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FREE-RADICAL REACTIONS IN CLOUDWATER: THE ROLE OF TRANSITION METALS IN HYDROGEN PEROXIDE PRODUCTION AND DESTRUCTION

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FREE-RADICAL REACTIONS IN CLOUDWATER: THE ROLE OF TRANSITION METALS IN HYDROGEN PEROXIDE PRODUCTION AND DESTRUCTION

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ABSTRACT

Cloudwater hydrogen peroxide is a principal oxidant for dissolved S(IV). Low-intensity cobalt-60 radiolysis permits the study of free-radical reactions producing H_2O_2 in aqueous solutions under conditions characteristic of the ambient atmosphere. Results using this technique have confirmed model predictions that H_2O_2 production is frequently the major fate of $O_2(-I)$ radicals. However, dissolved iron can significantly decrease the apparent yield of H_2O_2, principally because of destruction of H_2O_2 by Fe(II). In spite of its greater efficiency in catalyzing the production of H_2O_2 from $O_2(-I)$, faster oxidation reactions for Cu(I) and the generally lower atmospheric abundance of copper suggest that it will not be as effective as iron in atmospheric H_2O_2 destruction.

1. Introduction

Water droplets in clouds, in addition to scavenging gaseous species, provide a medium for the chemical transformation of dissolved substances. One important example is the oxidation of dissolved S(IV) by hydrogen peroxide, which is a principal source of cloudwater acidity (Daum et al., 1982; Venkatram et al., 1990). Aqueous-phase hydrogen peroxide concentrations up to several hundred micromolar have been measured, with seasonal and diurnal variations consistent with the view that this species is generated largely by atmospheric photochemical processes

(Kelly et al., 1985; Olszyna et al., 1988). Because the extent of S(IV) oxidation in clouds may be limited by the concentration of hydrogen peroxide, atmospheric consequences of sulfur emissions can be accurately described only with a thorough understanding of hydrogen peroxide sources and sinks.

1.1 Sources of Hydrogen Peroxide

H_2O_2 in the atmosphere is a product of atmospheric free radical reactions. These reactions are initiated by the photolysis of ozone, leading to the production of OH radicals

$$O_3 \rightarrow O_2 + O(^1D) \tag{1}$$

$$O(^1D) + H_2O \rightarrow 2\ OH \tag{2}$$

Hydroxyl radicals can be converted to hydroperoxyl radical by reactions such as

$$OH + CO \xrightarrow{O_2} HO_2 + CO_2 \tag{3}$$

Principal sink reactions for free radicals are

$$OH + NO_2 \rightarrow HONO_2 \tag{4}$$

and

$$2\ HO_2 \rightarrow H_2O_2 + O_2 \tag{5}$$

In clouds, the large Henry's law constants for H_2O_2 and HO_2, $7.4\times10^4\ M^{-1}\ s^{-1}$ at 25°C (Lind et al., 1987) and $9\times10^3\ M^{-1}\ s^{-1}$ at 25°C (Weinstein-Lloyd and Schwartz, 1991), respectively, lead at equilibrium to substantial transfer of these species to cloud droplets. The solubility of HO_2 is enhanced by its dissociation in the aqueous phase to give H^+ and O_2^- with a pK_a of 4.69 (Bielski et al., 1985)

$$HO_2 \rightleftarrows H^+ + O_2^- \tag{6}$$

In the absence of other reactive species in solution, HO_2 and its conjugate base, collectively denoted $O_2(-I)$, react at a pH-dependent rate to form H_2O_2

$$2\ O_2(-I) \xrightarrow{2H^+} H_2O_2 + O_2 \qquad (7)$$

Although unreactive toward most organic substances, $O_2(-I)$ can be removed by reaction with ozone and with oxidized and reduced transition metal ions

$$O_2(-I) + O_3 \xrightarrow{2H^+} OH + 2\ O_2 \qquad (8)$$

$$O_2(-I) + M(Ox) \rightarrow H_2O_2 + M(Red) \qquad (9)$$

$$O_2(-I) + M(Red) \rightarrow O_2 + M(Ox) \qquad (10)$$

1.2 Hydrogen Peroxide Sinks

Principal pathways for loss of aqueous H_2O_2 include oxidation of dissolved S(IV)

$$S(IV) + H_2O_2 \xrightarrow{2H^+} S(VI) + 2\ H_2O \qquad (11)$$

and reduced transition metal ions.

$$M(Red) + H_2O_2 \rightarrow M(Ox) + OH + OH^- \qquad (12)$$

Laboratory determinations of the rate of reaction (11) in pure solutions (Overton, 1985) and in precipitation (Lee et al., 1986) indicate that, depending on pH and ambient reaction concentrations, either H_2O_2 or S(IV) can be depleted during a typical cloud lifetime.

Reaction (12), first suggested by Fenton (1899) to account for the observed hydroxylation of organic compounds in the presence of Fe(II) and hydrogen peroxide, remains the subject of active research (Rush and Koppenol, 1986; Rahwal and Richter, 1987). The rate coefficient for this reaction depends strongly on the identity of the metal ion and its state of complexation, as well as on solution pH. Although Fenton reagents, i.e., acidic solutions of hydrogen peroxide containing reduced transition metal ions such as Fe(II) and Cu(I), are routinely used as OH radical sources, recent studies suggest that the oxidant generated by reaction

(12) in neutral and basic solutions is not OH radical but ferryl (Fe(IV)) or cupryl (Cu(III)) ion (Rush and Koppenol, 1986; Rahwal and Richter, 1987; Johnson et al., 1988).

2. EXPERIMENTAL APPROACHES

In principle, the rates and products of important aqueous-phase free radical reactions in the atmosphere can be investigated by direct observation in the atmosphere, or by theoretical modeling based on laboratory measurements. However, in-situ measurement of concentrations of free radicals, together with those of presumed precursors and products has been hindered by extremely low concentrations, which are expected to be in the nanomolar range for $O_2(-I)$ and several orders of magnitude lower for OH(aq).

Consequently, the most useful approach is model calculation, employing representative values of solar intensity and concentration of trace constituents, together with reactions and rate coefficients determined from laboratory experiments. However, one aspect of model calculations that needs to be verified is the applicability of rate coefficients determined in the laboratory, usually by pulse radiolysis, to atmospheric conditions. Laboratory measurements employ high free radical concentrations (10^{-6} M) and ultrapure solutions, whereas in cloudwater estimated concentrations of $O_2(-I)$ and OH are 10^{-8} M and 10^{-12} M, respectively (Jacob, 1986; McElroy, 1986) and they coexist with a suite of trace organic and inorganic species. Such conditions favor reactions with dissolved solutes rather than the radical-radical reactions often observed in the laboratory.

In the laboratory, free radicals can be produced in synthetic or authentic cloudwater by photolysis or radiolysis. In photolysis, free radicals are formed when energy is absorbed by the solute, whereas in radiolysis, the aqueous solvent absorbs virtually all the radiation, thus protecting the solutes. Cobalt-60 γ-radiolysis of dilute aqueous solutions is a particularly appropriate technique for producing oxy free radicals at a rate comparable to the expected rate of gas-to-liquid transfer in the atmosphere.

3. FREE RADICAL PRODUCTION BY ^{60}Co RADIOLYSIS

3.1 Background

Because of the importance of water radiolysis in nuclear reactors and irradiated biological systems, this process was the subject of intense research during the 1950's and 1960's. The physical processes, free-radical intermediates and stable products resulting from the interaction of water with ionizing radiation are well-characterized. Excess energy imparted to the water molecule by a γ-ray is lost by bond rupture or ionization

$$H_2O \xrightarrow{\gamma} H_2O^* \qquad (13)$$

$$\begin{array}{ll} H_2O^* \rightarrow H + OH & \qquad (14) \\ \downarrow & \qquad (15) \\ H_2O^+ + e^- & \end{array}$$

High energy electrons formed in reaction (15) undergo thermalization and are ultimately trapped by solvent

$$e^- \rightarrow e^-_{aq} \qquad (16)$$

Because of the pattern of energy loss in tracks and spurs, some free radicals are formed in close proximity; the recombination of such species is the source of so-called primary H_2 and H_2O_2

$$2\ H \rightarrow H_2 \qquad (17)$$

$$2\ OH \rightarrow H_2O_2 \qquad (18)$$

The primary products and their G-values, i.e., the yields expressed as the number of each species per 100 eV deposited in the sample, are summarized below:

$$H_2O \rightarrow OH(2.75),\ e^-_{aq}(2.65),\ H(0.65),\ H_2O_2(0.70),\ H_2(0.45) \qquad (19)$$

Following these primary processes, subsequent reactions occur between primary radiolysis products and dissolved substrates. A number of techniques have been developed to study such reactions. For example, all three primary radicals can be converted into $O_2(-I)$ by using oxygenated solutions containing sodium formate

$$e^-_{aq} + O_2 \rightarrow O_2^- \qquad (20)$$

$$H + O_2 \rightarrow HO_2 \qquad (21)$$

$$OH + HCO_2^- \rightarrow H_2O + CO_2^- \qquad (22)$$

$$CO_2^- + O_2 \rightarrow CO_2 + O_2^- \qquad (23)$$

Superoxide ion and hydroperoxyl radical rapidly establish equilibrium via reaction (6). Reactions (20) through (23) are sufficiently rapid that, in solutions containing millimolar sodium formate, conversion of primary radicals to $O_2(-I)$ occurs within several microseconds. As in the atmosphere, disproportionation to form H_2O_2 is the primary fate of $O_2(-I)$ radicals in the absence of other reactive species.

3.2 Irradiation Sources

Three sources were employed in these studies. Each source consists of a stainless steel-clad cylinder containing ^{60}Co, buried in concrete beneath the laboratory floor and shielded by water (Schwarz and Allen, 1954). Samples in an aluminum can are lowered into the cylinders and exposed for measured time periods. In their present configuration, these sources produce free radicals at 76, 11 and 0.24 nanomole per liter per second, as determined by ferrous sulfate dosimetry.

3.3 Previous Studies

We have previously investigated the yield of H_2O_2 from $O_2(-I)$ radicals produced by low-intensity γ-radiolysis in actual precipitation samples and in synthetic cloudwater samples, i.e., dilute aqueous solutions of

NH_4^+, NO_3^-, H^+, SO_4^{2-}, Na^+, Cl^-, H_2O_2, Fe(II), Mn(II), Cu(II) and HCHO (Weinstein-Lloyd and Schwartz, 1991). In synthetic samples in the absence of transition metals, the yield of H_2O_2 was consistent with conversion of primary radicals to $O_2(-I)$, followed by complete conversion of $O_2(-I)$ to H_2O_2 via the disproportionation reaction (7), for a wide range of radiation doses and dose rates (Figure 1). However, measured H_2O_2

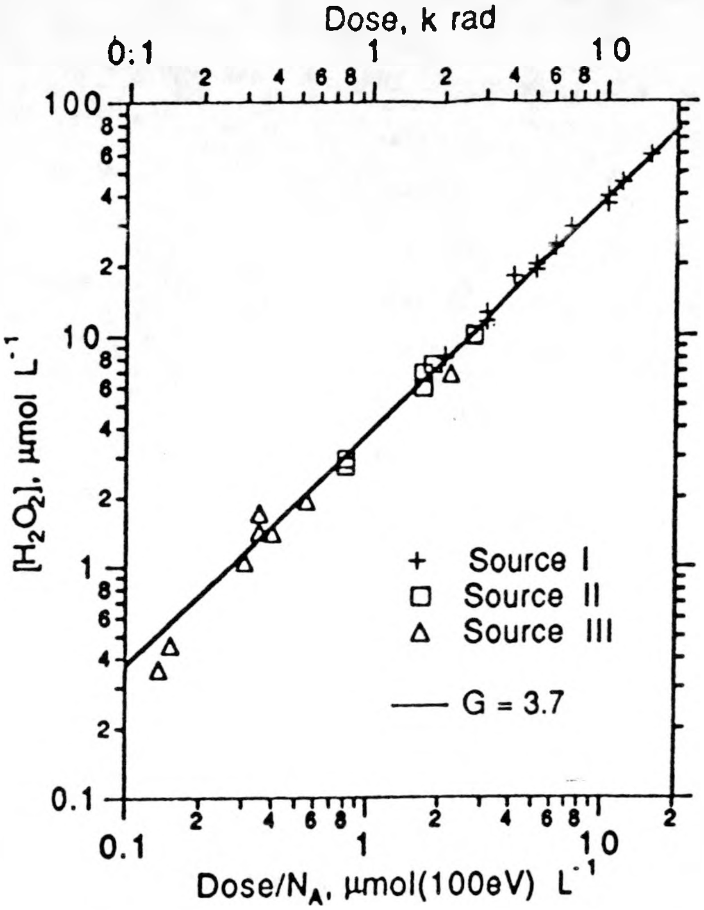

FIGURE 1. Yield of H_2O_2 in synthetic cloudwater as a function of radiation dose in 100 eV L^{-1} divided by Avogadro's constant N_A. Solid line represents G-value of 3.7 H_2O_2 molecules produced per 100 eV absorbed radiation energy (from Weinstein-Lloyd and Schwartz, 1991).

concentrations in irradiated authentic precipitation samples were generally not consistent with those expected from simple disproportionation of $O_2(-I)$ radicals. Departure from the expected results in such samples was generally greater for samples containing atmospheric H_2O_2 and for lower intensity irradiation (Weinstein-Lloyd and Schwartz, 1991).

4. TRANSITION METALS

4.1 Occurrence

Metal-containing particles are introduced into the atmosphere by geological weathering, combustion, and industrial processing of metals. A review of field measurements of transition metal concentrations in rainwater by Graedel et al. (1986) shows wide variability, with higher concentrations occurring near industrial sites. The most abundant transition metal in the atmospheric environment is iron. Typical iron concentrations are several micromolar; concentrations of copper, manganese and nickel are generally one order of magnitude lower. Although relatively few details are available about metal speciation, most of these measurements were made after filtration, thus minimizing the contribution of large particles to the reported metal concentration.

At least one field study (Behra and Sigg, 1990) and several model calculations, e.g., Jacob et al. (1989) indicate that a substantial proportion of metal may exist in the reduced form, suggesting the involvement of Fenton chemistry in cloudwater reactions.

4.2 Radiolysis of Synthetic Cloudwater with Transition Metals

Because transition metals are among the few species which are reactive toward $O_2(-I)$, we have investigated the yield of H_2O_2 in irradiated solutions containing known concentrations of Fe(III) and Cu(II) in addition to H_2O_2 and the major inorganic ions normally present in precipitation. Iron was studied because of its prevalence in the atmosphere and copper because it is the most efficient known catalyst for the formation of H_2O_2 from $O_2(-I)$ radicals (Rabani et al., 1973).

Our measurements of hydrogen peroxide concentrations in irradiated solutions containing 1 μM metal ion are shown as symbols in Figure 2 for iron and in Figure 3 for copper. The figures show the concentration of H_2O_2 expected from $O_2(-I)$ radicals if no reaction with transition metal occurred, as well as expected concentrations based on source intensities and rate coefficients for the mechanism summarized in Table 1. The observed reduction in apparent yield is due to free-radical reactions rather than direct reaction between H_2O_2 and oxidized metal, as demonstrated by appropriate blank experiments. The increased departure in observed concentration from the "expected" value as source intensity decreases is quantitatively accounted for by considering rates of the various reactions involved.

For the low free radical concentrations of these experiments, formation of H_2O_2 from direct reaction between two $O_2(-I)$ radicals is much slower than the catalyzed reaction consisting of

$$O_2(-I) + Fe(III) \rightarrow O_2 + Fe(II) \qquad (9')$$

$$O_2(-I) + Fe(II) \rightarrow H_2O_2 + Fe(III) \qquad (10')$$

The analogous set of reactions occurs for copper, although some evidence exists that the intermediate in the copper-catalyzed disproportionation may be CuO_2^+ rather than Cu(I) (Zuberbühler, 1976).

$$O_2(-I) + Cu(II) \rightarrow O_2 + Cu(I) \qquad (9")$$

$$O_2(-I) + Cu(I) \rightarrow H_2O_2 + Cu(II) \qquad (10")$$

Reactions (9) and (10) constitute a transition-metal-ion-catalyzed pathway for conversion of two $O_2(-I)$ radicals to H_2O_2, which increases the rate of disproportionation, but leaves the yield unchanged. Departure from the solid line in Figures 2 and 3 is the result of destruction of

TABLE 1. Reactions and Rate Coefficients for Radiolysis Studies

Reaction	Rate Coefficient*	Reference
(6) $HO_2 \rightleftarrows H^+ + O_2^-$	$K_{eq}/M = 2.05(-5)$	Bielski et al.(1985)
(7a) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	8.3(5)	Bielski et al. (1985)
(7b) $HO_2 + O_2^- \xrightarrow{H^+} H_2O_2 + O_2$	9.7(7)	Bielski et al. (1985)
(20) $e_{aq}^- + O_2 \rightarrow O_2^-$	1.9(10)	Buxton et al. (1988)
(21) $H + O_2 \rightarrow HO_2$	2.1(10)	Buxton et al. (1988)
(22) $OH + HCO_2^- \rightarrow H_2O + CO_2^-$	3.5(9)	Buxton et al. (1988)
(23) $CO_2^- + O_2 \rightarrow CO_2 + O_2^-$	2.4(9)	Adams and Wilson (1969)
<u>Iron Reactions</u>		
(9'a) $HO_2 + Fe(III) \rightarrow Fe(II) + O_2 + H^+$	3.1(5)	Sehested et al. (1969)
(9'b) $O_2^- + Fe(III) \rightarrow Fe(II) + O_2$	1.5(8)	Rush and Bielski (1985)
(10'a) $HO_2 + Fe(II) \xrightarrow{H^+} Fe(III) + H_2O_2$	1.2(6)	Rush and Bielski (1985)
(10'b) $O_2^- + Fe(II) \xrightarrow{2H^+} Fe(III) + H_2O_2$	1.0(7)	Rush and Bielski (1985)
(12') $Fe(II) + H_2O_2 \rightarrow Fe(III) + OH + OH^-$	6.0(1)	Po and Sutin (1968)
<u>Copper Reactions</u>		
(9"a) $HO_2 + Cu(II) \rightarrow Cu(I) + O_2 + H^+$	1(8)	Rabani et al. (1973)
(9"b) $O_2^- + Cu(II) \rightarrow Cu(I) + O_2$	4.81(9)	Amar et al. (1982)
(10"a) $HO_2 + Cu(I) \xrightarrow{H^+} Cu(II) + H_2O_2$	2.3(9)	Kozlov and Berdnikov (1973)
(10"b) $O_2^- + Cu(I) \xrightarrow{2H^+} Cu(II) + H_2O_2$	1(10)	Rabani et al. (1973)
(12") $Cu(I) + H_2O_2 \rightarrow Cu(II) + OH + OH^-$	4.7(3) 1(2)	Kozlov and Berdnikov (1973) Masarwa et al. (1988)
(25) $Cu(I) + O_2 \rightarrow Cu(II) + O_2^-$	1(6) 1(3) 1(1)	Zuberbühler (1976) Nord (1955) Zuberbühler (1976)

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* Except where indicated, second order rate constant units are l mol^{-1} s^{-1}; read 1(-5) as 1×10^{-5}.

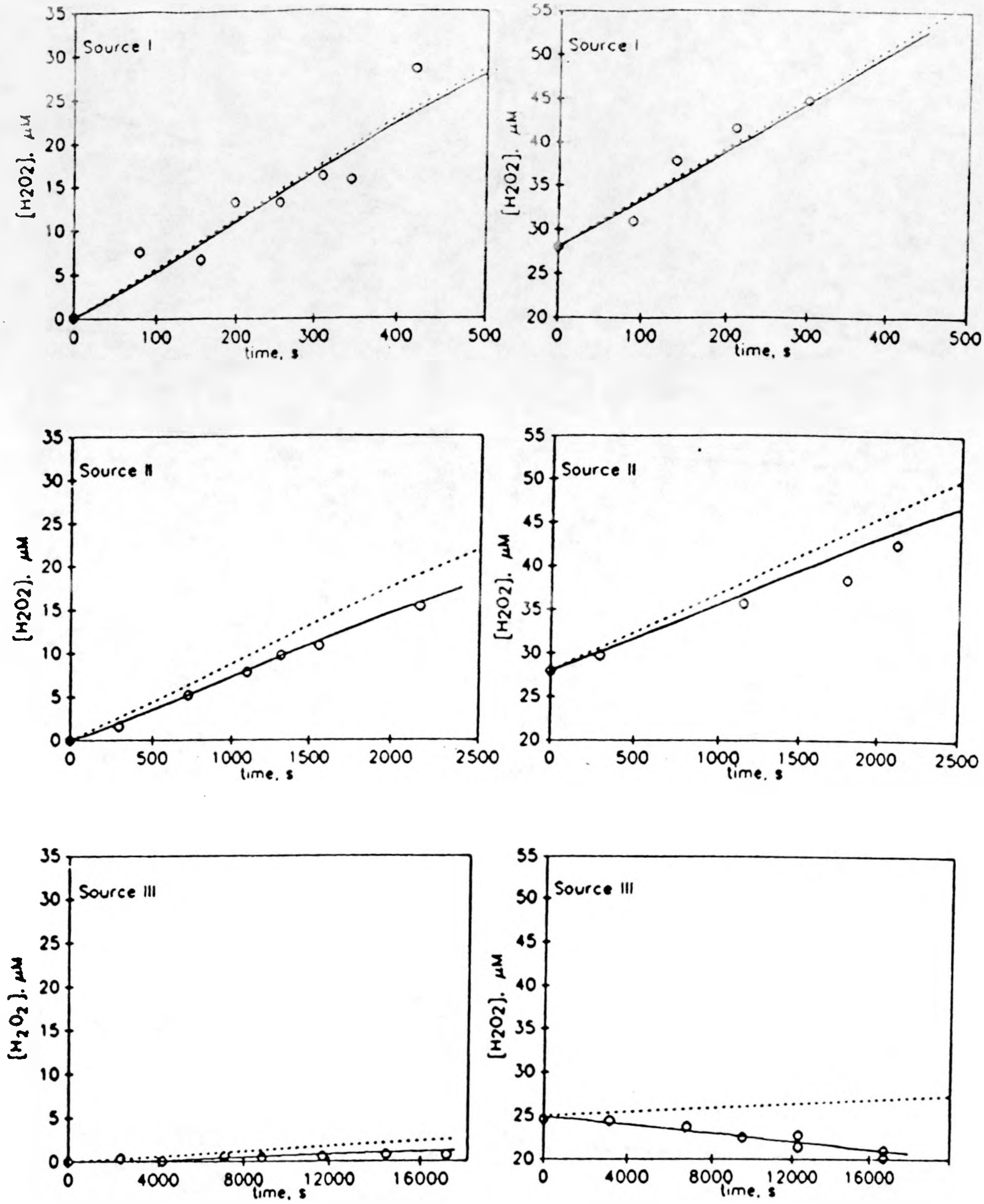

FIGURE 2. Concentration of H_2O_2 as a function of time in irradiated synthetic cloudwater containing 1 μM Fe(III) sulfate. Samples also contained 1 to 2 mM NaOOCH/HCOOH, 25 μM NH_4NO_3, and 35 μM NaCl. pH was adjusted with H_2SO_4 to 2.7. Dashed lines represent G = 3.7; solid lines represent modeled H_2O_2 concentration based on the reactions in Table 1 (from Weinstein-Lloyd and Schwartz, 1991).

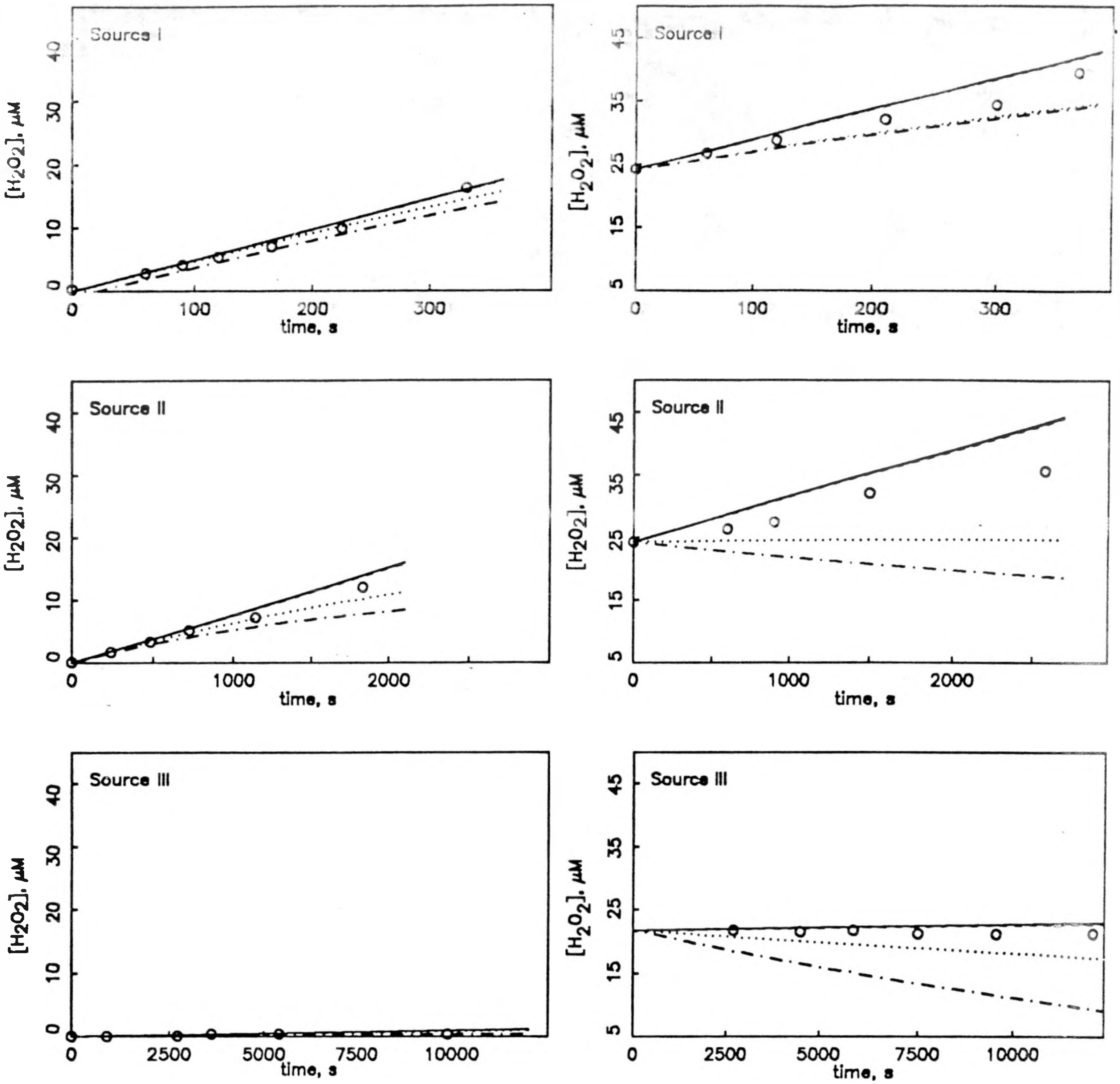

FIGURE 3. Concentrations of H_2O_2 as a function of time in irradiated synthetic cloudwater containing 1 μM Cu(II)sulfate. Samples also contained 1 mM NaOOCH/HCOOH, 12 μM NH_4NO_3, and 18 μM NaCl. pH was adjusted with H_2SO_4 to 4. Solid line represents G = 3.7; other lines represent modeled H_2O_2 concentration based on reaction in Table 1. ----:$k_{12''}$=1(2),k_{25}=1(6); ····:$k_{12''}$=4.7(3),k_{25}=1(3); -·-·: $k_{12''}$=4.7(3),k_{25}=1(1)

H_2O_2 by the reduced transition metal ion produced in reaction (9), i.e., by reaction (12). This departure is greatest when H_2O_2 concentration is high, thereby increasing the rate of reaction (12), as seen in the right-hand panels of Figures 2 and 3. Destruction of H_2O_2 is also greater in source III, where the low steady-state $O_2(-I)$ concentration minimizes loss of Fe(II) by reaction (10) and long irradiation times are employed. Although rate coefficients for reactions (12') and (12") depend strongly

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + OH + OH^- \qquad (12')$$

$$\mathrm{Cu(I)} + H_2O_2 \rightarrow \mathrm{Cu(II)} + OH + OH^- \qquad (12")$$

on solution composition, measurements indicate that the Cu reaction is several orders of magnitude faster than the Fe reaction. In spite of this, the very fast reaction (10") and the fast oxidation of Cu(I) by O_2 conspire to keep the concentration of reduced copper ion low enough to prevent substantial destruction of H_2O_2. The several curves in Figure 3 illustrate sensitivity to the choice of rate constant for reaction (12"), and for the rate of the Cu(I)-O_2 reaction

$$\mathrm{Cu(I)} + O_2 \rightarrow \mathrm{Cu(II)} + O_2^- \qquad (25)$$

Much of the difference in reported rate constants for these reactions is due to complexation of the metal. Rate coefficients used represent the highest and lowest values reported in the literature. The results appear to rule out a rate constant for reaction (25) as high as 10^6, and are consistent with reported rate constants for reaction (12") between 10^2 and $5x10^3$.

4.3 Atmospheric Implications

The effect of dissolved transition metal ions on the rate of formation of H_2O_2 by aqueous phase reactions in clouds has significant atmospheric implications. Using the gas-aqueous model of Schwartz (1984), we have previously demonstrated that micromolar concentrations of iron in cloudwater can significantly increase the rate of H_2O_2 production, but can result in net destruction of preexisting H_2O_2 in cloudwater via Fenton chemistry when H_2O_2 concentration is high (Weinstein-Lloyd and Schwartz, 1991). Based on the rate constants in Table 1, copper ions are also expected to catalyze the rate of production of atmospheric H_2O_2, although the lower steady state concentration of Cu(I) and the generally lower abundance of copper compared to iron should limit the destruction of atmospheric H_2O_2 by Cu(I).

5. CONCLUSION

Low-intensity ^{60}Co radiolysis produces O_2(-I) radicals in samples at concentrations characteristic of those in the ambient atmosphere. In the absence of O_2(-I) scavengers, the principal fate of these radicals is H_2O_2 production. However, when transition metals are present, these ions can be reduced by O_2(-I) and subsequently react with H_2O_2 via Fenton chemistry, thereby decreasing the apparent H_2O_2 yield. Such reactions may be of importance in cloudwater, which often contains transition metals in trace concentrations.

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