Carbon Monoxide and Nitric Oxide Consumption in Polluted Air: The Carbon Monoxide–Hydroperoxyl Reaction

Abstract. *A recent laboratory measurement of the ratio of the rate constant for the reaction* $CO + HO_2 \rightarrow CO_2 + OH$ *relative to that for* $H + HO_2 \rightarrow 2OH$ *indicates that the former reaction is probably faster than* $CO + OH \rightarrow CO_2 + H$. *On this basis a simple analysis is given showing that the calculated lifetime of nitric oxide in polluted atmospheres would be appreciably longer than that estimated on the assumption that the carbon monoxide–hydroperoxyl reaction may be neglected. A fast carbon monoxide–hydroperoxyl reaction implies that the cyclic consumption of carbon monoxide (an atmospheric sink) could occur even with no nitric oxide present.*

The role of CO in the chemistry of polluted atmospheres has recently come under increasing scrutiny, primarily because of the direct experimental finding (*1*) that the reaction

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

is much faster than had previously been thought, with a rate constant at room temperature k_1 of 1×10^{11} cm^3 mole^{-1} sec^{-1} and a low activation energy ($E_1 \approx 1$ kcal/mole). This finding led Westberg *et al.* to suggest (*2*) that the rapid conversion of NO to NO$_2$ in the atmosphere might be explained by the reaction sequence consisting of reaction 1 followed by

$$H + O_2 + M \rightarrow HO_2 + M \qquad (2)$$

$$NO + HO_2 \rightarrow NO_2 + OH \qquad (3)$$

thus regenerating OH and opening the way for repeated cycles that would consume CO and NO. This sequence also provides for a CO sink, which would help to explain the relatively short lifetime of CO in the atmosphere. Reaction 2 is known to be very fast with a well-defined rate constant k_2 (*3, 4*) of 7×10^{15} cm^6 mole^{-2} sec^{-1}. I know of no measurement of k_3, although there have been a number of guesses.

My purpose in this report is to point out the possible significance in this connection of a recent experimental finding (*4*) on the reaction

$$CO + HO_2 \rightarrow CO_2 + OH \qquad (4)$$

which is usually neglected (or ignored) in considerations of atmospheric pollution problems as being probably very slow. However, fairly direct, fast-flow experiments on the H-O$_2$ system with added CO have yielded a value for the ratio of k_4 to k_5

$$H + HO_2 \rightarrow 2OH \qquad (5)$$

at room temperature. Although this experiment was subject to considerable error, the resulting ratio was $k_4/k_5 \approx 0.06$. The absolute value of k_5 has not been measured, but it is most unlikely to be a slow reaction, and, in fact, it is probably very fast. It is a simple step involving the abstraction of an O atom by an H atom (38 kcal/mole, exothermic). The quite analogous reaction

$$H + NO_2 \rightarrow NO + OH$$

which requries the breaking of a stronger bond (29 kcal/mole, exothermic), is known (*5*) to be extremely fast with a rate constant of 3×10^{13} cm^3 mole^{-1} sec^{-1} at room temperature. Thus, if reaction 5 is fast as expected and has a rate constant of at least 1×10^{13} cm^3 mole^{-1} sec^{-1}, the experimental value of the k_4/k_5 ratio implies that $k_4 \geqq 6 \times 10^{11}$ cm^3 mole^{-1} sec^{-1}. It is argued in (*4*) that such a result is really not surprising, since reaction 4 is considerably more exothermic than reaction 1—64 kcal/mole as compared to 25 kcal/mole—and there is no apparent reason why it should not be the faster of the two.

Unfortunately, the technique used for measuring the k_4/k_5 ratio could not be employed to determine the k_3/k_5 ratio (because the reaction H + NO + M is fast whereas the reaction H + CO + M is not), so that k_3 remains unknown. Reaction 3 is much less exothermic (10 kcal/mole) than reaction 4, and the only other obvious difference is that reaction 3 involves two doublet reactants giving doublet products whereas reaction 4 involves singlet CO and CO$_2$. Reaction 3 is not spin-forbidden, however. In view of the lower exothermicity of reaction 3, one might guess that $k_3 < k_4$, but the shortcomings of this guess are obvious.

If we keep in mind the assumptions used above, it is possible to illustrate the kinetic behavior of CO and NO when reaction 4 is added to the simple sequence of reactions 1 through 3. This analysis is not meant to "model" an actual atmospheric situation in detail since it is obviously oversimplified. No other sources or sinks for HO$_2$ or OH are included, and, if the steady-state approximation is applied to [H], an excellent assumption in view of the fact that k_2 is large and in view of the high concentrations of O$_2$ and M in the atmosphere, then the constancy of $[HO_x] = [HO_2] + [OH]$ from reactions 1 through 4 alone follows. Use of the steady-state approximation for [OH] also gives

$$[OH] = \frac{[HO_x]}{1 + (k_4/k_1 + k_3[NO]/k_1[CO])^{-1}} \qquad (6)$$

and the rate equations for CO and NO become

$$\frac{1}{[CO]}\frac{d[CO]}{dt} = -[HO_x]\left(\frac{2k_4 + k_3[NO]/[CO]}{1 + k_4/k_1 + k_3[NO]/k_1[CO]}\right) \qquad (7)$$

$$\frac{1}{[NO]}\frac{d[NO]}{dt} = -\frac{k_3[HO_x]}{1 + k_4/k_1 + k_3[NO]/k_1[CO]} \qquad (8)$$

These are coupled rate equations which for exact solution must be handled numerically by computer. However, certain simplifications may be made. As long as we require the (quite likely) condition that $k_3 \leqq k_4$, and inasmuch as in the common polluted atmosphere the condition exists that $[NO] \ll [CO]$, Eqs. 7 and 8 may be approximated by

$$\frac{d\ln[CO]}{dt} \approx -[HO_x]\left(\frac{2k_4}{1 + k_4/k_1}\right) \qquad (9)$$

$$\frac{d\ln[NO]}{dt} \approx -[HO_x]\left(\frac{k_3}{1 + k_4/k_1}\right) \qquad (10)$$

so that the decays of the two species are essentially uncoupled and we have simply

$$\frac{[CO]}{[CO]_0} \approx \exp\left(-\frac{2k_4[HO_x]t}{1 + k_4/k_1}\right)$$

$$(t_{1/2})_{CO} \approx \frac{0.69(1 + k_4/k_1)}{2k_4[HO_x]} \qquad (11)$$

$$\frac{[NO]}{[NO]_0} \approx \exp\left(-\frac{k_3[HO_x]t}{1 + k_4/k_1}\right)$$

$$(t_{1/2})_{NO} \approx \frac{0.69(1 + k_4/k_1)}{k_3[HO_x]} \qquad (12)$$

where $[CO]_0$ and $[NO]_0$ refer to concentrations at $t = 0$. Equations 11 and 12 have been checked by comparison with exact computer solutions of Eqs.

7 and 8. Equation 12 is a somewhat poorer approximation than Eq. 11 for $t > t_{1/2}$ because CO decays faster than NO, and eventually the neglect of the term $k_3[\mathrm{NO}]/k_1[\mathrm{CO}]$ in Eq. 8 becomes unjustified, but by that time nearly all the CO has disappeared anyway.

If we accept the ratio $k_4/k_1 \geqq 6$, an analysis of Eqs. 9 and 11 indicates that reaction 1 is still essentially the rate-controlling step for CO consumption, because (approximating still further)

$$d \ln[\mathrm{CO}]/dt \approx -2k_1[\mathrm{HO}_x]$$

Thus Weinstock's estimate (*6*) of the [OH] required to maintain the global [CO] at 0.1 part per million (ppm) on the basis of reaction 1 alone would only need to be divided by ~ 2; that is, $[\mathrm{HO}_x] \approx 1.5 \times 10^{-9}$ ppm for a CO input rate of 2×10^{14} g/year. The actual $[\mathrm{HO}_x]$ is, of course, an unknown quantity in the atmosphere. Presumably OH is generated in sunlight by such steps as

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

and

$$\mathrm{O} + \mathrm{RH} \rightarrow \mathrm{R}\cdot + \mathrm{OH}$$

(where RH is any hydrocarbon) and it is likely that the main sinks (at least at night) for OH arise from the reactions

$$\mathrm{OH} + \mathrm{NO_2} + \mathrm{M} \rightarrow \mathrm{HNO_3} + \mathrm{M}$$

and

$$\mathrm{OH} + \mathrm{NO} + \mathrm{M} \rightarrow \mathrm{HNO_2} + \mathrm{M}$$

both of which have recently been found to be very fast (*7*). In sunlight the $\mathrm{HNO_3}$ and $\mathrm{HNO_2}$ may be photolyzed to recover OH. If $k_3 \approx k_4$, an analysis of Eqs. 10 and 12 shows that reaction 1 is also rate-controlling for NO consumption, but clearly, if $k_3 \ll k_4$, this is no longer true and we would have

$$d \ln[\mathrm{NO}]/dt \approx -(k_1k_3/k_4)[\mathrm{HO}_x]$$

If we now exclude reaction 4 from the mechanism by letting $k_4 = 0$, the rigorous Eqs. 7 and 8 reduce to

$$\frac{d[\mathrm{CO}]}{dt} = \frac{d[\mathrm{NO}]}{dt} = -[\mathrm{HO}_x]\frac{k_3[\mathrm{NO}]}{1 + k_3[\mathrm{NO}]/k_1[\mathrm{CO}]} \quad (13)$$

If we make the same simplification as before by restricting ourselves to $k_3[\mathrm{NO}]/k_1[\mathrm{CO}] \ll 1$, Eq. 13 may be solved to give

$$\frac{[\mathrm{NO}]}{[\mathrm{NO}]_0} \approx \exp\,[-k_3[\mathrm{HO}_x]t]$$

$$(t_{1/2})_{\mathrm{NO}} \approx \frac{0.69}{k_3[\mathrm{HO}_x]} \quad (14)$$

Comparing Eqs. 12 and 14, we see that the effect of including reaction 4 in the mechanism with $k_4 \geqq k_3$ is to lengthen (*8*) the computed lifetime of NO by the factor $(1 + k_4/k_1)$ over that predicted without reaction 4. As discussed above, it is likely (not proven) that $k_4/k_1 \geqq 6$, so that the computed $(t_{1/2})_{\mathrm{NO}}$ could be increased by a factor of 7 or more.

On the basis of the sequence of reactions 1 through 3 alone, since

$$d[\mathrm{CO}]/dt = d[\mathrm{NO}]/dt$$

the CO consumption would cease when $[\mathrm{NO}] \rightarrow 0$. The OH would then no longer be regenerated, and the steady-state cycle would be broken. Actually, as noted above, other reactions extraneous to the cycle probably govern $[\mathrm{HO}_x]$ in the real atmosphere.

Thus, in summary, it seems quite likely that reaction 4 is fast—probably faster than reaction 1—and that it would have an appreciable effect on calculated NO lifetimes in polluted atmospheres; that is, the NO lifetime would be considerably longer than the lifetime estimated from the sequence of reactions 1 through 3 alone. The effect of reaction 4 on CO lifetimes is different (NO is not required at all for a quite efficient CO sink to function), since reactions 1, 2, and 4 alone constitute a cyclic system to consume CO. (For appreciable conversion of NO to $\mathrm{NO_2}$, however, the presence of some CO is required by this mechanism with or without reaction 4.) If $[\mathrm{NO}] = 0$, the rigorous Eq. 7 has an exact solution given the approximate Eq. 11, which implies half the lifetime for CO computed without reaction 4 but with the same constant $[\mathrm{HO}_x]$.

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References and Notes

1. G. Dixon-Lewis, W. E. Wilson, A. A. Westenberg, *J. Chem. Phys.* **44**, 2877 (1966).
2. K. Westberg, N. Cohen, K. W. Wilson, *Science* **171**, 1013 (1971).

→ M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc. Ser. A Math. Phys. Sci.* **275**, 559 (1963); T. Hikida, J. A. Eyre, L. M. Dorfman, *J. Chem. Phys.* **54**, 3422 (1971).

4. A. A. Westenberg and N. deHaas, *J. Phys. Chem.* **76**, 1586 (1972).
5. L. F. Phillips and H. I. Schiff, *J. Chem. Phys.* **37**, 1233 (1962).
6. B. Weinstock, *Science* **166**, 224 (1969).
7. A. A. Westenberg and N. deHaas, in preparation.
8. It is not the presence of CO itself that lengthens the NO lifetime. The cycle of reactions 1 through 3 alone would still lead to a faster conversion of NO to $\mathrm{NO_2}$ than when $[\mathrm{CO}] = 0$ (there would then be no $\mathrm{NO_2}$ formation without another step, probably $\mathrm{NO} + \mathrm{NO} + \mathrm{O_2} \rightarrow 2\mathrm{NO_2}$), but reaction 4 decreases the effect, obviously because CO competes with NO for the $\mathrm{HO_2}$. That the presence of CO enhances the conversion of NO to $\mathrm{NO_2}$ has been experimentally confirmed (*2*).

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Apollo 16 Geochemical X-ray Fluorescence Experiment: Preliminary Report

Abstract. *The lunar surface was mapped with respect to magnesium, aluminum, and silicon as aluminum/silicon and magnesium/silicon intensity ratios along the projected ground tracks swept out by the orbiting Apollo 16 spacecraft. The results confirm the observations made during the Apollo 15 flight and provide new data for a number of features not covered before. The data are consistent with the idea that the moon has a widespread differentiated crust (the highlands). The aluminum/silicon and magnesium/silicon concentration ratios correspond to those for anorthositic gabbros through gabbroic anorthosites or feldspathic basalts. The x-ray results suggest the occurrence of this premare crust or material similar to it at the Descartes landing site.*

An integrated geochemical package was carried in the Command-Service Module during the Apollo 16 flight to the Descartes highland area. This package, which was identical to the one carried aboard Apollo 15, included the x-ray, gamma-ray, and alpha-particle spectrometers. These experiments were flown to extend our observations to larger areas of the moon and to allow us to extrapolate from the data obtained on the surface to the rest of the moon. Thus, the purpose of the orbital mapping experiment and, in particular, the x-ray fluorescence experiment was to tie in the information obtained from the analysis of the returned lunar samples from the various sites to the global geochemical picture.

There was some overlap of orbital coverage between the two missions so that the reproducibility of our results could be determined and the results could be compared. The total coverage for the two missions is greater than 20 percent of the total surface of the moon.