The Hydroperoxyl Radical in Atmospheric Chemical Dynamics: Reaction with Carbon Monoxide

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The transient species HO₂ has long been postulated to play an important role in atmospheric chemistry (1). Of considerable interest has been the reaction sequence 1, 2, and 3

\[ \text{HO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{OH} \] (1)

\[ \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \] (2)

\[ \text{H} + \cdot \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \] (3)

where M is a third body. This chain sequence would represent a very efficient mechanism for conversion of CO to CO₂ in the atmosphere. The possible importance of this coupled set of reactions 1, 2, and 3 do, in fact, represent an efficient sink for the conversion of CO to CO₂. Westenberg's measurements further imply that the efficient conversion of CO to CO₂ could take place even in the absence of nitric oxide. Our purpose here is to report on recent measurements in our laboratory which indicate that reaction 1 cannot be of significance in defining the chemical dynamics of either the troposphere or the stratosphere.

In most of the experiments in this study, the production of HO₂ was via the third order reaction 3. Recent measurements in our laboratory by the flash photolysis–resonance fluorosence technique have given the absolute rate constant for this reaction at 300°K as 1.95 \times 10^{-12} \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1} for

\[ \text{M} = \text{Ar} \text{ and } 6.26 \times 10^{-25} \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1} \text{ for } \text{M} = \text{N}_2 \] (7). Foner and Hudson (8) also obtained direct mass spectrometric evidence indicating the formation of HO₂ from the photolysis of H₂O₂. The mechanism of formation was believed to be that of reactions 5 and 6.

The experimental apparatus used in this study consisted of a 300-cm³ Pyrex photolysis cell equipped with a 1-inch Suprasil window (transmitting wavelengths above 1650 Å), a Hg resonance lamp, and a high-vacuum submanifold system through which the gases H₂O, CO, O₂1₈,1₈, and Ar could be metered into the photolysis cell. The output of the Hg resonance lamp was examined on a vacuum ultraviolet monochromator and was found to consist of nearly equal amounts of the two lines, 1849 and 2537 Å. In these experiments, no attempt was made to block the 2537-Å line since neither the reactants (H₂O, CO, O₂, Ar) nor the product (CO₂) absorbed significantly at this wavelength. Blank experiments with H₂O absent from the photolysis mixture indicated that production of CO₂ from mechanisms involving reactive species other than OH and HO₂ (9) was always less than 2 percent of the total product CO₂ observed. Analysis of the products, CO₂1₈,1₈ and O₂1₆,1₆, was carried out by using a mass spectrometer (Consolidated Electrodynamics Corporation model 21-620). All reactants used in these experiments were research grade and had stated purities of 99+ percent. Both the CO and the O₂1₈,1₈ were passed slowly through a liquid N₂ cold trap filled with glass beads before being used in photolysis experiments. In the case of CO, traces of iron carbonyl and CO₂ were removed. For O₂1₈,1₈ small amounts of CO₂1₆,1₆ had to be separated from the oxygen. Blank experiments carried out at the highest pressures of CO and Ar used in the reported experiments showed the residual CO₂ pressure al-
ways to be less than 1 mtorr. All experiments carried out at 300 K.

Experiments performed in this study were done with the gases in 0.918, 1.8, 3.4, and 6 mtorr of CO2 product. From a consideration of the mechanism for the photolysis of H2O at 1849 Å in the presence of O18, 1.8, and CO, that is,

\[ \text{H}_2\text{O} + hv \rightarrow \text{H} + \cdot \text{OH} \quad (7) \]
\[ ^{16}\text{OH} + \text{CO} \rightarrow \text{CO}^{18}\text{O} + ^{16}\text{H} \quad (2) \]
\[ \text{H} + \text{O}^{18}\text{O} + \text{Ar} \rightarrow \text{HO}^{18}\text{O} + \text{Ar} \quad (3) \]
\[ \text{HO}^{18}\text{O} + \text{CO} \rightarrow \text{CO}^{18}\text{O} + ^{16}\text{OH} \quad (1) \]
\[ ^{16}\text{OH} + \text{CO} \rightarrow \text{CO}^{16}\text{O} + ^{16}\text{H} \quad (2') \]
\[ \text{HO}^{18}\text{O} + \text{HO}^{18}\text{O} \rightarrow \]
\[ \text{H}_2\text{O}^{18}\text{O} + ^{16}\text{O} \quad (4) \]
\[ \text{H}_2\text{O} + \cdot \text{H} \rightarrow \cdot \text{OH} \quad (5') \]

the following qualitative observation can be made: If the chain length for the reaction sequence 1, 2', 3, and 5' leads to the mathematical relationship:

\[ \frac{[\text{R(CO}^{16}\text{O}]/[\text{R(CO}^{18}\text{O}])]}{[\text{R(CO}^{16}\text{O}]/[\text{R(CO}^{18}\text{O}])]}^{1/2} \approx \frac{2k_a[\text{CO}]}{k_1} + \frac{J_1[\text{H}_2\text{O}]}{J_1[\text{H}_2\text{O}]}^{1/2} \]

where \( R(CO^{16}\text{O}) \) and \( R(CO^{18}\text{O}) \) are the rates of formation of labeled and unlabeled \( CO_2 \) in units of molecules per cubic centimeter per second. (The second term on the right hand side of equation 1 has been separated from the first term under experimental conditions such that \( J_1[\text{H}_2\text{O}] < k_1[\text{H}_2\text{O}] \) and \( J_1[\text{H}_2\text{O}] < k_1[\text{H}_2\text{O}] \). A plot of the ratio \( \text{R(CO}^{16}\text{O}]/[\text{R(CO}^{18}\text{O}])^{1/6} \) against \( \text{[CO]} \), therefore, should yield a slope equal to the rate constant ratio \( 2k_a/ \[k_1]^{1/2} \). Figure 1 shows the results of this type of plot with the solid line representing a least squares fit of four data points. It is apparent from this plot that the best fit to the data is a slope approximately equal to 0, thus indicating a vanishingly small rate constant for reaction 1. In an effort to obtain an upper limit for the value of the rate constant for reaction 1, error limits of \( \pm 30 \) percent were placed on each of the data points in Fig. 1 and the maximum possible slope was then drawn through these error limits. By using the preferred value of \( k_1 \) (10) of \( 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1} \), a maximum value for \( k_1 \) was calculated as \( 1.5 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1} \) (11). This extremely low value of \( k_1 \), is to be compared with the value recently reported by Westenberg and de Haas (5) of approximately \( 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1} \). Because of the enormous disagreement in these values of \( k_1 \), carefnul consideration was given to possible sources of errors in each of the respective experimental systems. One such possibility would be the absence of or extremely low concentrations of HO2 in this work as compared with Westenberg's. To test this hypothesis, a new experiment was performed in which the HO2 was formed from the reaction sequence 5 and 6. In this experiment, 1.5 torr of \( H_2O_2 \) was photolyzed at 1849 Å in the presence of 500 mtorr of CO and 1 torr of \( O_2 \). In this case the oxygen was not labeled and the reactivity of \( HO_2 \) toward CO was indicated by a comparison of the total experimental yield of \( CO_2 \) with the theoretical or calculated yield. In this experiment, the 1849 Å intensity was 5 \times 10^{10} \text{ photons cm}^{-2} \text{ sec}^{-1} (12) and the photolysis time 10 minutes. Using the known extinction coefficient for \( H_2O_2 \) at 1849 Å (35 cm\(^{-1}\) atm\(^{-1}\) (13)), it was calculated that if each OH radical generated one \( HO_2 \) (reaction 6) and this in turn reacted with CO to produce one \( CO_2 \) molecule, the yield of \( CO_2 \) would have been approximately 300 mtorr. What was observed, in fact, was 6 mtorr of \( CO_2 \) product. From a consideration of the rate constants for reactions 6 and 3 and also the relative concentrations of \( H_2O_2 \) and CO, it can be calculated that 4 to 8 percent of the initially formed OH should have reacted with CO to form \( CO_2 \). The 2 percent yield observed experimentally indicates that within the uncertainty of the measurements and calculations (±10 percent), \( HO_2 \) generated via reactions 5 and 6 shows no greater reactivity toward CO than that produced in the original set of experiments from process 3.

More recent experiments in our laboratory, using the photochemical \( O_2^{18}\text{O} \) isotope technique, have demonstrated that \( HO_2 \) generated via processes 7, 2', and 3 readily reacts with both \( SO_2 \) and NO (14). Rate constants for these reactants were found to be \( 3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1} \) (± factor of 3) for reaction with NO and \( 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1} \) (± factor of 2) for \( SO_2 \) (14). These latter results, in addition to demonstrating the presence of \( HO_2 \) in the photochemical experiments, imply that the \( HO_2 \) and \( HO_2-SO_2 \) reactions are probably of considerable importance in both tropospheric and stratospheric chemistry.

Concerning other possible reasons for the large difference in the value of \( k_1 \) measured by Westenberg and de Haas (5) and in this laboratory, one likely possibility is that the \( HO_2 \) generated in Westenberg's experiment reacted with the CO while still in a non-Boltzmann distribution. The non-Boltzmann distribution for \( HO_2 \) would result from the high exothermicity of reaction 3, that is, 47 kcal. Thus, the stabilized \( HO_2 \) from this reaction could easily have internal energy in excess of 40 kcal. In the experiment of Westenberg and de Haas, a flow system was employed in which the total pressure was usually 5 torr or less. In the experiments reported here both high pressures (40 to 200 torr) and a strong quenching environment (for example, 20 torr of \( H_2O \)) were employed. In the \( H_2O_2 \) experiment, the \( HO_2 \) formed via the second order reaction 5 would also not be expected to contain large amounts of excess internal energy even though the enthalpy change, \( \Delta H \), for this reaction is -29 kcal. In this system any internal energy appearing in the reaction products would be expected to appear primarily in that product involving the formation of a new chemical bond (that is, \( H-OH \) (15)).
reaction of the thermallyized HO₂ radical with CO is exceedingly slow ($k_1$ probably less than $10^{-20}$ cm$^3$ mole$^{-1}$ sec$^{-1}$) and that this reaction should not, therefore, be of any significance in atmospheric chemistry. The large discrepancy between the results of Westenberg and de Haas and our results might be explained in terms of the reacting hydroperoxyl radical being in a non-Boltzmann distribution in the former study. Finally, the most important reactions of thermallyized HO₂ in the atmosphere would appear to be those with the trace gases NO and SO₂.

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References and Notes

2. Other competing atmospheric reactions for the species OH and H include the following:

\[
\begin{align*}
\text{H} + \text{O}_3 &\rightarrow \text{OH} + \text{O}_2 \\
\text{OH} + \text{RH} (\text{sat}) &\rightarrow \text{H}_2\text{O} + \text{R} \\
\text{OH} + \text{RH} (\text{unsat}) &\rightarrow \text{products} \\
\text{OH} + \text{NO}_2 + \text{M} &\rightarrow \text{HNO}_3 + \text{M} \\
\text{OH} + \text{NO} + \text{M} &\rightarrow \text{HNO}_2 + \text{M} \\
\text{OH} + \text{H}_2\text{O}_2 &\rightarrow \text{HO}_2 + \text{H}_2\text{O} 
\end{align*}
\]

where R is either a saturated or unsaturated hydrocarbon radical. The uncertainty in the rate constants for reactions 2 and 3 and a to f range from a low of 2±15 percent to a high of 2±10 factor of 6.


9. In the absence of H₂O, the following reactions could have resulted in a limited production of CO$_2$:

\[
\begin{align*}
\text{O} + \nu &\rightarrow 2\text{O} \\
\text{O} + \text{CO} + \text{M} &\rightarrow \text{CO}_2 + \text{M} \\
\text{O} + \text{O}_3 + \text{M} &\rightarrow \text{O}_2 + \text{M} \\
\text{O}_3 + \text{CO} &\rightarrow \text{CO}_2 + \text{O}_2 
\end{align*}
\]


11. If it is assumed that chain termination occurs not via reaction 4 but rather a process such as diffusion of HO₂ to the walls, the upper limit for the rate constant for reaction 1 is found to be $\lesssim 10^{-10}$ cm$^3$ mole$^{-1}$ sec$^{-1}$. On the other hand, if the principal loss mechanism for HO₂ is due to reaction with impurities, the upper limit for $k_1$ is found to be $\lesssim 1 \times 10^{-18}$ cm$^3$ mole$^{-1}$ sec$^{-1}$. In the latter case the impurity level for CO was placed at 0.1 percent (CO) and a rate constant of $10^{-18}$ cm$^3$ mole$^{-1}$ sec$^{-1}$ was selected for the reaction of HO₂ with this impurity. Since hydrogen peroxide was observed as a product in these studies both of the above possibilities can probably be discounted.

12. The intensity of the H$_2$ resonance lamp at 1849 A was determined from a measurement of the yield of H$_2$ (quantum yield, $\phi$, approximately 1.4) in the photolysis of N$_2$O.

Deep-Sea Benthic Community Respiration:
An in situ Study at 1850 Meters

Abstract. The in situ oxygen uptake of sediments at 1850 meters on the continental slope south of New England is two orders of magnitude less than the uptake of sediments from shallow shelf depths. After treatment of the sediments with Formalin there was no measurable chemical oxygen uptake, which shows that the total uptake is biological (community respiration).

The deep-sea benthos live under conditions of low food supply and high hydrostatic pressure. Measurements of the rate of food supply to these organisms are lacking, but it is assumed to be low because of the logarithmic decrease in animal numbers and biomass with depth (1) and because of the comparatively low organic content in deep-ocean sediments (2). Metabolic effects of high pressure have not been studied in deep-sea benthic animals, but Jannasch et al. (3) found microbial degradation to be 10 to 100 times slower in the deep sea than in controls at the same temperature but at surface pressure. Therefore, one can predict that deep-sea communities will show an inverse relationship between water depth and oxygen uptake due to pressure. This occurs in an environment increasingly food limited with depth.

Pamatmat (4) measured benthic metabolic rates on sediment cores retrieved from 2800 and 2900 m. These samples were subjected to changes in both pressure and temperature before measurements were made. Also, attempts have been made to calculate the oxygen requirements of deep-sea benthos by using respiration data for similar species of shallow-water animals (5). We report here the first in situ measurements of oxygen uptake, as a measure of metabolic activity, made on undisturbed deep-sea benthic communities.

We visually placed in situ respirometers (bell jars) at a deep-sea bottom station, located 217 km south of Cape Cod at 39°46'N, 70°40'W, from the research submersible D.S.R.V. Alvin at 1850 m. This environment is characterized by a bottom current of 0.25 to 0.5 cm/sec, foraminiferal ooze sediment, and temperatures ranging from 3.7° to 4.5°C (6). The respirometer unit consisted of two capped Plexiglas cylinders serving as chambers which, when placed on the sediment, enclosed areas of 48 cm$^2$. A polarographic oxygen electrode (7) in each chamber fed a signal through an operational amplifier to a Rustrak recorder housed in a glass, pressure-resistant sphere atop the unit. Power was supplied from batteries in the sphere. Each chamber was stirred by a magnetically driven stirrer. Measurements of the total oxygen uptake were made over a period of 48 to 72 hours during which the oxygen concentration changed by 12 to 18 percent. Formalin injections, used to poison the biological oxygen demand, were made with an ampule mounted within each chamber; the ampule was broken by a plunger operated by Alvin's mechanical arm.

Table 1. In situ measurements of oxygen consumption of bottom sediments from various locations.

<table>
<thead>
<tr>
<th>Location</th>
<th>Total uptake (mg m$^{-2}$ hr$^{-1}$)</th>
<th>Community respiration (mg m$^{-2}$ hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bermuda subtidal, 21°C</td>
<td>22.9</td>
<td>22.9</td>
</tr>
<tr>
<td>Woods Hole outfall, 22°C</td>
<td>67.8</td>
<td>52.8</td>
</tr>
<tr>
<td>Buzzards Bay, 22°C</td>
<td>54.6</td>
<td>46.8</td>
</tr>
<tr>
<td>Puget Sound subtidal, 7°C</td>
<td>7.6</td>
<td>7.6</td>
</tr>
<tr>
<td>Slope, 1850 m</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>


16. Supported in part by the Climatic Impact Assessment Program, Office of the Secretary, Department of Transportation. The work reported on was performed at Goddard Space Flight Center and the University of Maryland and is part of a thesis submitted by W.A.P. to the faculty of the University of Maryland in partial fulfillment of the requirements for the master's degree in chemistry.  