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Reviewed work(s):
Source: *Science*, New Series, Vol. 179, No. 4070 (Jan. 19, 1973), pp. 280-282
Published by: American Association for the Advancement of Science
Stable URL: http://www.jstor.org/stable/1735678
Accessed: 28/06/2012 16:35

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15. Supported by grant GA 21472 from the National Science Foundation and grant N22-201-72G from the National Oceanic and Atmospheric Administration. Lamont-Doherty Geological Observatory Contribution No. 1821.

6 October 1972; revised 15 November 1972 ■

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

Abstract. *From measurements of the photochemical rate of production of* $CO_2^{16,18}$ *and* $CO_2^{16,16}$*, produced from the low intensity photolysis of mixtures of CO,* H_2O*, Ar, and* $O_2^{18,18}$*, the rate constant for the reaction* $HO_2 + CO \rightarrow CO_2 + OH$ *has been determined at 300°K to be less than or equal to* 10^{-20} *cubic centimeter per molecule per second. These measurements indicate that the reaction of thermalized* HO_2 *is of negligible importance as a sink mechanism for converting CO to* CO_2 *in either the troposphere or the stratosphere.*

The transient species HO_2 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

$$HO_2 + CO \rightarrow CO_2 + OH \qquad (1)$$

$$OH + CO \rightarrow CO_2 + H \qquad (2)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (3)$$

where M is a third body. This chain sequence would represent a very efficient mechanism for conversion of CO to CO_2 in the atmosphere. The possible importance of this coupled set of reactions, however, depends on whether or not the rates of the above processes are greater than those for possible competing reactions involving the transient species H, OH, and HO_2. Essential to this evaluation, therefore, are the rate constants for reactions 1, 2, and 3, as well as for possible competing reactions. With regard to reactions 2 and 3 and several other atmospheric reactions of H and OH, the rate constants are reasonably well known for purposes of this evaluation (*2*). In the case of reaction 1 and other competing reactions involving the HO_2 species, the situation is much less satisfactory. In fact, until quite recently, the only available rate constant for reaction 1 was that provided by Baldwin *et al.* (*3*), who calculated the value of k_1 at temperatures in the vicinity of 770°K from measurements of the rate constant ratio k_1/k_4. Reaction 4 in this system was the disproportionation reaction

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (4)$$

An extrapolation of these rate data (*4*) to 300°K yields a value of approximately 10^{-24} cm^3 molec^{-1} sec^{-1} for k_1.

More recently Westenberg and de Haas (*5*) have estimated a rate constant for reaction 1 at 300°K of approximately 1×10^{-12} cm^3 molec^{-1} sec^{-1}, 12 orders of magnitude greater than Baldwin's estimate. Westenberg (*6*) has suggested, therefore, that the coupled set of reactions 1, 2, and 3 do, in fact, represent an efficient sink for the conversion of CO to CO_2. Westenberg's measurements further imply that the efficient conversion of CO to CO_2 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 HO_2 was via the third order reaction 3. Recent measurements in our laboratory by the flash photolysis–resonance fluorescence technique have given the absolute rate constant for this reaction at 300°K as 1.95×10^{-32} cm^6 molec^{-2} sec^{-1} for $M = Ar$ and 5.26×10^{-32} cm^6 molec^{-2} sec^{-1} for $M = N_2$ (*7*). Foner and Hudson (*8*) have also detected the HO_2 radical mass spectrometrically when produced from reaction 3, thus demonstrating the production of this species in the H-O_2-M system. In a limited number of experiments, we generated HO_2 via the photolysis of H_2O_2. In this system, an excess of H_2O_2 over CO ensured that most of the initially formed OH reacted with H_2O_2 to produce HO_2; for example

$$H_2O_2 + h\nu \rightarrow 2OH \qquad (5)$$

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \qquad (6)$$

Foner and Hudson (*8*) also obtained direct mass spectrometric evidence indicating the formation of HO_2 from the photolysis of H_2O_2. The mechanism of formation was believed to be that of reactions 5 and 6.

Table 1. Data for the reaction of HO_2 with CO. The concentrations of the reactants were 20 torr H_2O and 1 torr $O_2^{18,18}$. The total pressure was 200 torr (Ar + CO) and the photolysis time approximately 14 minutes at an intensity of 3×10^{14} photons cm^{-2} sec^{-1}. The total yield of CO_2 was 8 to 14 mtorr. In blank experiments the yield of CO_2 was about 0.4 mtorr. The reproducibility of the results was ± 15 percent; the results presented here are the averages from 25 experiments.

CO (torr)	Relative yield	
	$CO_2^{16,16}$	$CO_2^{18,18}$
1	100	6.3
10	100	6.8
40	100	6.2
150	100	6.4

The experimental apparatus used in this study consisted of a 300-cm^3 Pyrex photolysis cell equipped with a 1-inch Suprasil window (transmitting wavelengths above 1650 Å), a Hg resonance lamp, and a high-vacuum (10^{-6} mm) submanifold system through which the gases H_2O, CO, $O_2^{18,18}$, 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 (H_2O, CO, O_2, Ar) nor the product (CO_2) absorbed significantly at this wavelength. Blank experiments with H_2O absent from the photolysis mixture indicated that production of CO_2 from mechanisms involving reactive species other than OH and HO_2 (*9*) was always less than 2 percent of the total product CO_2 observed. Analysis of the products, $CO_2^{16,18}$ and $CO_2^{16,16}$, 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 $O_2^{18,18}$ were passed slowly through a liquid N_2 cold trap filled with glass beads before being used in photolysis experiments. In the case of CO, traces of iron carbonyl and CO_2 were removed. For $O_2^{18,18}$ small amounts of $CO_2^{18,18}$ 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 CO_2 pressure always to be less than 1 mtorr. All experiments performed in this study were carried out at 300°K.

The results from those experiments involving the mixtures H_2O, CO, $O_2^{18,18}$, and Ar are shown in Table 1. From Table 1 it is apparent that only approximately 1/15 of the total amount of CO_2 produced was labeled with oxygen-18. More importantly, it is observed that varying the [CO] from 1 to 150 torr produced no significant change in the relative yield of $CO_2^{16,18}$. From a consideration of the mechanism for the photolysis of H_2O at 1849 Å in the presence of $O_2^{18,18}$, Ar, and CO, that is,

$$H_2O^{16} + h\nu \rightarrow H + {}^{16}OH \tag{7}$$

$${}^{16}OH + CO^{16} \rightarrow CO_2^{16,16} + H \tag{2}$$

$$H + O_2^{18,18} + Ar \rightarrow HO_2^{18,18} + Ar \tag{3}$$

$$HO_2^{18,18} + CO^{16} \rightarrow CO_2^{16,18} + {}^{18}OH \tag{1}$$

$${}^{18}OH + CO^{16} \rightarrow CO_2^{16,18} + H \tag{2'}$$

$$HO_2^{18,18} + HO_2^{18,18} \rightarrow H_2O_2^{18,18} + O_2^{18,18} \tag{4}$$

$$H_2O_2^{18,18} + h\nu \rightarrow 2HO^{18} \tag{5'}$$

the following qualitative observation can be made: If the chain length for the reaction sequence 1, 2′, and 3 is unity or greater, the ratio $CO_2^{18,16}/CO_2^{16,6}$ will always be greater than unity. As shown in Table 1 this is not the case even for pressures of CO as high as 150 torr. (The small but constant production of $CO_2^{16,18}$ in these experiments is believed to arise from the photolysis of $H_2O_2^{18,18}$ reaction 5′.)

A steady state treatment of reactions 7, 2, 3, 1, 2′, 4, and 5′ leads to the mathematical relationship:

$$\frac{R(CO_2^{16,18})}{[R(CO_2^{16,16})]^{1/2}} = \frac{2k_1[CO]}{(k_4)^{1/2}} + \frac{J_{5'}[H_2O_2]}{(J_7[H_2O])^{1/2}} \tag{I}$$

where $R(CO_2^{16,18})$ and $R(CO_2^{16,16})$ 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 I has been separated from the first term under experimental conditions such that $J_{5'}[H_2O_2] < k_4[HO_2]^2$ and $J_{5'}[H_2O_2] < J_7[H_2O]$.) A plot of the ratio $R(CO_2^{16,18})/[R(CO_2^{16,16})]^{1/2}$ against [CO], therefore, should yield a slope equal to the rate constant ratio $2k_1/(k_4)^{1/2}$. 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 ±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_4 *(4, 10)* of 3.3×10^{-12} cm^3 molec^{-1} sec^{-1}, a maximum value for k_1 was calculated as 1.5×10^{-20} cm^3 molec^{-1} sec^{-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} cm^3 molec^{-1} sec^{-1}. Because of the enormous disagreement in these values of k_1, careful 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 HO_2 in this work as compared with Westenberg's. To test this hypothesis, a new experiment was performed in which the HO_2 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 5×10^{15} photons cm^{-2} 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.

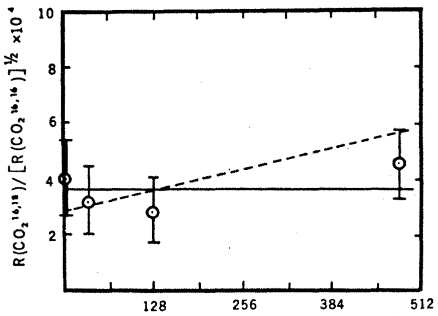

Fig. 1. Plot of the ratio $R(CO_2^{16,18})/[R(CO_2^{16,16})]^{1/2}$ against the concentration of CO.

More recent experiments in our laboratory, using the photochemical $O_2^{18,18}$ 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 3×10^{-13} cm^3 molec^{-1} sec^{-1} (± factor of 3) for reaction with NO and 3×10^{-16} cm^3 molec^{-1} sec^{-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 both the HO_2-NO 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, ΔH, 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)*.

In summary, the experimental results reported in this work indicate that the reaction of the thermalized HO_2 radical with CO is exceedingly slow (k_1 probably less than 10^{-20} cm^3 molec^{-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 thermalized HO_2 in the atmosphere would appear to be those with the trace gases NO and SO_2.

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

$$H + O_3 \rightarrow OH + O_2 \quad (a)$$
$$OH + RH\ (sat.) \rightarrow H_2O + R \quad (b)$$
$$OH + RH\ (unsat.) \rightarrow products \quad (c)$$
$$OH + NO_2 + M \rightarrow HNO_3 + M \quad (d)$$
$$OH + NO + M \rightarrow HNO_2 + M \quad (e)$$
$$OH + H_2O_2 \rightarrow HO_2 + H_2O \quad (f)$$

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 ± 15 percent to a high of ± a factor of 6.
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9. In the absence of H_2O, the following reactions could have resulted in a limited production of CO_2:

$$O_2 + h\nu \rightarrow 2O$$
$$O + CO + M \rightarrow CO_2 + M$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$O_3 + CO \rightarrow CO_2 + O_2$$

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11. If it is assumed that chain termination occurs not via reaction 4 but rather a process such as diffusion of HO_2 to the walls, the upper limit for the rate constant for reaction 1 is found to be ~ 10^{-19} cm^3 molec^{-1} sec^{-1}. On the other hand, if the principal loss mechanism for HO_2 is due to reaction with impurities, the upper limit for k_1 is found to be ~ 1×10^{-18} cm^3 molec^{-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^{-13} cm^3 molec^{-1} sec^{-1} was selected for the reaction of HO_2 with this impurity. Since hydrogen peroxide was observed to be a product in these studies both of the above possibilities can probably be discounted.
12. The intensity of the Hg resonance lamp at 1849 Å was determined from a measurement of the yield of N_2 (quantum yield, Φ, approximately 1.4) in the photolysis of N_2O.
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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.

18 September 1972; revised 25 October 1972 ■

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 metabolism at the surface 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.

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

Location	O_2 (ml m^{-2} hr^{-1}) Total uptake	O_2 (ml m^{-2} hr^{-1}) Community respiration
Bermuda subtidal, 21°C (*12*)	22.9	22.9
Woods Hole outfall, 22°C (*9*)	67.8	52.8
Buzzards Bay, 22°C (*9*)	54.6	46.8
Puget Sound subtidal, 7°C (*4*)	7.6	
Slope, 1850 m	0.5	0.5

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 oxgen 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.