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MASTER

THE SOLUBILITY AND DISSOCIATION KINETICS OF HYDROXYMETHYL HYDROPEROXIDE IN AQUEOUS SOLUTION

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ABSTRACT

The Henry's Law solubility of hydroxymethyl hydroperoxide (HMP) and its equilibrium and reaction kinetics in aqueous solution were studied. The equilibrium constants of $H_2O_2 + CH_2O <=> HMP$ (1) and $HMP + CH_2O <=> BHMP$ (2) are $K_1 = 2.35 \times 10^{-2} e^{2610/T} M^{-1}$ and $K_2 = 1.04 \times 10^{-3} e^{2779/T} M^{-1}$, respectively. Both the forward and reverse rates of reaction (1) were base catalyzed between pH 5 and 8. The temperature dependences of these two rate constants at pH 7.07 between 5 and 35 °C are $k_1 = 6.0 \times 10^{13} e^{-9450/T} M^{-1}s^{-1}$ and $k_{-1} = 1.0 \times 10^{15} e^{-11800/T} s^{-1}$. The Henry's Law constant of HMP was determined to be 4.1×10^5 and 6.5×10^5 M atm^{-1} at 22.0 and 10.0 °C, respectively. Exhibiting a large solubility, HMP is expected to be efficiently scavenged by hydrometeors. Because of its rapid decomposition at neutral pH, aqueous HMP is expected to be stable only at pH $\leq$ 5.5.

1. INTRODUCTION

Atmospheric organic peroxides are produced from oxidation of hydrocarbons initiated by O_3 and OH radicals (Becker *et al.*, 1990; Gab *et al.*, 1985; Hanst and Gay, 1983; Martinez *et al.*, 1981). Among the several organic peroxides identified in the atmosphere, hydroxymethyl hydroperoxide (HMP) is of particular interest (Hellpointner and Gab, 1989) because of its phytotoxicity (Marklund, 1971, 1973; Sobels, 1956) and its possible role in forest decline (Becker *et al.*, 1990). In order to assess the atmospheric budget and the environmental importance of this peroxide, knowledge of physical and chemical properties governing its atmospheric lifetime must be determined first. We report in this paper the determination of the Henry's Law solubility and reaction kinetics of HMP in aqueous solution. The information thus determined is needed for assessing the atmospheric lifetime of HMP against wet scavenging by hydrometeors such as cloudwater droplets.

In aqueous solution, HMP is in equilibrium with H_2O_2 and H_2CO, i.e.,

$$CH_2(OH)_2 + H_2O_2 \underset{k_{-1}}{\overset{k_1}{<==>}} H_2O + HOCH_2O_2H \qquad (1), (-1)$$

Reacting with CH_2O, HMP further forms bis(hydroxymethyl)peroxide (BHMP):

$$HOCH_2O_2H + CH_2(OH)_2 <=> HOCH_2OOCH_2OH + H_2O \qquad (2)$$

The equilibria and kinetics of these two reactions have been studied, albeit at reagent concentrations considerably higher than that of the ambient atmosphere, i.e., by 3-4 orders of magnitude (Dunicz *et al.*, 1951; Marklund, 1971). One the other hand, k_1 has recently been studied by Berner and Bizjak (1988) at micromolar concentrations.

2. EXPERIMENTAL

Materials. All the chemicals used were of reagent grade. They include: H_2O_2 (30%), CH_2O (37%), 1 M HCl and NaOH volumetric standards, $NaHSO_3$, KCl, Na_2HPO_4, tris(hydroxymethyl)aminomethane (Tris), and CH_3CO_2Na. N_2 (UHP, 99.999%) was used as the purging gas in the solubility measurements. Millipore Milli-Q water (resistivity $\geq$ 18 Mohm at 25°C) was used for the preparations of solutions.

pH and Temperature Controls. The pH of reaction mixtures was controlled by 1 - 5 mM of the following buffers: phosphate for pH 6 - 8, acetate for pH 4 - 5.5, Tris for pH ~ 8, and HCl for pH $\leq$ 3.3, and was measured by a research grade pH meter (Beckman, Model 4500) equipped with a combination electrode (Orion, Ross electrode). The temperature of the reaction mixtures was maintained constant within ± 0.1 °C using a circulating water bath (Neslab, model RTE-9).

Peroxide Measurement. An amperometric technique was used to measure H_2O_2 in the micromolar concentration range (Lee *et al.*, 1986a). The Oxidase Meter (Yellow Spring Instrument Company, Inc., model 25) used consists of a concentric Pt-Ag electrode pair, a power supply, a current measurement circuit, and a record output. With a 700 mV bias voltage applied to the electrodes, H_2O_2 is oxidized to O_2 on the platinum anode and O_2 is reduced to H_2O on the silver cathode, the resulting current being linearly proportional to $[H_2O_2]$. The detection limit of this device is about 0.1 μM (S/N = 3) and the response time constant is < 0.1 s. The amperometric device does not respond to HMP or BHMP, and these organic peroxides were determined as H_2O_2 following decomposition by dilution (Zhou and Lee, 1991). The response of this device is pH dependent and a detailed characterization has been reported (Shen and Lee, 1986).

Kinetics Measurement. The kinetics of reaction (1) was studied by adding a small portion of H_2O_2 (typically 100 μL) to a 2-20 mM CH_2O solution maintained at a desirable pH, and monitoring the decrease of H_2O_2 as a function of time. Since $[CH_2O]$ was maintained at much greater level than $[H_2O_2]$, i.e., by a factor of $\geq$ 200, the disappearance of H_2O_2 conforms to a first-order kinetics (figure 1a), i.e.,

$$\ln(([H_2O_2]_t - [H_2O_2]_\infty)/([H_2O_2]_0 - [H_2O_2]_\infty)) = -k_{obs}t \qquad (3)$$

where the subscripts 0, t and ∞ denote time 0, t and infinity, and k_{obs} is an apparent pseudo first-order rate constant defined as:

$$k_{obs} = k_{-1} + k_1[CH_2O] \qquad (4)$$

By plotting k_{obs} against $[CH_2O]$, we obtain k_1 and k_{-1} as the slope and intercept, respectively. However, since the intercept is small and subject to large uncertainties, k_{-1} was not determined by this technique. In stead, it was determined by following the formation of H_2O_2 accompanying the decomposition of HMP, i.e., reaction (-1). In this approach, an HMP stock solution was prepared by mixing millimolar levels of H_2O_2 and CH_2O at pH~7 where the equilibria establish rapidly (≤5 min). To initiate an experimental run, a small portion of this solution was added into a buffer solution (dilution factor of 100) and the increase of H_2O_2 from the decomposition of HMP was continuously monitored. Since HMP is completely dissociated under the diluted condition, k_{-1} is readily evaluated by the expression,

$$\ln (([H_2O_2]_T - [H_2O_2]_t)/([H_2O_2]_T - [H_2O_2]_0)) = -k_{-1}t \qquad (5)$$

where the subscript T denotes total. A typical plot of Eq. 5 is shown in Figure 1b. It should be pointed out that k_{-1} was determined with the initial [BHMP] varying between <1% and 15 % of the total peroxide ($[CH_2O] = 2 - 20$ mM). The fact that k_{-1} remained constant within the experimental uncertainty of ± 5% indicates that equilibrium (2) is established sufficiently fast that it does not interfere with the kinetics measurement of reaction (-1).

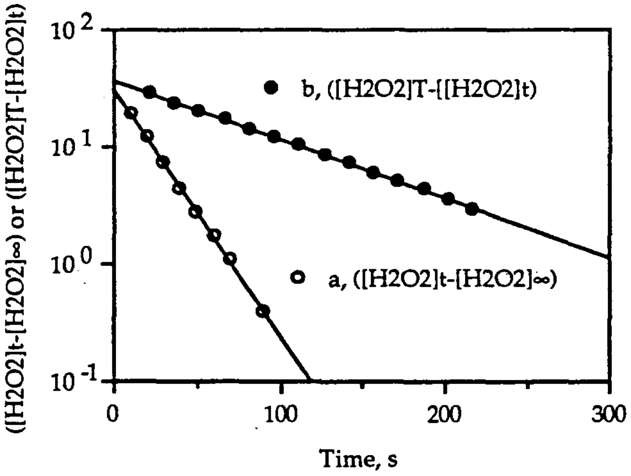

Figure 1. The kinetics of the formation of HMP from H_2O_2 (10 μM) and CH_2O (5 mM), (a), and of the decomposition of HMP in a diluted solution, (b); T= 22.0°C and pH = 7.07.

Equilibrium Measurement. An apparent equilibrium constant defined by

$$K_{app} = ([HMP]_\infty + [BHMP]_\infty)/([H_2O_2]_\infty[CH_2O]) \qquad (6)$$

was determined from the equilibrium concentrations of CH_2O, H_2O_2 and total organic peroxides, HMP + BHMP, in a H_2O_2-H_2CO mixture. Combining Eq. (6) with the equilibrium constants K_1 and K_2, we obtain

$$K_{app} = K_1 + K_1K_2[CH_2O] \qquad (7)$$

K_1 and K_2 can then be determined from the intercept and slope of this equation.

Solubility Measurement. A bubbler gas-liquid reactor containing known concentrations of peroxides was used to generate gaseous peroxides. Since the convective mixing of the reactor is rapid, gas-liquid equilibrium of a dissolved species having Henry's Law constant > 0.3 M atm^{-1} is established under typical conditions of gas flow $F_g \geq 1.0$ L min^{-1} and liquid volume $V_l \leq 50$ mL (Park and Lee, 1988; Lee and Schwartz, 1981). In a typical run, 50 mL of 5 - 30 mM total peroxides and 5 - 30 mM CH_2O maintained at pH 7.20 was bubbled through with pre-humidified N_2 at 1.00 ± 0.05 L min^{-1}. The peroxides in the effluent gas were collected by a scrubber connected down stream. The scrubber (ASTMD1607-69, Public Health Service Publication, 1965) exhibited a collection efficiency of ≥99%. The collection time was between 20 - 60 minutes. Since $[H_2O_2]$ and ([HMP] + [BHMP]) in the mother solution and the total peroxide concentration as H_2O_2 in the scrubbing solution can be determined, the partial pressure of organic peroxides, $p_{HMP} + p_{BHMP}$ (obtained by correcting the contribution of H_2O_2), can be related to ([HMP] + [BHMP]) of the mother solution by an operational Henry's Law constant:

$$H_{op} = ([HMP] + [BHMP])/(p_{HMP} + p_{BHMP}) \quad (8a)$$

which can be rearranged to :

$$H_{op} = H_1H_2(1 + K_2[CH_2O])/(H_2 + H_1K_2[CH_2O]) \quad (8b)$$

where H_1 and H_2 are the Henry's Law constants of HMP and BHMP, respectively. Eq. (8b) can be further rearranged into

$$(1 + K_2[CH_2O])/H_{op} = 1/H_1 + (K_2/H_2)[CH_2O] \quad (9)$$

By plotting $(1 + K_2[CH_2O])/H_{op}$ against $[CH_2O]$, we obtain $1/H_1$ and K_2/H_2 as the intercept and the slope, respectively.

HMP - S(IV) Reaction. A competition technique was employed to determine the reaction rate of HMP with S(IV), using H_2O_2 - S(IV) reaction as a reference. Typically, 2 - 10 µM or 20 - 100 µM of S(IV) was added to an acidic solution (pH 3 - 4) containing 20 µM or 200 µM (H_2O_2 + HMP) to initiate the concurrent reactions of S(IV) with H_2O_2 and HMP, i.e.,

$$H_2O_2 + S(IV) \xrightarrow{k_{10}} \text{products} \quad (10)$$

$$HMP + S(IV) \xrightarrow{k_{11}} \text{products} \quad (11)$$

After S(IV) was depleted (≤ 2 min), the residual $[H_2O_2]$ and [HMP] were measured with the amperometric device. At a constant pH, k_{10} and k_{11} are related to these residual concentrations by:

$$\ln([HMP]_r / [HMP]_0) = (k_{11} / k_{10}) \ln([H_2O_2]_r / [H_2O_2]_0) \quad (12)$$

where subscripts *0* and *r* represent initial and residual. The value of k_{11} was obtained from the slope of Eq. (12), k_{11}/k_{10}, and the known value of k_{10} (Lee *et al.*, 1986a; McArdle and Hoffmann, 1983).

3. RESULTS AND DISCUSSION

Equilibrium Constants. The values of the equilibrium constants of K_1 and K_2 determined from a plot of K_{app} *vs* [CH_2O] (Figure 2) at 25.0 °C are 157 M^{-1} and 11 M^{-1}, respectively. They are in reasonable agreement with the values of 126 and 14.0 M^{-1} reported by Marklund (1971), and are at significant variance from $K_1 = 12 - 45\ M^{-1}$ and $K_2 = 15 - 42\ M^{-1}$ reported by Dunicz *et al.* (1951) for the same temperature. The temperature dependence of K_1 and K_2 was studied between 5 and 35°C (Table 1) and the Arrhenius plot (Figure 3) of the data yielded $K_1 = 0.0235\ e^{2610/T}$ and $K_2 = 0.00104\ e^{2779/T}$. The effects of pH and ionic strength on K_1 and K_2 were found to be insignificant.

Table 1 Summary of equilibrium and rate constants at pH 7.07. ($n \geq 3$ for all values. Standard deviations ≤ 5 % for k_1, k_{-1} and K_1, 10 % for K_2.)

T (°C)	k_1 ($M^{-1}\ s^{-1}$)	$10^2 \times k_{-1}$ (s^{-1})	K_1 (M^{-1})	K_2 (M^{-1})
5.0	0.103	0.0388	275	26.5
10.0	0.195	0.0761	241	16.6
22.0	0.497	0.497	163	12.7
25.0	0.967	0.593	157	10.8
35.0	2.81	2.26	111	9.6

Rate Constants. The apparent first-order rate constant determined for reaction (1), k_{obs}, is plotted in Figure 4 as a function of [CH_2O] according to Eq (5). The values of k_1 evaluated from the slopes (Table 1) are in good agreement with the literature values. For example, the value at 22.0 °C, $1.92 \times 10^{-2}\ M^{-1}\ s^{-1}$, compares well (all at pH 5.50) with $3.1 \times 10^{-2}\ M^{-1}\ s^{-1}$ (25 °C) by Marklund (1971) and $2.0 \times 10^{-2}\ M^{-1}\ s^{-1}$ (22 °C) by Berner and Bizjak (1988). The values of k_{-1} determined between 5 and 35 °C are also

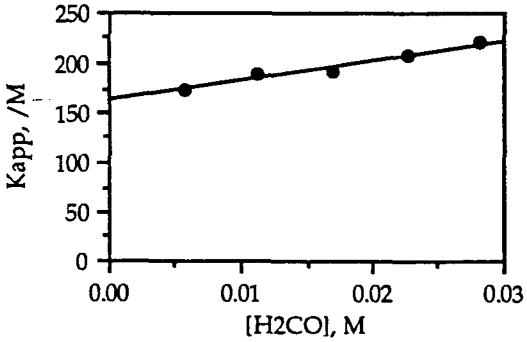

Figure 2. Dependence of K_{app} on [CH_2O] at pH 7.07 and 22.0 °C.

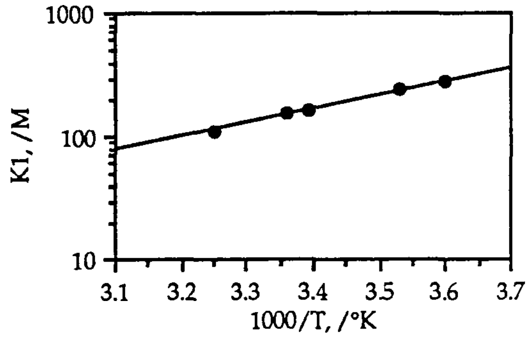

Figure 3. Temperature dependence of K_1 at pH 7.07.

listed in Table 1. The temperature dependence of k_1 and k_{-1} between 5 and 35 °C and at pH 7.07 can be expressed as: $k_1 = 6.0 \times 10^{13}e^{-9450/T}$ (Figure 5) and $k_{-1} = 1.0 \times 10^{15}e^{-11800/T}$. The pH dependence of k_1 and k_{-1} were studied between pH 4 and 8, and both reactions were found to be base catalyzed (Figure 6).

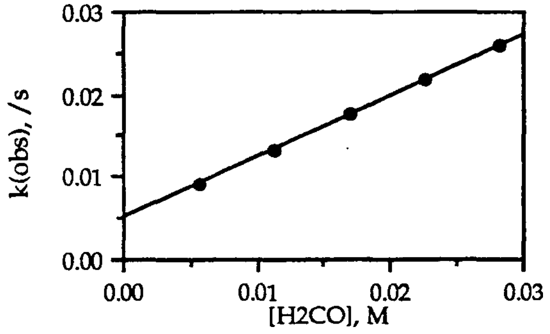

Figure 4. Dependence of k_{obs} on $[CH_2O]$ at 22.0 °C and pH 7.07.

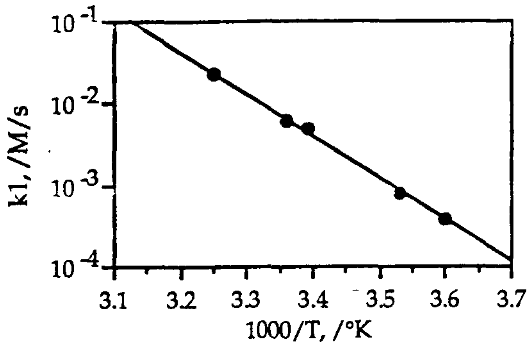

Figure 5. Temperature dependence of k_1 at pH 7.07.

Henry's Law Constants. The Henry's Law constant of H_2O_2 determined in this work, 1.1×10^5 and 2.7×10^5 M atm^{-1} at 22.0 and 10.0 °C, respectively, are used for making corrections of the contribution of H_2O_2 to total peroxide partial pressures. These values are in good agreement with the literature values of 1.4×10^5 M atm^{-1} at 20 °C (Yoshizumi *et al.*, 1984), 1.0×10^5 and 1.1×10^5 M atm^{-1} at 25 and 20 °C, respectively (Martin and Damschen, 1981), and 7.4×10^4 M atm^{-1} at 25 °C (Lind and Kok, 1986).

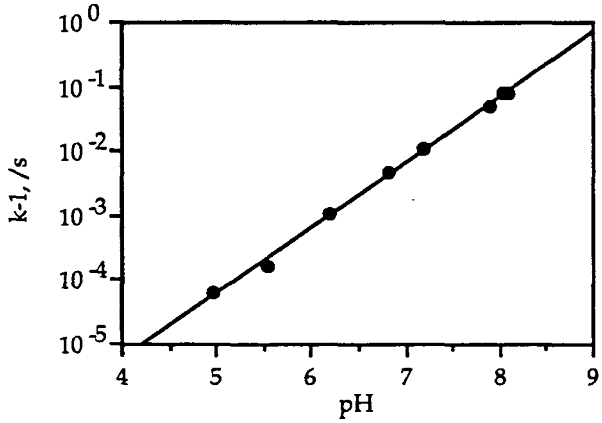

Figure 6. Dependence of k_{-1} on pH at 25.8°C.

The operational Henry's Law constant of the organic peroxides, H_{op} defined by Eq. (8), was determined as a function of $[CH_2O]$. The plot of $H_{op}/(1 + K_2\,[CH_2O])$ *vs* $[CH_2O]$ (Eq. 9) allowed H_1 and H_2 to be determined as $(4.1 \pm 0.5) \times 10^5$ and $(2.3 \pm 1.0) \times 10^6$ M atm^{-1} (22.0 °C), respectively; the values at 10.0 °C are $(6.5 \pm 1.1) \times 10^5$ and $(3.6 \pm 2.0) \times 10^6$ M atm^{-1}, respectively. It may be interesting to note that the Henry's Law constants of HMP and BHMP are exceptionally large. In fact, they are greater than that of H_2O_2. However, this large Henry's Law solubility exhibited by HMP and

BHMP is consistent with the assumption that gem-diol compounds are highly soluble as implied in solubility measurements of aldehydes. In these studies, an apparent solubility is defined as $H^* = H(1 + K_{hyd})$, where H is the intrinsic Henry's Law constant of the unhydrated aldehyde and $K_{hyd} = [RCH(OH)_2]/[RCHO]$; H is determined from the observed H* and known K_{hyd} (Betterton and Hoffmann, 1988). Implicit in this treatment is the assumption that the hydrated species is so soluble that its contribution to the total gas-phase aldehyde is negligible. For a contribution from the hydrated species of, say $\leq 1\%$, the Henry's Law constant of the hydrated species should satisfy the inequality $H_{hyd} \geq 100H^*$. Using CH_2O as an example, we obtain $H_{hyd} = 3 \times 10^5$ M atm^{-1} (25 °C) for methylene glycol, using $H^* = 3 \times 10^3$ M atm^{-1} (Betterton and Hoffmann, 1988; Zhou and Mopper, 1990). Since the substitution of hydroxyl group for hydroperoxyl group gives rise to a negligible effect on the Henry's Law constants, e.g., the values are 220 and 230 M atm^{-1} for CH_3OH (Gaffney and Senum, 1984) and CH_3OOH (Lind and Kok, 1986), respectively, $CH_2(OH)_2$ and $HOCH_2O_2H$ are expected to exhibit similar solubilities. The large Henry's Law constant determined for HMP in fact lends support to the assumption that $CH_2(OH)_2$ is highly soluble.

HMP-S(IV) Reaction. With the competition kinetics technique applied to the study of reactions (10) and (11), we obtain $k_{11}/k_{10} = 0.23$ from Eq. (12) ($r^2 = 0.962$, $n = 17$) at 22.0 °C and pH between 3 and 4. Since $k_{10} = 9.6 \times 10^7 [H^+]$ M^{-1} s^{-1} (Lee *et. al.*, 1986), $k_{11} = 2.2 \times 10^7 [H^+]$ M^{-1} s^{-1}. This value is comparable to those of other organic peroxides: $1.7 \times 10^7 [H^+]$ M^{-1} s^{-1} for CH_3O_2H at 23 °C and $3.5 \times 10^7 [H^+]$ M^{-1} s^{-1} for $CH_3C(O)O_2H$ at 18 °C (Lind *et al.*, 1987).

Atmospheric Implications. Hellpointner and Gab (1989) proposed two pathways for the formation of hydroxyalkyl hydroperoxides in the atmosphere: H_2O_2 addition to aldehydes in the aqueous phase, and H_2O addition to Criegee intermediates in the gas phase. The first pathway, however, is deemed unimportant under ambient conditions because of the small equilibrium ratio of $[HMP]/[H_2O_2]$ (<0.02) stipulated by the typical $[H_2CO]$ (<100 μM) found in atmospheric water (e.g., Lee el al., 1986b). This ratio has been observed to be ~10% in rainwater of pH ≤ 5.5. (Hellpointner and Gab, 1989). The equilibrium of reaction (1) is such that aqueous HMP is decomposed rather than formed under ambient conditions.

Owing to its extremely high aqueous solubility, gaseous HMP is expected to be efficiently scavenged by atmospheric droplets (Jacobs, 1985; Chameides, 1984; Levine and Schwartz, 1982) similar to H_2O_2. Consequently, gaseous HMP should be removed from the atmosphere more effectively than, say, CH_3O_2H (MHP). In deed, the ratio [HMP]/[MHP] was found to be ~3 in rainwater samples, 1 - 2 orders of magnitude greater than the ratio of ~0.1 in the gas phase (Hellpointner and Gab, 1989). The aqueous concentration ratio of ~3 may represent a lower limit because of possible decomposition of HMP prior to chemical analysis.

The half life of aqueous HMP via decomposition is pH dependent and is given by $\tau_{1/2} = (8.1 \times 10^{-9} \times [H^+])\, e^{11800/T}$ s for pH 5 - 8. $\tau_{1/2}$ is in the order of hours below pH 5.5 and of minutes at neutral pH. Such a stability is consistent with the observation that HMP was detected only in acidic rainwater samples (Hellpointner and Gab, 1989).

The possible contribution of HMP to the oxidation of S(IV) is examined in light of the present kinetics results. For [HMP]/[H_2O_2] = 0.1 under typical atmospheric conditions, only 2% S(IV) would be oxidized by HMP compared to that by H_2O_2. However, under conditions of higher HMP concentrations, such as that reported by Kok and Hewitt (1989), *i.e.*, [HMP] ~ [H_2O_2], up to 20% of S(IV) oxidation may be responsible by this organic peroxide.

HMP has been recognized to have several toxic effects on plants, among which is the irreversible inhibition of horseradish peroxidase enzyme (Marklund, 1973). Since HMP is produced from the reaction of O_3 with biogenic alkenes (Hewitt *et al.*, 1990), the die-back of alkenes producing species, such as red spruce and Norway spruce, has been attributed to the toxic effect of HMP, rather than that of O_3 (Hellpointner and Gab, 1989; Hewitt *et al.*, 1990). The high solubility of HMP determined in this work may be consistent with such a proposal because surface deposition of HMP may be facilitated by the large solubility. Finally, acidic precipitation may also enhance the toxicity of HMP by increasing its stability.

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5. REFERENCES

Becker, K. H., Brockmann, K. J., and Bechaea, J. (1990) Production of hydrogen peroxide in forest air by reaction of ozone with terpenes, *Nature,* **346,** 256-258.

Benner, W. H., and Bizjak, M. (1988) Pseudo first-order reaction rate constant for the formation of hydroxymethyl hydroperoxide from formaldehyde and hydrogen peroxide, *Atmos Environ,* **22,** 2603-2605.

Betterton, E. A. and Hoffmann, M. R. (1988) Henry's Law constants of some environmentally important aldehydes, *Environ. Sci. Technol.,* **22,** 1415-1418.

Chameides, W. L. (1984) The photochemistry of a remote marine stratiform cloud. *J. Geophys. Res.* **89,** 4739-4755.

Dunicz, B. L., Perrin, D. D., and Style, D. W. G. (1951) The reaction between aldehydes and hydrogen peroxide in acid solution; Part I, formaldehyde, *Trans Faraday Soc.,* **47,** 1210-1215.

Gab, S. E. Hellpointner, Turnerm, W. V., and Korte, F. (1985) Hydroxymethyl hydroperoxide and bis(hydroxymethyl) peroxide from gas-phase ozonolysis of naturally occurring alkenes, *Nature,* **316,** 535-536.

Gaffney, J. S. and Senum, G. I. (1984) Peroxides, peracids, aldehydes and PANs and their links to natural and anthropogenic organic soureces. In the Proceedings of

"Gas-Liquid Chemistry of Natural Waters", Brookhaven National Laboratory, Upton, NY, April 1984.

Hanst, P. L., and Gay, Jr., B. W. (1983) Atmospheric oxidation of hydrocarbons: formation of hydroperoxides and peroxyacids, *Atmos. Environ.*, **17**, 2259-2265.

Hellpointner, E. and Gab, S. (1989) Detection of methyl, hydroxymethyl and hydroxyethyl hydroperoxides in air and precipitation, *Nature,* **337**, 631-634.

Hewitt, C. N., Kok, G. L. and Fall, R. (1990) Hydroperoxides in plants exposed to ozone mediate air pollution damage to alkene emitters, *Nature,* **344**, 56-58.

Jacob, D. (1985) Comment on "the photochemistry of a remote stratiform cloud" by W.L. Chamedies, *J. Geophys. Res.*, **90D**, 5864.

Kok, G. L., and Hewitt, C. N. (1980) Measurement of hydrogen peroxide and organic hydroperoxides at Niwot Ridge, Colorado, *EOS Trans. AGU,* **70**, 1019.

Lee, Y. -N. and Schwartz, S. E. (1981) Reaction kinetics of nitrogen dioxide with liquid water at low partial pressure, *J. Phys. Chem.*, **85**, 840-848.

Lee, Y. -N., Shen, J., Klotz, P. J., Schwartz, S. E., and Newman, L. (1986a) Kinetics of hydrogen peroxide-sulfur (IV) reaction in rainwater collected at a Northeastern U.S. site, *J.Geophys. Res.*, **91D**, 13264-13274.

Lee, Y. -N., Shen, J. and Klotz, P. J. (1986b) Chemical composition of precipitation at Long Island, NY, *Water, Air and Soil Pollution*, **30**, 143-152.

Levine, S. Z. and Schwartz, S. E. (1982) In-cloud and below-cloud scavenging of nitric acid vapor, *Atmos. Environ.*, **16**, 1725.

Lind, J. D. and Kok, G. L. (1986) Henry's Law determinations for aqueous solutions of hydrogen peroxide, methylhydroperoxide, and peroxyacetic acid., *J. Geophys. Res.*, **91**, 7889-7895.

Lind, J. D., Lazrus, A. L., and Kok, G. L. (1987) Aqueous phase oxidation of sulfur (IV) by hydrogen peroxide, methylhydroperoxide, and peroxyacetic acid, *J. Geophys. Res.*, **92**, 4171-4177.

Marklund, S. (1971) The simultaneous determination of bis(hydroxymethyl) peroxide (BHMP), hydroxymethylhydroperoxide (HMP), and H_2O_2 with titanium (IV). Equilibria between the peroxides and the stabilities of HMP and BHMP at physiological conditions, *Acta Chem, Scand.*, **25**, 3517-3531.

Marklund, S. (1973) Mechanisms of the irreversible inactivation of horseradish peroxidase caused by hydroxymethylhydroperoxide, *Archs. Biochem. Biophys.*, **154**, 614-622.

Martin, L. R. and Damschen, D. E. (1981) Aqueous oxidation of sulfur dioxide by hydrogen peroxide at low pH, *Atmos. Environ.*, **15**, 1615-1621.

Martinez, R. I., Herron, J. T., and Huie, R. E. (1981) The mechanism of ozone-alkene reactions in the gas phase. A mass spectrometric study of the reactions of eight linear and branched-chain alkenes, *J. Am. Chem. Soc.*, **103**, 3807-3812.

McArdle, J. V., and Hoffmann, M. R. (1983) Kinetics and mechanism of the oxidation of aquated sulfur dioxide by hydrogen peroxide at low pH, *J. Phys. Chem.*, **87**, 5425-5429.

Park, J. -Y. and Lee, Y. -N. (1988) Solubility and decomposition kinetics of nitrous acid in aqueous solution, *J. Phys. Chem.*, **92**, 6294-6302.

Public Health Service Publication. (1965) Selection Methods for the Measurement of Air Pollutants, No. 999-AP-11.

Shen, J. and Lee, Y. -N. (1986) Computer-assisted study of the kinetics of H_2O_2-S(IV) reaction in precipitation samples. BNL Foraml Report-52013, Brookhaven National Laboratory, Upton, New York, 11973.

Sobels, F. H. (1956) Organic peroxides and mutagenic effects in Drosophia. *nature,* **177**, 979-982.

Yoshizumi, K., Aoki, K., Houchi, I., Okita, T., Kobayashi, T., Kamakura, S., and Tajima, M. (1984) Measurements of the concentration in rainwater and of the Henry's Law constant of hydrogen peroxide, *Atmos. Environ.*, **18**, 385-401.

Zhou, X. and Mopper, K. (1990) Apparent partition coefficients of 15 carbonyl compounds between air and seawater and between air and freshwater; Implications for air-sea exchange. *Environ. Sci. Technol.*, **24**, 1864-1869.

Zhou, X. and Lee, Y. -N., Aquous solubility and reaction kinetics of hydroxymethyl hydroperoxide. *J. Geophys. Res.* (1991). In preparation.