

Ozone loss in soot aerosols

R. S. Disselkamp, M. A. Carpenter, J. P. Cowin, C. M. Berkowitz, E. G. Chapman,
R. A. Zaveri, and N. S. Laulainen

Pacific Northwest National Laboratory, Atmospheric Sciences Technical Group and Environmental Molecular Sciences Laboratory, Richland, Washington

Abstract. The fractal-like structure of atmospheric soot (e.g., elemental carbon) provides a large surface area available for heterogeneous chemistry in the upper troposphere and lower stratosphere [Blake and Kato, 1995]. One potentially important reaction is ozone decomposition on soot. Although extensively studied in the laboratory, a wide range of reaction probabilities have been observed ($\gamma \sim 10^{-3}$ to $\gamma \sim 10^{-7}$) which have been attributed to differences in reactivity between fresh (i.e., nonoxidized) versus aged (i.e., oxidized) soot [Schurath and Naumann, 1998]. The importance in understanding soot-ozone chemistry is particularly important in light of recent nighttime field measurements [Berkowitz *et al.*, 2000] made over Portland, Oregon. The data revealed episodes of an anticorrelation between ozone mixing ratio and aerosol surface area density. During these episodes a single scattering albedo in the range 0.8-0.9 was measured, indicating an increased absorptive component of the aerosol, perhaps due to elemental carbon. In addition, an increase in the concentration of aerosols contained in the small size range of the fine mode (<0.1 - $0.15 \mu\text{m}$) was observed, suggestive of new aerosol formation. In this article we attempt to explain these field observations. One explanation of the field observations is ozone loss occurring on atmospheric soot aerosol. Here we present laboratory results obtained using a static aerosol reactor that indicate that direct ozone loss on soot aerosol is unlikely under ambient conditions in the troposphere. An alternative and more likely explanation of the field data is based on ozone-mediated organic aerosol production. This could occur by either nighttime nitrate radical oxidation or direct ozone oxidation of hydrocarbons as suggested previously [Starn *et al.*, 1998; Griffin *et al.*, 1999; Kamens *et al.*, 1999; Yu *et al.*, 1999; De Gouw and Lovejoy, 1998].

1. Introduction

The motivation for this investigation arises from increasing concern about the interaction of aerosols with important atmospheric trace gas species, such as ozone, NO_x , HNO_3 , and other compounds [World Meteorological Organization (WMO), 1998]. It has been recognized that heterogeneous reactions of NO_y species on the surface of aerosols play an important role on the distribution of NO_y , O_3 , and other oxidants. These reactions can occur on many types of aerosols. The reactions of N_2O_5 and NO_3 on sulfate aerosols and mineral dust are believed to be the major sink for odd nitrogen and a major source of HNO_3 in the nighttime troposphere [Mozurkewich and Calvert, 1988; Mamane and Gottlieb, 1989]. The inclusion of coarse parameterizations of these reactions in regional and global models reduces concentrations of NO_x , O_3 , and OH by 10-50% [Dentener and Cruzen, 1993; Zhang *et al.*, 1994; Dentener *et al.*, 1996]. This finding provides a plausible interpretation for the poor performance of most photochemical models. Lary *et al.* [1997] suggest that NO_x generated through heterogeneous processes could lead to O_3 loss in the lower stratosphere and O_3 production in the upper troposphere, making it difficult to obtain an accurate ozone budget.

Within this framework, there is a need to confirm past laboratory investigations of the kinetics of ozone loss on various aerosol substrates and to broaden these studies to include the influence of relative humidity. Knudsen cells and flow tube reactors have been the main working tools for such investigations. Unfortunately, these earlier methods have recognized shortcomings (diffusion of reactant gas into bulk soot material in the case of Knudsen cells studies and short reactant gas-aerosol interaction time for flow tube investigations). New technologies offer the potential of evaluating these earlier measurements without these difficulties and enable relative humidities, aerosol concentration, and trace gas concentration representative of the atmosphere to be studied.

Numerous investigations of the kinetics of ozone loss on soot material have been performed previously. However, with reported reaction probabilities ranging from 10^{-3} to less than 10^{-7} , uncertainty still exists regarding the importance of O_3 -soot chemistry. In principle, differences in reaction probabilities can be due to either differences in experimental technique employed (Knudsen cell, aerosol flow tube, or static chamber apparatus), soot materials studied, or soot oxidation arising from prolonged exposure to ozone. The relative importance of these possible causes of data variation among experiments is not clear. For example, one Knudsen cell measurement reported $\gamma \sim 10^{-3}$ on fresh (i.e., nonoxidized) Degussa FW2 soot [Rogaski *et al.*, 1997]. A second Knudsen cell measurement on fresh charcoal reported a reaction probability of $\gamma \sim 10^{-3}$ that decreased to $\gamma \sim 10^{-5}$ upon oxidation

of the surface [Stephens *et al.*, 1986]. Similar results were obtained by flow tube studies where reaction probabilities of $\gamma \sim 10^{-3}$ for spark-generated fresh graphitic soot [Fendel *et al.*, 1995], and $\gamma \sim 10^{-4}$ and 10^{-5} for flame-generated fresh and oxidized soot, respectively [Il'in *et al.*, 1990]. Recent static aerosol chamber studies [Mohler *et al.*, 1996; Schurath and Naumann, 1998] have examined O_3 -soot chemistry over several days, under conditions approaching those of the atmosphere (100 ppbv O_3 , 200 $\mu\text{g}/\text{m}^3$ soot mass concentration). The prolonged exposure of soot to ozone in these experiments enabled a characterization of the effect of soot oxidation (i.e., aging) on ozone-soot chemistry. Reaction probabilities of $\gamma \sim 10^{-5}$ [Mohler *et al.*, 1996] and $\gamma < 10^{-7}$ [Schurath and Naumann, 1998] were reported in samples studied up to 3 days.

We used Fourier transform infrared (FTIR) spectrometry and a static aerosol chamber to examine ozone reactions on the surface of soot aerosols. This paper begins by describing the experimental apparatus and characteristic results showing the loss of ozone under a range of conditions that test the robustness of the laboratory system. The results are then used to evaluate the importance of ozone uptake by soot in the natural atmosphere as observed by Berkowitz *et al.* [2000]. Although field observations suggest a soot-like material is associated with ozone loss, our results show that the mechanism is more complicated than simple uptake onto soot (elemental carbon) aerosol.

2. Ozone-Soot Aerosol Laboratory Experiments

Laboratory experiments are useful in providing detailed information about chemical processes that occur in the atmosphere. Although our experiments are performed using soot and ozone concentrations greater than those that exist in the atmosphere, we will assume our results can be extrapolated to atmospheric conditions. Experiments were performed using a previously described apparatus [Narus *et al.*, 1996] and method of generating static soot aerosol samples [Disselkamp *et al.*, 2000]. Here we give a brief description of the apparatus and method of generating aerosol samples. A schematic illustration of the experimental apparatus is shown in Figure 1. The aerosol chamber has an internal sample volume of 28 L and was maintained at 298 ± 4 K during the course of the experiments. A white cell (infrared analysis, 11 m path length) interfaced to an FTIR spectrometer (Nicolet Magna-IR 560 spectrometer) enabled a spectroscopic interrogation of the chamber. The chamber is teflon-coated, yielding an ozone lifetime in excess of 3 hours within the cleaned, passivated, dry chamber. Chamber cleaning was performed prior to each experiment by introducing soap (Alconox) with deionized water via a spray head to remove particulate debris from the chamber walls. A liquid nitrogen cryopump was then used to dry the chamber after cleaning.

Experiments were performed using a four-step procedure: (1) The chamber was evacuated to $\sim 1.3 \times 10^{-5}$ atm and a background spectrum collected; (2) Ozone entrained in humidified zero air was added to the chamber yielding a total pressure of ~ 0.52 atm and an ozone partial pressure of $\sim 3.5 \times 10^{-5}$ atm (~ 35 ppmv); (3) Acquisition of infrared spectra was initiated such that spectra were obtained at 6 min time intervals; (4) After 14 spectra were collected, an O_3 -soot aerosol sample was formed by forcing soot powder (~ 24 mg)

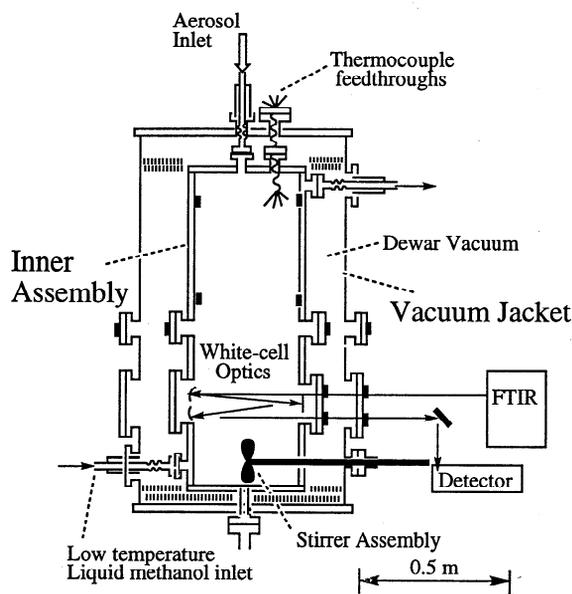


Figure 1. A schematic illustration of the aerosol chamber interfaced to an Fourier transform infrared (FTIR) spectrometer is shown. The transfer optics between the FTIR and chamber, and the gas/aerosol manifold located at the top of the chamber, have been omitted for clarity.

through stainless steel wire mesh screens (25 and 100 mesh) and into the chamber using nitrogen gas at 13.6 atm (final chamber pressure ~ 1.3 atm, soot introduction time ~ 5 s). Spectra obtained before and after soot introduction to the chamber enabled ozone-wall reaction processes and ozone-wall plus ozone-soot reaction processes to be characterized. Each absorption spectrum was computed from an average of 350 sample and background interferogram scans using 1 cm^{-1} resolution. Relative humidities $>9\%$ were measured using a relative humidity sensor (Vaisala model HMP234), whereas lower relative humidity was measured from a weakly absorbing water transition in the infrared spectra calibrated using the relative humidity sensor. Experiments were performed using relative humidities of 0.5%, 9.0%, and 33%. Relative humidities $>33\%$ were not studied because the ozone lifetime in the chamber ($1/e$ decay time) prior to soot introduction (i.e., caused by wall reaction) was less than $t \sim 20$ min, making an estimate of O_3 loss due to chemistry alone difficult. Three types of soots were investigated. One type was Degussa FW1, a carbon black having a specific surface area of $460 \text{ m}^2/\text{g}$ generated from the combustion of liquid coal-tar. A second type was Degussa FW2, identical to Degussa FW1 except that it had been posttreated with NO_2 to generate functional groups at the surface. The third material studied was crystalline graphite powder (Dixon-Ticonderoga) having a specific surface area of $500 \text{ m}^2/\text{g}$. The Degussa FW1 soot was used as a more realistic (e.g., combustion generated) type assumed to be a surrogate for fresh atmospheric soot, whereas Degussa FW2 allowed a comparison to be made with a previous study [Rogaski *et al.*, 1997].

Figure 2 presents results representative of all the experiments performed, and was obtained from an analysis of an experiment employing 24 mg of Degussa FW2 soot. Both O_3 and CO_2 partial pressure versus time is shown. These two species were the only compounds identified in infrared

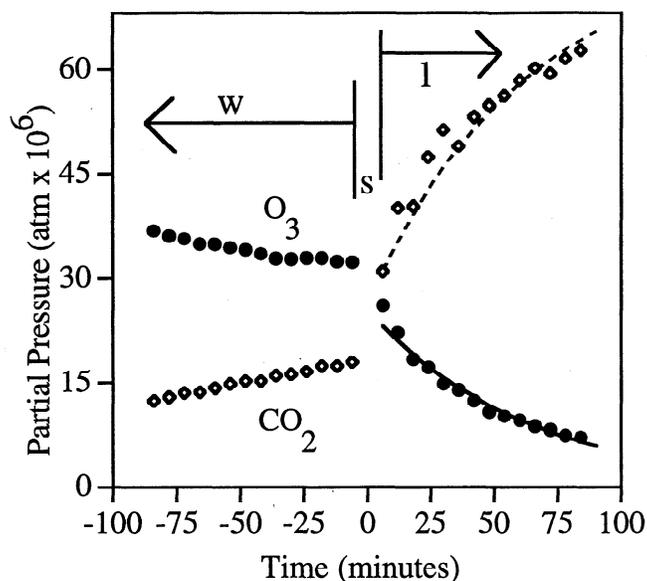


Figure 2. The partial pressures of O_3 and CO_2 versus time are shown. Time equal to zero corresponds to the moment when 24 mg of Degussa FW2 soot was introduced into the chamber. The solid and dashed lines represent model results fit to the experimental data (see text). The w , s , and l labels correspond to a wall reaction time (w) and wall plus chemistry reaction times (short time, s ; long time, l).

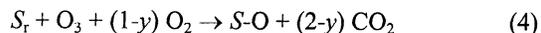
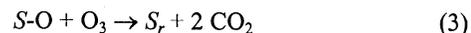
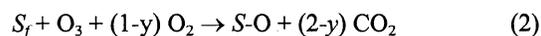
spectra, aside from water, at all relative humidities employed. Time equal to zero corresponds to soot introduction to the chamber; therefore negative time is a probe of ozone decay without soot (i.e., a characterization of wall reaction processes) and positive time to that of wall reaction plus ozone-soot chemistry. Several interesting features can be extracted from Figure 2. Prior to soot introduction to the chamber, the slow decrease in O_3 partial pressure, from 3.4×10^{-5} atm at $t=-84$ min to 2.8×10^{-5} atm at $t=-6$ min, indicates that the chamber is chemically inert with respect to ozone decomposition. Conversely, upon soot introduction to the chamber, a rapid uptake of O_3 occurs (2.8×10^{-5} atm at $t=-6$ min to 2.0×10^{-5} atm at $t=6$ min) followed by a slow O_3 decay with a lifetime of 57 min at $t>6$ min (illustrated by the solid line). Therefore a distinct two-stage reaction process is observed. Also note that a decrease in O_3 partial pressure is mirrored by an increase in CO_2 partial pressure. The stoichiometry of CO_2 production from O_3 oxidation of soot, upon soot introduction to the chamber, is contained in the expression

$$P_{CO_2}(t) = P_{CO_2}(t=-6 \text{ min}) + n P_{O_3}(t=-6 \text{ min}) \{1 - \exp[-(t-6)/\tau]\}, \quad (1)$$

where n is the stoichiometric coefficient of CO_2 production and τ is the (observed) O_3 lifetime of 57 min. With the stoichiometric coefficient of CO_2 production as the only unknown, a fit of experimentally measured CO_2 partial pressure to (1) yields a value of $n = 2.0$, illustrated as the dashed line in Figure 2. This is a surprisingly large value. A value of $n > 1.5$ can be explained by O_2 participating in the reaction process, which has been observed previously [Smith et al., 1988; Smith and Chughtai, 1996]. The CO_2 production quantum yield from O_3 exhibited considerable variation in our experiments, ranging from 1.0 to 2.0, with an average value of

1.7. A slight positive correlation between an increase in the stoichiometric coefficient and an increase in relative humidity was observed. Less than 1 mol % of CO relative to CO_2 was produced. Our lack of CO production is inconsistent with previous investigations [Stephens et al., 1986; Smith et al., 1988]. The cause of this discrepancy is not known.

A reaction sequence consistent with the experimental results can be written as



where S_f and S_r denote a fresh soot surface and a reacted (perhaps free-radical site-containing) soot surface [Akhter et al., 1985], respectively, and $S-O$ denotes an oxidized soot surface. The stoichiometric parameter y , although variable from 0.0 to 1.0 in the experiments, has an average value of 0.45 (derived from $n=1.7$). In one scenario the oxidation mechanism contained in (2)-(4) can explain the data of Figure 2 and the work of others [Smith et al., 1988; Smith and Chughtai, 1996] if (2) and (4) occur rapidly ($\gamma \sim 10^{-3}$) whereas (3) occurs slowly ($\gamma \sim 10^{-8}$, value obtained from discussion below). The initial, fast, uptake of O_3 of Figure 1 ($t=-6$ min to $t=6$ min) arises from (2), whereas the slow, rate-limiting, decay of O_3 ($t>6$ min) may occur via (3). Further analysis has revealed that the reaction order in our experiments varies from 1.0 to 1.2, and therefore is approximately first order. Assuming a first-order process, the reaction probability for the loss of O_3 , γ , is contained in

$$\ln [P_{O_3}(t)/P_{O_3}(t_0)] = -\{(\gamma c \Sigma S)/4\} (t-t_0), \quad (5)$$

where the term contained in the braces is the inverse of the laboratory measured O_3 lifetime, $1/\tau$, c is the mean-molecular speed of O_3 at 298 K (3.6×10^4 cm/s), Σ is the soot specific surface area (cm^2/g), S is the soot mass concentration (g/cm^3), and $t-t_0$ is time (s). Since the experiments performed here used a pressure of ~ 1.3 atm and hence may be in the transitional regime for ozone transport to soot and require the use of the Fuchs-Sutugin correction factor [Seinfeld and Pandis, 1998] in (5), this correction factor under our experimental conditions ($\tau=57$ min) becomes unity (mass transfer can be neglected) due to the small value of the computed reaction probability ($\gamma \sim 10^{-8}$) for each of our experiments. Qualitatively similar results were obtained at all relative humidities studied. The only difference was the wall reaction rate that was greatly increased at high relative humidity, thus limiting our study to relative humidity from 0.5% to 33%. Whether the decay of ozone on soot is still first order at ~ 35 ppbv ozone mixing ratio is something we cannot determine from our data. A shorter half-life for ozone loss will occur if the loss process is greater than first order with respect to ozone partial pressure. For example, it can be readily computed that the half-life for ozone loss for a second order process at 35 ppbv ozone and 7.5×10^{-7} cm^2/cm^3 soot surface area density is 0.24 years. This time is still sufficiently long as to not represent an important process in the atmosphere. If the reaction order is greater than 2.0, which is however unlikely, it is possible that ozone-soot chemistry may become important.

Results similar to those illustrated in Figure 2 have been

obtained by others [Smith and Chughtai, 1996; Schurath and Naumann, 1998; Stephens et al., 1989]. In one study [Smith and Chughtai, 1996] a distinct two-stage reaction process was observed. Our result, which demonstrates that CO₂ production occurs during the initial reaction stage ($t=6$ min to $t=6$ min) and indicates that O₃ loss is not catalytic, is inconsistent with their study of *n*-hexane soot. In addition, a static chamber study [Schurath and Naumann, 1998] yielded a second-stage reaction probability of $\gamma \sim 10^{-7}$, similar to our value of $\gamma \sim 10^{-8}$; however, their lack of CO₂ measurements did not enable an analysis of the stoichiometric coefficient of CO₂ production, nor the initial ozone uptake on fresh soot, to be made. A study by Stephens et al. [1989] yielded a reaction order of 0.86 ± 0.13 , which is close to the values obtained here.

3. Atmospheric Implications

Our laboratory results can be analyzed to determine the likelihood of significant O₃ decomposition on atmospheric elemental carbon soot aerosol. Our analysis proceeds by first computing the maximum amount of O₃ that can be taken up on fresh soot emissions ($\gamma \sim 10^{-3}$, short-time behavior) assuming a representative aerosol surface area density of 7.5×10^{-7} cm²/cm³ [Hauglustaine et al., 1996]. Next, we utilize the reaction probability of $\gamma \sim 10^{-8}$ for O₃ loss on oxidized soot to compute an O₃ lifetime to again address the feasibility of significant O₃ destruction on atmospheric soot. We begin with computing the average area of the active site (i.e., S-O moieties of (2) and (4)) on soot responsible for ozone loss, given by

$$\zeta = (m \Sigma) / [\text{O}_3]_u, \quad (6)$$

where ζ is the average area of the S-O active site ($\text{\AA}^2/\text{site}$), m is soot mass density (g/cm³), Σ is soot specific surface area taken as the manufacturer's measured BET value ($\text{\AA}^2/\text{g}$), and $[\text{O}_3]_u$ is the quantity of O₃ taken up by the soot during the initial stage of the reaction process (molecules/cm³). The quantities m , Σ , and $[\text{O}_3]_u$ are known from the laboratory experiments, yielding an average value for ζ of $135 \text{\AA}^2/\text{site}$. From this value the quantity of O₃ taken up in the atmosphere can be computed to be $[\text{O}_3]_u = (7.5 \times 10^{-7} \text{ cm}^2/\text{cm}^3) / (135 \text{\AA}^2/\text{site}) (10^{-16} \text{ cm}^2/\text{\AA}^2) = 5.6 \times 10^7$ molecules/cm³, or a mixing ratio of $\sim 2 \times 10^{-12}$. Therefore O₃ loss by uptake on fresh soot emissions, according to (2), is negligible. The lifetime of O₃ according to (3) can be estimated using (5) and the reaction probability of $\gamma \sim 10^{-8}$, the mean-molecular speed of ozone (3.6×10^4 cm/s at 298 K), and the aerosol surface area density of 7.5×10^{-7} cm²/cm³, yielding $\tau = 470$ years. Therefore, on the basis of our laboratory measurements and assuming similarities between atmospheric soot and the elemental carbon soot which we investigated, O₃-soot heterogeneous chemistry cannot account for significant O₃ decomposition in the atmosphere. Recent models have suggested that ozone loss on atmospheric soot may be important [Bekki, 1997; Lary et al., 1997]. However, in one study a large accommodation coefficient for ozone loss on soot of 10^{-3} was used [Bekki, 1997] and in a second investigation HNO₃ → NO_x reduction ($\gamma \sim 10^{-2}$), in addition to ozone loss on soot ($\gamma = 10^{-5}$), was modeled [Lary et al., 1997]. Even under high urban soot loading conditions (10 $\mu\text{g}/\text{m}^3$) ozone loss on soot with $\gamma \sim 10^{-8}$ will be unimportant.

These results have applicability to recent nighttime measurements of ozone and aerosols made downwind of Portland, Oregon. Berkowitz et al. [2000] detected several events during which high aerosol surface area was correlated with reduced ozone mixing ratios within the top of the atmospheric mixed layer downwind of this urban area. Results from a simple empirical uptake model suggested that a causal relation exists. Their observations of the single scattering albedo of the aerosols during these events suggested aerosols with a significant carbonaceous component were associated with this ozone loss. However, the results of our laboratory study suggest that if the aerosols were in fact carbonaceous (no samples were taken on which to do actual aerosol speciation), they were not elemental carbon in nature. Nevertheless, reasonable scenarios can be proposed that account for the field data. Alternative explanations of their data are that the observed anti-correlation is merely coincidental, or that ozone-mediated aerosol production occurs via the oxidation of organic hydrocarbons. This oxidation can occur either by direct ozone reaction or during nighttime chemistry by the nitrate radical (i.e., $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$), as suggested previously [Starn et al., 1998; Griffin et al., 1999; Kamens et al., 1999; Yu et al., 1999; De Gouw and Lovejoy, 1998]. In one study, isoprene and its oxidation products, methyl vinyl ketone (MVK) and methacrolein (MACR), together with the trace gas product $[\text{O}_3][\text{NO}_2]$ were measured at a forest-impacted urban site. This study indicated that nitrate radical initiated isoprene oxidation occurred within the boundary layer. Unfortunately, aerosol formation was not measured. It is reasonable to expect that similar conditions could have existed during the nighttime Portland observations. Additional studies incorporating NO_x and hydrocarbon measurements are needed to support this aerosol formation hypothesis.

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C. M. Berkowitz, M.A. Carpenter, E. G. Chapman, J. P. Cowin, R. S. Disselkamp, N. S. Laulainen, and R. A. Zaveri, Pacific Northwest National Laboratory, 902 Battelle Blvd., Richland, WA 99352. (carl.berkowitz@pnl.gov; michael.carpenter@pnl.gov; elaine.chapman@pnl.gov; jp.cowin@pnl.gov; robert.disselkamp@pnl.gov; nels.laulainen@pnl.gov; rahul.zaveri@pnl.gov)

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