be deaminated to ammonia, which is universally available to phytoplankton.

Coastal waters already receive the sewage of roughly half the population of the United States. To replace a portion of the phosphate in this sewage with a nitrogenous compound and to then discharge it into an environment in which eutrophication is nitrogen-limited may be simply adding fuel to the fire.

JOHN H. RYTHER
WILLIAM M. DUNSTAN
Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543

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Carbon Monoxide: Its Role in Photochemical Smog Formation

Abstract. *The photochemistry of trace amounts of isobutene and oxides of nitrogen in an atmosphere of air was studied both in the presence and in the absence of small amounts of carbon monoxide. Carbon monoxide accelerates the reaction as measured by nitric oxide oxidation or ozone formation. This finding has relevance to photochemical smog formation.*

Until recently, the reactivity of carbon monoxide in polluted atmospheres has been all but ignored. Leighton (*1*) noted that the reaction of CO with O, H, or O_3 was demonstrably too slow to be significant. He did not discuss the reaction of CO with OH because, prior to 1966, the activation energy for that reaction was believed to be at least 7 kcal/mole (*2*), which would give a negligible reaction rate constant of approximately $10^5 M^{-1}$ sec^{-1} at atmospheric temperature. More recently, it has been demonstrated that the reaction of CO with OH (see reaction 1 below) has an activation energy of approximately 1 kcal/mole and that the rate constant at 25°C is $8 \times 10^7 M^{-1}$ sec^{-1} (*2*), thus making this reaction of possible significance in the atmosphere.

Recently Heicklen *et al.* proposed a mechanism to explain the previously unaccountably rapid rate of conversion of NO to NO_2 in polluted atmospheres (*3*). The mechanism involves three parallel chain reactions, each with OH as the chain carrier. Two chain reactions involve OH attack on hydrocarbons; the third involves the reaction of OH with CO and consists of the following steps (where M represents O_2 or N_2):

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

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

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

The net reaction from these three steps is

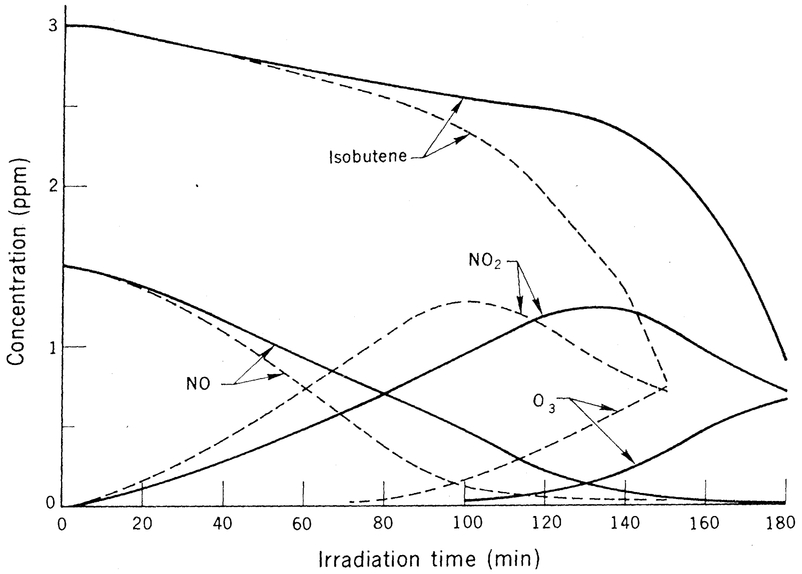
$$CO + O_2 + NO \rightarrow CO_2 + NO_2 \quad (4)$$

Experimental evidence is presented here for the effect of CO on the oxidation of NO in polluted atmospheres.

Experiments were performed in a 7.68-m^3, Teflon-lined, constant-temperature, stirred smog chamber (*4*). In each experiment approximately 3 parts per million (ppm) of isobutene, 1.5 ppm of NO or NO_2, and varying amounts of CO were mixed with an atmosphere of pure air and irradiated with light approximating the intensity and spectral characteristics of sunlight. Figures 1 and 2 show some of the results. A mixture consisting of NO, isobutene, carbon monoxide, and air was chosen for study because, in many ways, it simulates the chemical reactivity of a dilute mixture of automobile exhaust and air. The concentrations of hydrocarbon, NO, and CO used in these experiments are about an order of magnitude higher than those found in polluted atmospheres, but they are in roughly the correct proportions. High pollutant concentrations and the relatively high volume-to-surface ratio ($V/S = 0.227$ m) of the smog chamber helped to minimize the importance of wall reactions; identical results were obtained when the walls were newly cleaned or when they were well seasoned by numerous experiments.

As may be seen in Figs. 1 and 2, continuous measurements were made of the concentrations of O_3 [by means of an oxidant meter (Mast Development) with the use of Bufalini's method (*5*)], NO_2 (Saltzman reagent), $NO + NO_2$ (dichromate oxidation and Saltzman reagent), CO (infrared absorption), and isobutene (gas chomatography). Formaldehyde, peroxyacetyl nitrate (PAN), acetone, methyl nitrate, isobutene oxide, total hydrocarbon, and total oxidant were also monitored; for simplicity, these species have been omitted from the graphs since the effect of CO on their concentration was what would have been predicted from the altered O_3 concentration.

The air used in these experiments was purified by methods described elsewhere (*4*). Chemically pure grade isobutene, NO, and NO_2 were used without further purification. Carbon monoxide was purified by passage through a packed column cooled to liquid nitrogen temperatures to remove iron carbonyl, which is present in CO taken from conventional steel cylinders. In our CO samples the $Fe(CO)_5$ concentration was 0.15 percent. The purification procedure employed is effective only if carried out carefully, in which case it removes more than 99 percent of the iron carbonyl present. One of the experiments shown in Fig. 1 was performed with CO generated in a glass system by the reaction of H_2SO_4 with



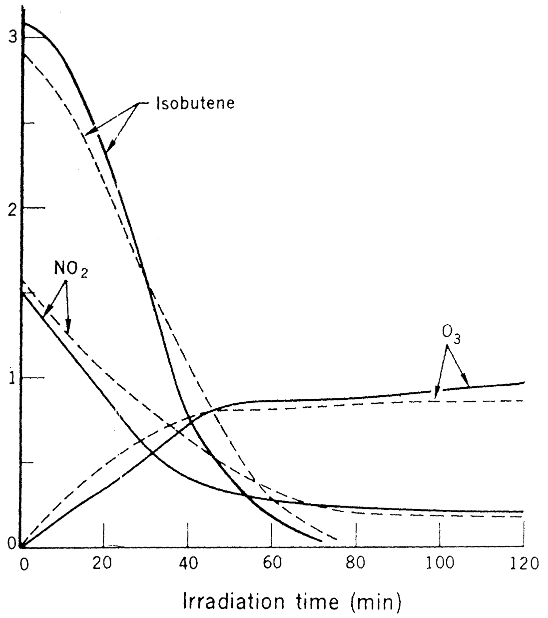


Fig. 1 (left). The effect of carbon monoxide on ozone formation. Curves shown are the results of photochemical experiments performed in an irradiated smog chamber starting with an atmosphere of air, 3 ppm of isobutene, 1.5 ppm of NO, less than 0.04 ppm of NO_2, and either 0 ppm of CO (solid lines) or 100 ppm of CO (dashed lines). The relative humidity was 70 percent; the temperature, 28°C. The NO, NO_2, and O_3 curves were corrected for the rapid reaction between NO and O_3 that occurred during the transfer of samples from the smog chamber to the measuring instruments. The results shown in this figure are averages of eight experiments. The experimental reproducibility is good: in matched pairs of experiments, the time required for the conversion of NO to NO_2 (defined as when $[NO] = [O_3]$) was always 31 ± 3 minutes shorter in the presence of added CO than in its absence. Nonreplicated measurements were made with different ratios of NO, CO, and isobutene, and carbon monoxide accelerated the conversion of NO to NO_2 in these experiments as well. Fig. 2 (right). The effect of carbon monoxide on ozone formation. Curves shown are the results of experiments similar to those shown in Fig. 1, but with 1.5 ppm of NO_2 instead of NO. The difference in the ozone curves in the presence of either 0 ppm of CO (solid lines) or 70 ppm of CO (dashed lines) is explained in the text. We have no explanation for the corresponding differences in the isobutene and NO_2 curves; however, these curves were not nearly so reproducible as the O_3 curves.

HCOOH. The results were identical to those obtained with CO taken from a steel cylinder and purified.

In Fig. 1 species concentrations are compared in the absence and in the presence of CO when the starting oxide of nitrogen is principally NO. In Fig. 2 the analogous curves for NO_2 are shown. These curves depict averages of several replications. Figure 1 demonstrates that CO markedly accelerates the disappearance of olefin, the conversion of NO to NO_2, and the appearance of ozone. However, the final ozone concentration is not noticeably altered. The effect of CO when NO_2 is the primary oxide of nitrogen is not so pronounced, as Fig. 2 indicates. The increase in the initial rate of ozone formation, although apparently slight as shown in Fig. 2, is not due to experimental uncertainty, but is a real effect. It actually represents an increase of about 50 percent in $d[O_3]/dt$ at the beginning of the experiment.

The detailed explanation of these experiments is subject to some speculation, but we believe that the following conclusions are established beyond reasonable doubt. First, it is apparent that CO is not inert in the production of photochemical smog, and smog chamber measurements made in the past in which CO was used as a tracer gas and its nonreactivity was assumed must be reevaluated. Second, and more important in the understanding of smog production, the experiments clearly implicate OH as a major chain carrier in the smog-producing system consisting of olefin, an oxide of nitrogen, CO, and air. There is no reaction other than reaction 1 by which CO plausibly can influence NO oxidation in this system. Finally, although we are not yet prepared to assess the magnitude of the role of CO in the real atmosphere, with its many different hydrocarbons, qualitatively it seems that the presence of CO will accelerate the early-morning conversion of NO to NO_2, thus hastening the appearance of oxidants.

The rate of ozone formation is closely controlled by the relative concentrations of NO and NO_2. Ozone is produced primarily by the photodissociation of NO_2 followed by the rapid combination of O atoms with O_2:

$$NO_2 + h\nu \rightarrow NO + O \qquad (5)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (6)$$

and is consumed principally by reaction with NO:

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (7)$$

Thus the ozone concentration increases in proportion to the amount of NO oxidized to NO_2. Quantitatively,

$$[O_3] \cong (k_5/k_7)\,[NO_2]\,/\,[NO] \qquad (8)$$

where k_5 is the product of the light absorbed (per unit time per unit volume) by NO_2 and its dissociation quantum efficiency and k_7 is the rate constant for reaction 7; in our system k_5/k_7 is $6.5 \times 10^{-10}M$. This relationship holds well at all times during the course of the smog experiments, even though, at times, either $[O_3]$ or [NO] is too small to show on the graphs of Figs. 1 and 2.

The results included in Fig. 1 and in the first 40 minutes of the reaction in Fig. 2 show that CO accelerates the oxidation of NO to NO_2 and the rate of ozone formation. This result is what would be expected from reactions 1 through 3. However, as is shown in Fig. 2, when the ozone concentration becomes greater than about 0.6 ppm, and, hence, by reaction 8, $[NO_2]/[NO]$ is greater than 30, CO decelerates the further oxidation of NO to NO_2 and the rate of ozone formation. This behavior can be explained by a chain reaction consisting of reactions 1, 2, 9, and 10:

$$HO_2 + NO_2 \rightarrow HNO_2 + O_2 \quad (9)$$

$$HNO_2 + h\nu \rightarrow OH + NO \quad (10)$$

This chain reaction converts NO_2 to NO and will compete with reactions 1 through 3 under conditions of large $[NO_2]/[NO]$.

The carbon monoxide had 0.15 percent $Fe(CO)_5$ as its principal impurity (the hydrocarbon impurities were negligible, being less than 5 ppm). When iron carbonyl was not removed from the CO, the rate of oxidation of NO to NO_2 was accelerated even more than is shown in Fig. 1. In the presence of unpurified CO, only 60 minutes elapsed before all the NO was converted to NO_2 (defined as when $[NO] = [O_3]$). By comparison, with purified CO, 100 minutes elapsed (see Fig. 1); without CO, 130 minutes elapsed. Since the concentration of $Fe(CO)_5$ is an order of magnitude smaller than that of the NO, its pronounced effect can be explained only by a chain reaction. Because the carbonyl undergoes decomposition in sunlight (*6*) and is probably vulnerable to attack by oxygen atoms, a possible chain mechanism for its effect might include the following reactions:

$$Fe(CO)_5 + O \rightarrow Fe(CO)_4 + CO_2 \quad (11)$$

$$Fe(CO)_5 + \overset{h\nu}{\rightarrow} Fe(CO)_x + (5-x)CO, \quad x < 5 \quad (12)$$

$$Fe(CO)_x + O_2 \rightarrow Fe(CO)_xO_2 \quad (13)$$

$$Fe(CO)_xO_2 + (NO \text{ or } CO) \rightarrow Fe(CO)_xO + (NO_2, CO_2) \quad (14)$$

$$Fe(CO)_xO + (CO \text{ or } NO) \rightarrow Fe(CO)_x + (CO_2, NO_2) \quad (15)$$

Other reaction mechanisms may be equally possible, but reactions 11 through 15 do show that the observed effects of $Fe(CO)_5$ can be accounted for in a plausible manner. Iron carbonyl is highly reactive in other free-radical systems: trace amounts of $Fe(CO)_5$ either quench hydrocarbon-air flames or reduce their flame velocities substantially (*7*); this compound formerly was used as an antiknock agent in gasoline (*6*).

KARL WESTBERG
NORMAN COHEN
Aerospace Corporation,
El Segundo, California 90245
K. W. WILSON
Stanford Research Institute,
Irvine, California 92664

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Sulfur Isotopes in Swaziland System Barites and the Evolution of the Earth's Atmosphere

Abstract. *Sedimentary barites from the Swaziland System of South Africa (more than 3000 million years old) have sulfur-34 ratios that are enriched by only 2.5 per mil with respect to contemporary sulfides. To explain this small fractionation, it is proposed that oxygen pressure in the earth's atmosphere was very low and that local oxidation occurred in a photosynthetic layer of the ocean.*

In this report we interpret the significance of sulfur isotope data from an isolated occurrence of sulfate separated in time by 2000 million years from any well-understood deposits. We hope to show that the deposit is sedimentary, that its sulfate may reasonably represent contemporary oceanic sulfate, and that its sulfur isotope composition may indicate roughly the oxygen content of the early atmosphere.

Beds of barite alternating with green chert, shale, and pebble conglomerate occur in a 20-m-thick zone of the Fig Tree or Upper Onverwacht Group, Swaziland Sequence, in the Barberton Mountain Land, South Africa. These occurrences are mentioned by Visser (*1*), and several of them are shown on the 1 : 50,000 map of the Barberton area published by the South African Geological Survey in 1955; they appear as an 8-km-long band, 11 km southeast of Barberton. The barite is recrystallized, but we consider it to be sedimentary for the following reasons: (i) it occurs in conformable layers, and cross-cutting veins have not been observed; (ii) the zone of barite beds is persistent within the same horizon for several kilometers along strike; (iii) no accompanying sulfide mineralization has been observed; and (iv) the barite-chert association found here is common in sedimentary barite deposits.

Strontium isotopic data provide strong evidence that these deposits were formed prior to the main metamorphic event of 3000 million years ago that affected the Barberton Mountain Land. Whereas the $^{87}Sr/^{86}Sr$ ratio established in graywackes and shales by this metamorphic event was 0.712 (*2*), the $^{87}Sr/^{86}Sr$ ratio in eight Barberton barites ranges from 0.70088 to 0.70172 (*3*). This lower $^{87}Sr/^{86}Sr$ ratio precludes derivation of the cations from a source with a high Rb/Sr ratio and suggests that they were derived from the upper mantle during volcanism associated with sedimentation (*4*).

Table 1 lists $\delta^{34}S$ values (*5*) for barites and for sulfides from approxi-

Table 1. Values of $\delta^{34}S$ for barites and sulfides of the Swaziland System.

Sample	$\delta^{34}S$	Remarks
		Barites
A185	+3.5	Coarse green barite associated with chert, central zone
9B2	+3.1	
B11	+3.1	
B20	+3.8	
B14	+3.5	Barite and conglomerate, west workings
B15	+3.4	Elongated barite crystals, east workings
B17	+3.7	Barite in conglomerate, easternmost part of district
Approximately	*contemporaneous sulfides*	
A177	+1.1	Disseminated pyrite in graywacke, Fig Tree Group
R5	−0.1	Pyrite in Fig Tree iron formation
R6	+1.6	Pyrite from dolomite bed underlying barite
	−0.9	Galena in quartz vein, Rosetta mine (*19*)