GEOPHYSICAL RESEARCH LETTERS, VOL. 31, L22104, doi:10.1029/2004GL020910, 2004

# Atmospheric evolution of organic aerosol

M. J. Molina, A. V. Ivanov, S. Trakhtenberg, and L. T. Molina

Department of Earth, Atmospheric and Planetary Sciences and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

Received 3 July 2004; revised 9 September 2004; accepted 22 September 2004; published 23 November 2004.

[1] We report here results of an experimental study of the OH-initiated oxidation of solid organics in the presence of $O_2$, $NO_x$ and $H_2O$, using two kinds of self-assembled organic monolayers (alkane and aromatic), paraffin and pyrene films as proxies for organic aerosol. We show that the OH-initiated oxidation of the alkane surfaces leads to rapid volatilization. The gas-phase products detected include $HO_2$, $H_2O_2$, CO, $CO_2$, HCO, $CH_2O$, $CH_3CHO$, $CH_3OH$, and HCOOH. We conclude that volatilization is at least as efficient as wet deposition as a removal process for aliphatic particulates, whereas aromatic particulates show higher stability towards volatilization. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. **Citation:** Molina, M. J., A. V. Ivanov, S. Trakhtenberg, and L. T. Molina (2004), Atmospheric evolution of organic aerosol, *Geophys. Res. Lett.*, *31*, L22104, doi:10.1029/2004GL020910.

## 1. Introduction

[2] Numerous field measurements have shown that particulate organic carbon (OC) is abundant and ubiquitous in the troposphere [*Hildemann et al.*, 1996; *Jacobson et al.*, 2000]. OC aerosol can contribute significantly to the radiative forcing of the Earth's climate [*Dickerson et al.*, 1997] and may affect cloud formation [*Novakov and Corrigan*, 1996]. Little is known about OC aerosol chemistry, but its dominant removal pathway is believed to be through rainout (wet deposition) [*Rogge et al.*, 1993; *Liousse et al.*, 1996; *Hildemann et al.*, 1996]. For this reason the chemistry of organic aerosol has long been thought to be of minor importance in the atmosphere, and hence such chemistry is not normally included in atmospheric models. Nonetheless, the reactive probability of OH [*Bertram et al.*, 2001] and Cl [*Moise and Rudich*, 2001] with carbonaceous aerosol has been reported to be close to unity, whereas uptake of Br [*Moise and Rudich*, 2001], $NO_2$ [*Grassian*, 2002], $NO_3$ [*Moise and Rudich*, 2001], and $O_3$ [*Moise and Rudich*, 2002; *Eliason et al.*, 2003, 2004] is much less efficient.

[3] We report here results of a laboratory investigation of the OH-initiated oxidation of model organic surfaces aimed at elucidating the major pathways of chemical evolution of organic aerosol in the troposphere.

Copyright 2004 by the American Geophysical Union.
0094-8276/04/2004GL020910$05.00

## 2. Experimental

[4] Two types of surfaces were employed in this study: (1) well-organized self-assembled monolayers with thickness of ~2.5 nm deposited on either a silicon wafer or a glass slide, and (2) ~1-μm thick films deposited on glass slides. Octadecyltrichlorosilane (OTS) monolayers and paraffin films served as models for alkane aerosols, and phenyltrichlorosilane (PTS) monolayers and pyrene films as models for aromatic aerosols. The model surfaces were exposed to OH at concentrations ranging from $0.1$ to $100 \cdot 10^8$ molecule $cm^{-3}$ in the presence of $NO_x/O_2/H_2O$ in various proportions. The concentrations of $O_2$, NO, $NO_2$ and $H_2O$ were up to $3 \cdot 10^{16}$, $3 \cdot 10^{12}$, $3 \cdot 10^{12}$ and $6 \cdot 10^{14}$ molecule $cm^{-3}$, respectively. Oxidation of the organic films was monitored by surface analysis techniques: Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), contact angle goniometry (CA), and profilometry.

[5] OH loss and the formation of gas-phase products during heterogeneous oxidation of the organic surfaces were studied using a laminar flow reactor coupled to a chemical ionization mass spectrometer (CIMS), as described elsewhere [*Bertram et al.*, 2001]. Three different reactions (H + $NO_2$, H + $O_2$ + M at 10–12 Torr, and a microwave discharge of water vapor) were employed as OH sources. Oxygen was used as the main carrier gas. All the experiments were performed under fast flow conditions at 1.5–2.1 Torr total pressure and room temperature. Three types of experiments were carried out: (i) kinetics measurements of OH uptake and its time dependence were performed by inserting a Pyrex tube into the cylindrical flow reactor with the inside wall coated with the organic compound of interest; (ii) flat substrates coated with the organic monolayers were exposed inside the reactor to OH in the different gas-phase environments and were subsequently characterized with the surface analysis techniques listed above; and (iii) a finger-like liquid nitrogen trap placed between the downstream end of the flow tube and the CIMS detection zone was used to collect and identify the gas-phase products generated during the oxidation of thick films.

## 3. Results

[6] Blank experiments show that in the absence of OH the OTS, PTS, paraffin and pyrene surfaces do not react with $H_2O$, NO, $NO_2$, $O_2$, HONO, $HNO_3$ or mixtures of those components. Furthermore, none of those species react with each other on the organic surfaces. Evaporation of both paraffin and pyrene was found to be negligible [*Bertram et al.*, 2001].

[7] The CIMS measurements indicate that the presence of NO, $NO_2$ and $H_2O$ has no effect on the value of the OH

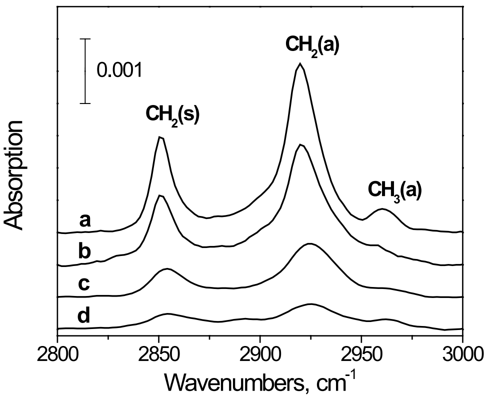

**Figure 1.** FTIR spectra of $CH_3$ and $CH_2$ groups of an OTS monolayer exposed to [OH] = $10^8$ molecule $cm^{-3}$ after the following exposure times: a. 0 min; b. 2.5 min; c. 5 min, d. 10 min.

reactive probability, $\gamma_{OH}$, on any of the surfaces under study. We observed $\gamma_{OH}$ >0.2 for paraffin and pyrene films, independent of time (the flow reactor technique provides only a lower limit to $\gamma_{OH}$ due to diffusion limitations). For OTS monolayers the initial $\gamma_{OH}$ of >0.2 was close to that of paraffin and pyrene, and it rapidly decreased reaching a stable value of $8 \cdot 10^{-3}$ after 15 min of exposure to [OH] at a level of $\sim 10^8$ molecule $cm^{-3}$, corresponding to the bare glass slide and indicating that the OTS monolayer was completely depleted. The same depletion effect was observed for the PTS monolayer with the observed lifetime being a factor of 4–5 longer than that of the OTS monolayer.

[8] The results of FTIR measurements on an OTS surface are shown in Figure 1. Practically all the $CH_X$ groups are removed from the surface after 10 minutes of exposure to $O_2$ and [OH] $\sim 10^8$ molecule $cm^{-3}$. We found the rate of $CH_X$ loss to be higher than that of the OH loss: one OTS chain (18 carbons) is removed as a result of the heterogeneous loss of 2–3 OH radicals.

[9] We observed loss of carbon in the reaction of all the organic surfaces with OH, independently of the OH source used. Within experimental error, the measured rate of carbon loss was the same in the presence and absence of NO. Figures 2a and 2b show an XPS survey and C (1s) spectra of an OTS monolayer exposed to OH for various time periods; the fractional carbon concentration gradually decreased from 45% before exposure to below 10%, which is characteristic of the residual content of cleaned silicon wafers [*Frydman et al.*, 1997] indicating full consumption of the organic layer. Increase of the fractional oxygen concentration and of the O/Si ratio and the broadening of the C (1s) peak indicate oxidation of the remaining organic layer. A chemical shift of the C (1s) line from its characteristic energy at 285 eV at about +1.5 eV, +3 eV, and +4.5 eV can be attributed to formation of C-O, carbonyl, and carboxyl groups, respectively [*Beamoson and Briggs*, 1992]. No nitrogen was detected on the samples, including those exposed to OH/$NO_x$-containing mixtures. Figures 2c and 2d show results of similar XPS measurements for a PTS monolayer; we observed qualitative behavior during oxidation analogous to that of the OTS samples. The observed linear time dependence of the initial monolayer depletion rate on OH concentrations indicates that the OH + OTS/PTS reactions are the rate-limiting steps of the oxidation.

[10] Results of wettability measurements show that after a 15-min exposure to [OH] $\sim 10^8$ molecule $cm^{-3}$ an OTS surface becomes completely hydrophilic (θ < 10°, characteristic of the bare glass), indicating complete consumption of the organic monolayer. For shorter exposure times, the water contact angles were below a 112° (characteristic of the unexposed OTS surface) and were in line with predictions based on the advanced Cassie equation [*Israelachvili and Gee*, 1989]. In contrast, a paraffin surface does not become completely hydrophilic, even after prolonged OH exposure (θ > 30°).

[11] Figure 3a shows a summary of the experimental carbon loss results for OTS monolayers. The points represent the experimental data obtained by FTIR, X-ray photoelectron spectroscopy (XPS), and contact angle goniometry (CA). These techniques yield the same surface decomposition rate, within error. Further, profilometry measurements show that the carbon loss rate for the paraffin film is, within error, the same as for the OTS monolayer. Gas phase species identified as products of the reaction of OH with the

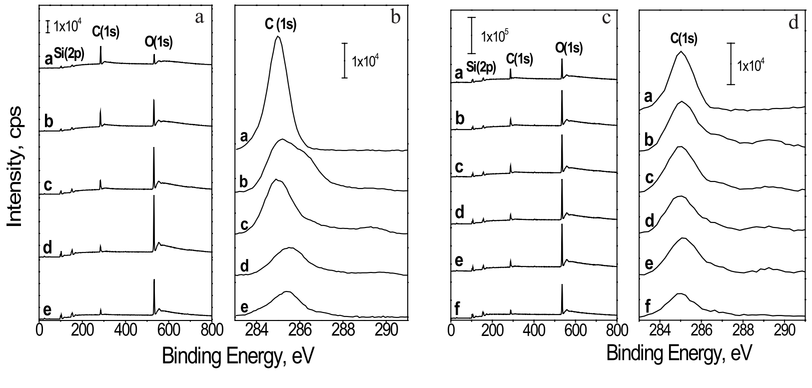

**Figure 2.** (a) XPS survey and (b) spectra of C (1s) for an OTS monolayer exposed to OH = $10^8$ molecule $cm^{-3}$ after the following exposure times: a. 0 min; b. 5 min; c. 10 min; d. 15 min; e. Si (100) wafer. (c) XPS survey and (d) spectra of C (1s) for a PTS monolayer exposed to OH of $2 \cdot 10^8$ molecule $cm^{-3}$ after exposure times of a. 0 min; b. 7 min; c. 18 min; d. 38 min; e. 60 min; f. Si (100) wafer.

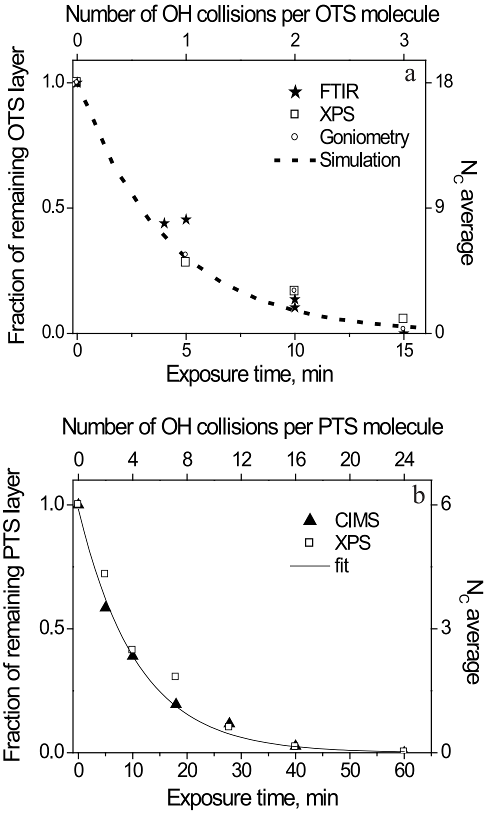

**Figure 3.** (a) Depletion of OTS exposed to [OH] = $10^8$ molecule $cm^{-3}$ in the presence of $[O_2]$ = $3 \cdot 10^{16}$ molecule $cm^{-3}$; (b) depletion of PTS exposed to [OH] = $2 \cdot 10^8$ molecule $cm^{-3}$ in the presence of $[O_2] = 3 \cdot 10^{16}$ molecule $cm^{-3}$.

paraffin film include $HO_2$, $H_2O_2$, CO, $CO_2$, $CH_2O$, $CH_3CHO$, $CH_3OH$, and HCOOH.

[12] Summary results for depletion of a PTS monolayer are shown in Figure 3a, which presents the normalized OH uptake coefficient and the intensity of the C (1s) XPS peak that yield, within experimental error, the same value for the carbon loss rate of the PTS monolayer. Carbon loss occurs more slowly than for OTS samples.

[13] The main gas-phase products of oxidation of pyrene surfaces exposed to an OH level of $10^{10}$ molecule $cm^{-3}$ were found to be $H_2O$, $HO_2$, $H_2O_2$, CO, $CO_2$, HCO and $CH_2O$; glyoxal and acetic acid were detected in trace amounts. Water generated in these experiments appears to come from the secondary chemistry of OH with the gas-phase products. This set of products is quite different from those reported by *Esteve et al.* [2003] in the oxidation of phenanthrene.

[14] Additional experiments with pyrene surfaces were performed at pressures of 50–100 Torr using a quartz-crystal-microbalance (QCM) technique to monitor changes in mass. A relatively fast mass loss was observed in the presence of OH. The loss was found to be a linear function of exposure time and initial OH concentrations.

## 4. Discussion and Conclusions

[15] Figure 4 shows the reaction mechanism we propose for the OH-initiated oxidation of the alkane surfaces, based on the corresponding gas-phase mechanism. The rate-limiting step is the reaction of the organic surface with OH; we note that this rate is enhanced by a factor of ~100 in comparison with the gas-phase reaction [*Bertram et al.*, 2001; *Moise and Rudich*, 2001; *Cohen*, 1991]. In the second step of the overall mechanism the surface alkyl radical R promptly transforms to the surface alkylperoxy radical $RO_2$ in the presence of $O_2$, as observed in recent EPR studies [*Remorov et al.*, 2002; *Attwood et al.*, 2003]. Subsequently, the long-chain surface alkyl peroxy radicals undergo self-reaction. As mentioned above, the rate of carbon loss is not affected by the presence of NO. We conclude that the $RO_2$ self-reaction occurs very efficiently on the organic surface. At sufficiently low OH and high NO levels the surface alkyl peroxy radicals might react preferentially with NO, but we were unable to detect either NO loss or $NO_2$ formation in our experiments. In the gas phase, it has been shown that the rate of the $RO_2$ self-reaction increases significantly as a number of C atoms, $N_C$, increases [*Kirchner and Stockwell*, 1996]. We also note that the product distribution of the $RO_2$ self-reaction differs for long-chain radicals: instead of formation of a peroxide, ROOR, the pathway forming two alkoxy radicals RO becomes dominant as $N_C$ increases [*Atkinson*, 1994; 1997a]. Typically, $N_C$ = 23–32 for OC aerosol [*Rogge et al.*, 1993], and hence the major products are expected to be alkoxy radicals, RO. As indicated in Figure 4, there are, in turn, several possible decomposition channels for the RO radicals: for the long-chain alkoxy radicals the C-C scission channel appears to proceed faster than isomerization (e.g., 1,5 H-shift) and prevails over the $HO_2$-reduction channel both for substituted and primary RO [*Atkinson*, 1994].

[16] We can therefore rationalize the rapid carbon loss observed in our alkane-surface oxidation experiments by assuming that the reaction mechanism leads predominantly to carbon-carbon bond scission. In fact, even if the alkoxy radical intermediate isomerizes or loses a hydrogen atom by reacting with $O_2$, the product would subsequently react with another OH radical, leading to the formation of more active (β-OH substituted or O-containing) alkoxy radicals that decompose faster [*Atkinson*, 1997b] and thus contributing subsequently also to the scission channel. The carbon loss

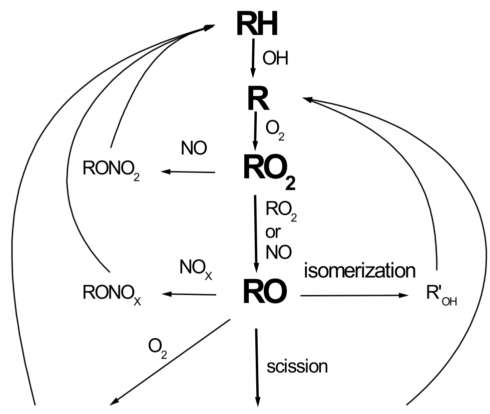

**Figure 4.** Proposed reaction mechanism of oxidative degradation of alkane surfaces.

effect appears to be analogous to the oxidative degradation observed in hydrocarbon polymers [*Mikheev et al.*, 2001], with the participation of radical intermediates.

[17] Our results indicate that the overall carbon loss rate is determined by the initial rate of OH attack, even in the absence of gas-phase NO. The dashed line in Figure 3a represents a simulation of the carbon loss rate based on this rate-determining step assumption.

[18] We conclude that the atmospheric oxidation of alkane aerosol, which is initiated predominantly by reaction with OH radicals [*Bertram et al.*, 2001; *Eliason et al.*, 2003], leads efficiently to volatilization of the aerosol. The concentrations of $O_2$ in our experiments are smaller than in the ambient air and hence the RO + $O_2$ path might be enhanced in the atmosphere relatively to our laboratory observations. By simulating the overall mechanism using literature gas-phase reaction rate values (except for the faster initial OH attack) and assuming that two neighboring surface $RO_2$ radicals react immediately with each other, we estimate that the atmospheric volatilization rate decreases by a factor of $\sim$3 relative to our laboratory measurement.

[19] The lifetime of OC aerosol has been estimated previously to be 4 to 5 days [*Rogge et al.*, 1993; *Liousse et al.*, 1996; *Hildemann et al.*, 1996], assuming wet deposition to be the dominant sink; dry deposition is negligible because of small deposition velocities [*Seinfeld and Pandis*, 1998]. At an average global OH concentration of $\sim 10^6$ molecule $cm^{-3}$ [*Prinn et al.*, 2001], and assuming that the carbon loss rate is directly proportional to the OH concentration we estimate the volatilization lifetime of a log-normally mass-distributed alkane aerosol with size of 0.01–0.2 $\mu$m to be $\sim$6 days. We conclude that volatilization and wet deposition occur at comparable rates for an alkane particle, and hence, volatilization is an important removal pathway for these aerosols in the troposphere.

[20] The proposed reaction mechanism based on our laboratory measurements of carbon loss rates describes well the oxidation of alkane aerosols initiated by OH radicals, and may also be applied to other condensed aliphatic compounds, such as carboxylic and dicarboxylic acids, aldehydes, ketones, esters, and alkenes, because oxidation mechanisms for these compounds, which comprise a major fraction of primary OC aerosol ($\sim$80%) [*Calvert et al.*, 2002], are expected to be similar to those of long-chain alkanes. Clearly, additional experiments need to be conducted to investigate the atmospheric chemistry of these other aerosol components.

[21] We also studied oxidation of aromatic surfaces with one (PTS) and four aromatic rings (pyrene). The reaction mechanism for cleavage of one-aromatic-ring and subsequent defragmentation (carbon loss) can be explained in terms of the analogous gas-phase chemistry, where a major reaction pathway proceeds via attachment of OH to the aromatic ring, with formation of a surface aromatic radical, which in the presence of oxygen rapidly generates a peroxy radical. Defragmentation via a series of C-C bond scissions finally leads to the formation of small oxygenated organic compounds (glyoxal, acetic acid, ethers) [*Calvert et al.*, 2002] that evaporate from the particle. The pyrene results indicate that aromatic ring cleavage prevails over aromatic ring-retaining processes.

[22] Preliminary results of methane-soot oxidation studies also indicate efficient carbon loss, and we expect the carbon loss mechanism proposed here can also be applied to describe the atmospheric oxidation of soot.

[23] **Acknowledgments.** This work was supported by grants from the National Science Foundation and the U.S. Air Force Office of Scientific Research. The authors are grateful to Kirsten Johnson for her help with the QCM experiments.

## References

Atkinson, R. (1994), Gas-phase tropospheric chemistry of organic compounds, *J. Phys. Chem. Ref. Data Monogr.*, *2*, 1.

Atkinson, R. (1997a), Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes, *J. Phys. Chem. Ref. Data*, *26*, 215–248.

Atkinson, R. (1997b), Atmospheric reactions of alkoxy and β-hydroxyalkoxy radicals, *Int. J. Chem. Kinet.*, *29*, 99–111.

Attwood, A. L., J. L. Edwards, C. C. Rowlands, and D. M. Murphy (2003), Identification of a surface alkylperoxy radical in the photocatalytic oxidation of acetone/$O_2$ over $TiO_2$, *J. Phys. Chem. A*, *107*, 1779–1782.

Beamoson, G., and D. Briggs (1992), *High Resolution XPS of Organic Polymers: The Scenta ESCA 300 Database*, 408 pp., John Wiley, Hoboken, N. J.

Bertram, A. K., A. V. Ivanov, M. Hunter, L. T. Molina, and M. J. Molina (2001), The reaction probability of OH on organic surfaces of atmospheric interest, *J. Phys. Chem. A*, *105*, 9415–9421.

Calvert, J. G., et al. (2002), *The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons*, 556 pp., Oxford Univ. Press, New York.

Cohen, N. (1991), Are reaction rate coefficients additive? Revised transition state theory calculations for OH + alkane reactions, *Int. J. Chem. Kinet.*, *23*, 397–417.

Dickerson, R. R., et al. (1997), The impact of aerosols on solar ultraviolet radiation and photochemical smog, *Science*, *278*, 827–830.

Eliason, T. L., S. Aloisio, D. J. Donaldson, D. J. Cziczo, and V. Vaida (2003), Processing of unsaturated organic acid films and aerosols by ozone, *Atmos. Environ.*, *37*, 2207–2219.

Eliason, T. L., J. B. Gilman, and V. Vaida (2004), Oxidation of organic films relevant to atmospheric aerosols, *Atmos. Environ.*, *38*, 1367–1378.

Esteve, W., H. Budzinski, and E. Villenave (2003), Heterogeneous reactivity of OH radicals with phenanthrene, *Polycyclic Aromat. Compd.*, *23*, 441–446.

Frydman, E., H. Cohen, R. Maoz, and J. Sagiv (1997), Monolayer damage in XPS measurements as evaluated by independent methods, *Langmuir*, *13*, 5089–5106.

Grassian, V. H. (2002), Chemical reactions of nitrogen oxides on the surface of oxide, carbonate, soot, and mineral dust particles: Implications for the chemical balance of the troposphere, *J. Phys. Chem. A*, *106*, 860–877.

Hildemann, L. M., W. F. Rogge, G. R. Cass, M. A. Mazurek, and R. T. Simoneit (1996), Contribution of primary aerosol emission from vegetation-derived sources to fine particle concentrations in Los Angeles, *J. Geophys. Res.*, *101*, 19,541–19,549.

Israelachvili, J. N., and M. L. Gee (1989), Contact angles on chemically heterogeneous surfaces, *Langmuir*, *5*, 288–289.

Jacobson, M. C., et al. (2000), Organic atmospheric aerosols: Review and state of the science, *Rev. Geophys.*, *38*, 267–294.

Kirchner, F., and W. R. Stockwell (1996), Effect of peroxy radical reactions on the predicted concentrations of ozone, nitrogenous compounds, and radicals, *J. Geophys. Res.*, *101*, 21,007–21,022.

Liousse, C., J. E. Penner, C. Chuang, J. J. Walton, H. Eddleman, and H. Cachier (1996), A global three-dimensional study of carbonaceous aerosol, *J. Geophys. Res.*, *101*, 19,411–19,432.

Mikheev, Y. A., G. E. Zaikov, and V. G. Zaikov (2001), Heterogeneous features of autooxidation of hydrocarbon polymers, *Polym. Degrad. Stability*, *72*, 1–21.

Moise, T., and Y. Rudich (2001), Uptake of Cl and Br by organic surfaces: A perspective on organic aerosols processing by tropospheric oxidants, *Geophys. Res. Lett.*, *28*, 4083–4086.

Moise, T., and Y. Rudich (2002), Reactive uptake of ozone by aerosol-associated unsaturated fatty acids: Kinetics, mechanism, and products, *J. Phys. Chem. A*, *106*, 6469–6476.

Novakov, T., and C. E. Corrigan (1996), Cloud condensation nucleus activity of the organic component of biomass smoke particles, *Geophys. Res. Lett.*, *23*, 2141–2144.

Prinn, R. G., et al. (2001), Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades, *Science*, *292*, 1882–1888.

Remorov, R. G., et al. (2002), Spectroscopic and kinetic evidence of surface radicals formation in heterogeneous reactions of solid paraffin wax with atmospheric radicals OH, Cl, paper presented at 17th International Symposium on Gas Kinetics, Univ. of Essen, Essen, Germany, 24–29 Aug.

Rogge, W. F., M. A. Mazurek, L. M. Hildemann, G. R. Cass, and B. R. T. Simoneit (1993), Quantification of urban organic aerosols at a molecular-level: Identification, abundance and seasonal-variation, *Atmos. Environ., Part A*, *27*, 1309–1330.

Seinfeld, J. H., and S. N. Pandis (1998), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 1326 pp., John Wiley, Hoboken, N. J.

---

A. V. Ivanov, L. T. Molina, M. J. Molina, and S. Trakhtenberg, Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA. (mmolina@mit.edu)