where

$$b = \frac{[\mathrm{N_2H_3^{\bullet}}]_\mathrm{s}}{[\mathrm{N_2H_3^{\bullet}}]^*} - 1 \quad (\mathrm{A10})$$

Equations A1, A3, and A9 give

$$\frac{\mathrm{d}[\mathrm{N_2}]}{\mathrm{d}t} = \frac{1}{V}\frac{\mathrm{d}N_{\mathrm{N_2}}}{\mathrm{d}t} = \frac{\frac{k_3k_4^2K_2}{k_6k_7}[\mathrm{Cu}]_T[\mathrm{H_2O_2}]\exp\left(\frac{t - t^*}{\tau}\right)}{b + \exp\left(\frac{t - t^*}{\tau}\right)} = \frac{\frac{k_4}{2k_7}[\mathrm{H_2O_2}]\exp\left(\frac{t - t^*}{\tau}\right)}{b + \exp\left(\frac{t - t^*}{\tau}\right)} \quad (\mathrm{A11})$$

Peroxide balance gives

$$[\mathrm{H_2O_2}]_0 - [\mathrm{H_2O_2}] = 2[\mathrm{N_2}] + [\mathrm{N_2H_2}] + \frac{[\mathrm{N_2H_3^{\bullet}}]}{2} \quad (\mathrm{A12})$$

$$\cong 2[\mathrm{N_2}] \quad (\mathrm{A13})$$

where $[\mathrm{H_2O_2}]_0$ is the initial peroxide concentration. Equations A10 and A13 give, upon rearrangement,

$$\frac{\mathrm{d}[\mathrm{N_2}]}{[\mathrm{H_2O_2}]_0 - 2[\mathrm{N_2}]} = \frac{\frac{k_4}{2k_7}\exp\left(\frac{t - t^*}{\tau}\right)}{b + \exp\left(\frac{t - t^*}{\tau}\right)}\mathrm{d}t = \frac{k_4}{2k_7}\left[1 - \frac{b}{b + \exp\left(\frac{t - t^*}{\tau}\right)}\right]\mathrm{d}t \quad (\mathrm{A14})$$

Integrating both sides of eq A14 implicitly between the time intervals t^* and t,

$$-0.5\ln\frac{[\mathrm{H_2O_2}]_0 - 2[\mathrm{N_2}]}{[\mathrm{H_2O_2}]_0 - 2[\mathrm{N_2}]^*} = \frac{k_4}{2k_7}\left|(t - t^*) - b\int_{t^*}^{t}\frac{\mathrm{d}t}{b + \exp\left(\frac{-t^*}{\tau}\right)\exp\left(\frac{t}{\tau}\right)}\right|$$

$$= \frac{k_4}{2k_7}\left|(t - t^*) - b\left[\frac{t - t^*}{b} - \frac{\tau}{\mathrm{b}}\ln\frac{b + \exp\left(\frac{t - t^*}{\tau}\right)}{b + 1}\right]\right|$$

$$= \frac{k_4}{2k_7}\ln\frac{b + \exp\left(\frac{t - t^*}{\tau}\right)}{b + 1} \quad (\mathrm{A15})$$

where $[\mathrm{N_2}]^*$, the nitrogen concentration at t^* (close to 0), may be assumed to be negligibly small. Equation A15 thus reduces to

$$1 - \frac{2[\mathrm{N_2}]}{[\mathrm{H_2O_2}]_0} \cong \left|\frac{b + 1}{b + \exp\left(\frac{t - t^*}{\tau}\right)}\right|^{(k_4/k_7)}$$

or upon rearrangement

$$[\mathrm{N_2}] \equiv \frac{N_{\mathrm{N_2}}}{V} = \frac{[\mathrm{H_2O_2}]_0}{2}\left|1 - \left|\frac{b + 1}{b + \exp\left(\frac{t - t^*}{\tau}\right)}\right|^{(k_4/k_7)}\right| \quad (\mathrm{A16})$$

$$[\mathrm{H_2O_2}] = [\mathrm{H_2O_2}]_0 - 2[\mathrm{N_2}] = [\mathrm{H_2O_2}]_0\left|\frac{b + 1}{b + \exp\left(\frac{t - t^*}{\tau}\right)}\right|^{(k_4/k_7)} \quad (\mathrm{A17})$$

Relationship between τ and τ_e. The characteristic time constant τ, which is introduced and defined in eq A8, may be shown to be identically equal to the induction period τ_e as follows. Referring to Figure 1 in the preceding paper, it is seen that τ_e and t_m, the reaction time at which the reaction attains a maximum rate, are related by

$$\left(\frac{\mathrm{d}[\mathrm{N_2}]}{\mathrm{d}t}\right)_{\max} = \frac{[\mathrm{N_2}]|_{t_\mathrm{m}}}{(t_\mathrm{m} - \tau_\mathrm{e})} \quad (\mathrm{A18})$$

where

$$\left(\frac{\mathrm{d}[\mathrm{N}_2]}{\mathrm{d}t}\right)_{\max}$$

and t_m are given by

$$\frac{\mathrm{d}^2[\mathrm{N}_2]}{\mathrm{d}t^2} = 0$$

Equation A11 gives

$$\frac{\mathrm{d}^2[\mathrm{N}_2]}{\mathrm{d}t^2} = \frac{k_4[\mathrm{H}_2\mathrm{O}_2]\mathrm{e}^{t/\tau}}{2k_7\tau^2(\mathrm{b}e^{t^*/\tau} + e^{t/\tau})^2}\left(be^{t^*/\tau} - \frac{k_4}{k_7}\mathrm{e}^{t/\tau}\right) \quad \text{(A19)}$$

Thus, t_m is given by

$$be^{t^*/\tau} - \frac{k_4}{k_7}\mathrm{e}^{t_\mathrm{m}/\tau} = 0$$

or

$$t_\mathrm{m} = \tau \ln\left(\frac{k_7}{k_4}be^{t^*/\tau}\right) = t^* + \tau \ln\left(\frac{k_7}{k_4}\mathrm{b}\right) \quad \text{(A20)}$$

At $t = t_\mathrm{m}$, eq A16 and A17 give

$$[\mathrm{N}_2]|_{t_\mathrm{m}} = \frac{1}{2}([\mathrm{H}_2\mathrm{O}_2]_0 - [\mathrm{H}_2\mathrm{O}_2]_{t_\mathrm{m}}) =$$

$$\frac{[\mathrm{H}_2\mathrm{O}_2]_0}{2}\left|1 - \left|\frac{b+1}{b + \frac{k_7}{k_4}\mathrm{b}}\right|^{(k_4/k_7)}\right| \quad \text{(A21)}$$

Equation A11 gives

$$\left(\frac{\mathrm{d}[\mathrm{N}_2]}{\mathrm{d}t}\right)_{\max} = \frac{\frac{k_4}{2k_7\tau}[\mathrm{H}_2\mathrm{O}_2]|_{t_\mathrm{m}}\frac{k_7}{k_4}\mathrm{b}}{b + \frac{k_7}{k_4}\mathrm{b}} =$$

$$\frac{[\mathrm{H}_2\mathrm{O}_2]_0}{2\left(1 + \frac{k_7}{k_4}\right)\tau}\left|\frac{b+1}{b + \frac{k_7}{k_4}b}\right|^{(k_4/k_7)} \quad \text{(A22)}$$

Equations A18, A21, and A22 give

$$\tau_\mathrm{e} = t^* + \tau \ln\left(\frac{k_7}{k_4}b\right) + \tau\left(1 + \frac{k_7}{k_4}\right)\left|1 - \left|\frac{b + \frac{k_7}{k_4}\mathrm{b}}{b+1}\right|^{k_4/k_7}\right| \quad \text{(A23)}$$

For τ_e to be equal to τ, it is required that t^* be small relative to τ and

$$\ln\left(\frac{k_7}{k_4}b\right) + \left(1 + \frac{k_7}{k_4}\right)\left|1 - \left|\frac{b + \frac{k_7}{k_4}b}{b+1}\right|^{k_4/k_7}\right| = 1.0 \quad \text{(A24)}$$

Experimentally, k_4/k_7 and b are found to be about 0.19 and 5.28, respectively. With these values, RHS of eq A23 = $t^* + \tau$. The results establish that, provided that t^* is negligibly small, $\tau = \tau_\mathrm{e}$.

Registry No. $\mathrm{N}_2\mathrm{H}_4$, 302-01-2; $\mathrm{H}_2\mathrm{O}_2$, 7722-84-1; Cu, 7440-50-8.

Vanadium(V)/Vanadium(III) Redox Couple in Acidic Organic Media. Structure of a Vanadium(III)–Tetraethylene Glycol Pentagonal-Bipyramidal Complex ($[\mathrm{V(teg)(Br)}_2]^+\mathrm{Br}^-$)

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Abstract: The vanadium(V)/vanadium(III) redox couple was investigated in an acidic organic medium by reduction of sodium metavanadate by hydrogen bromide with 1,2-dichloroethane as solvent in the presence of tetraglyme as a complexing agent. In the absence of dioxygen a vanadium(III)–tetraethylene glycol (teg) pentagonal-bipyramidal complex, $[\mathrm{V(teg)(Br)}_2]^+\mathrm{Br}^-$, is formed. In the presence of dioxygen a catalytical cycle is initiated whereby vanadium(V) oxidizes hydrogen bromide to molecular bromine. The reduced vanadium(III) species thereby formed is reoxidized by dioxygen to vanadium(V) as confirmed by ESR and UV–vis of the organic phase.

The coordination and oxidation chemistry of vanadium compounds in liquid organic media has recently received a great deal of research interest. This research has been fueled by the discovery of biological implications of vanadium chemistry. Thus a low-valent vanadium compound is found at the active site of nitrogenase in the bacterium *Azobactor chroococcumm*,[1] and a vanadium(V) complex is present in a bromoxidase enzyme in the marine algae *Ascophyllum nodosum*.[2] The bromoxidase enzyme is capable of catalyzing bromination reactions whereby bromide anions are oxidized by hydrogen peroxide, eq 1. Vanadium is

$$\mathrm{SH} + \mathrm{Br}^- + \mathrm{H}_2\mathrm{O}_2 + \mathrm{H}^+ \rightarrow \mathrm{SBr} + 2\mathrm{H}_2\mathrm{O} \quad (1)$$

also sequestered from sea water in the marine organisms known as "sea squirts" or tunicates.[3] These tunicates are exceptional in their ability to accumulate vanadium(III)[4] at concentrations of up to 1–2 M by reduction of anionic vanadium(V) species found

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