Reports

The Role of Biogenic Hydrocarbons in Urban Photochemical Smog: Atlanta as a Case Study

W. L. CHAMEIDES, R. W. LINDSAY, J. RICHARDSON, C. S. KIANG

The effects of natural hydrocarbons must be considered in order to develop a reliable plan for reducing ozone in the urban atmosphere. Trees can emit significant quantities of hydrocarbons to metropolitan areas such as Atlanta, and model calculations indicate that these natural emissions can significantly affect urban ozone levels. By neglecting these compounds, previous investigators may have overestimated the effectiveness of an ozone abatement strategy based on reducing anthropogenic hydrocarbons.

HAAGEN-SMIT'S PIONEERING WORK on photochemical smog first established that the photooxidation of hydrocarbons in the presence of nitrogen oxides produces ozone (O_3) (1). In urban areas with large emissions of anthropogenic hydrocarbons (AHCs) and nitrogen oxides (NO_x), this mechanism often drives summer O_3 levels above the 0.12 ppmv National Ambient Air Quality Standard (NAAQS) (2). In the United States, a plan for O_3 abatement was implemented in the 1970s through the Clean Air Act. Although the law calls for emission reductions in either AHCs or NO_x, its implementation by the Environmental Protection Agency (EPA) and the relevant state agencies has focused on AHC reductions (2, 3). However, despite large and costly reductions in AHC emissions during the past 10 years, O_3 levels in many areas have not decreased (4, 5); more than 60 cities remain in violation of the NAAQS, and almost 40% of these cities are in the South.

The apparent lack of success in U.S. efforts to reduce O_3 suggests that there may be flaws in our nation's O_3 abatement strategy or in its implementation. One possible flaw in the current AHC-based strategy relates to the assumption implicit in the strategy that AHC emissions are the dominant source of O_3-producing hydrocarbons to the urban atmosphere and that biogenic or natural hydrocarbons (NHCs) are negligible. Our studies, which have focused on the chemistry of a specific southern city (Atlanta, Georgia) where O_3 levels continue to exceed the NAAQS despite sizable AHC reductions (5), suggests that this assumption is not always appropriate.

In the United States, trees are the principal emitters of biogenic nonmethane hydrocarbons, and isoprene and α-pinene are the primary species emitted (6–10). Nationwide this source is estimated to produce 30×10^9 to 60×10^9 kg of carbon per year, whereas AHC sources account for only about 18×10^9 kg of carbon per year (6, 10). However, despite the large NHC source and smog chamber experiments that indicate that NHCs can effectively produce O_3 in the presence of NO_x and sunlight (11), the role of NHCs in urban photochemical smog has been discounted (12). One argument advanced for neglecting NHCs is that although NHC sources averaged over the entire United States may be significant compared to AHC sources, they should be relatively small in urban areas where anthropogenic emissions are most concentrated (10). However, an analysis of NHC sources in urban areas indicates that these sources are ubiquitous and quite significant; in southern cities such as Atlanta, NHC emissions appear to be as large as, if not larger than, AHC emissions (13–17).

It has also been argued that NHCs are negligible because their urban concentrations are much smaller than those of AHCs (10, 16). However, because NHCs are more reactive than AHCs, they react faster than AHCs and thus can have a significant effect in spite of their low concentrations.

In our model calculations simulating the formation of O_3 in Atlanta, NHCs had a large effect although they comprised only a few percent of the total hydrocarbon burden. These calculations were performed with the city-specific empirical kinetics modeling approach (EKMA) (18–20). The EKMA model (developed by the EPA) simulates the photochemistry of a well-mixed column of air extending from the surface to the top of the mixed layer as the column advects from its initial position at 0800 local standard time (LST) at the city center to some evening position downwind of the city. During advection, surface emissions add hydrocarbons and NO_x to the column, and variations in the mixing height cause air from above to be mixed into the column. The effects of changes in the local hydrocarbon source strength are explored by simultaneously varying the initial hydrocarbon concentration at 0800 LST and the daytime surface emission rates. Changes in the local NO_x source strength are explored by varying the equivalent NO_x parameters.

A 34-species photochemical mechanism, CB-4, was used in the model to simulate the chemistry within the air column. In CB-4 a carbon-bond mechanism is used in which nine functional groups represent the volatile organics emitted into the urban atmosphere (21). Although the chemistry of isoprene is explicitly included in the mechanism, this portion of the mechanism is not typically used; EPA recommends to EKMA users that isoprene be set equal to zero, thereby inactivating the NHC portion of the mechanism (19).

The model parameters were chosen to simulate O_3 in an air column advecting from downtown Atlanta to Conyers, Georgia (located 40 km southeast of Atlanta), on 4 June 1984, a typical O_3-episode day for Atlanta (22). This day was also simulated by the Georgia Department of Natural Resources (DNR) for their 1987 State Implementation Plan, and, except for the inclusion of an NHC source, the input data used in our simulations were the same as those used by DNR (23, 24).

Because vegetative emissions are light- and temperature-sensitive, the NHC emissions added to the model were distributed over the course of the day so that most of the NHCs were emitted in the afternoon. The NHC emission rate was initially 0, increased linearly until 1200 LST, remained constant from 1200 to 1500 LST, and then decreased linearly to 0 at 1900 LST. (Slightly higher O_3 levels were obtained when the NHC emissions were held constant with time.) We varied the total, integrated, daytime NHC emission rates from 0 to 50 kg km^{-2} (13). In all cases the initial NHC concentration was set at 0.

All NHC emissions were assumed to be isoprene (25). The chemistry of isoprene was simulated with (i) that specifically included in the CB-4 mechanism and (ii) the functional group chemistry of the CB-4 mechanism (each isoprene molecule treated as two olefins and one paraffin) (21). We report the results of the first approach, but both approaches generally yielded O_3 levels within a few percent of each other.

The maximum 1-hour averaged O_3 level

School of Geophysical Sciences, Georgia Institute of Technology, Atlanta, GA 30332.

calculated as a function of AHCs and NO_x with no NHC emissions is shown in Fig. 1A. The maximum O_3 level of 0.150 ppmv calculated for present-day AHC and NO_x levels (the dot in Fig. 1A) is in excellent (perhaps fortuitous) agreement with the maximum O_3 level measured at Conyers (0.147 ppmv). Because a reduction in AHC emissions from 34 to 24 kg km^{-2} reduces O_3 from 0.15 ppmv to the NAAQS of 0.12 ppmv in Fig. 1A, one would project on the basis of this figure that a 30% reduction in AHC emissions would be needed to bring Atlanta into compliance with the Clean Air Act. However, this projection changes considerably if NHCs are included.

The maximum O_3 levels calculated as a function of AHCs and NHCs with NO_x held at present-day levels are shown in Fig. 1B. The vertical dashed line indicates the results when AHCs are held constant at present-day levels; by following this line upward from the x-axis, one can explore the effects of adding NHC emissions to the existing NO_x and AHC emissions. As Lurmann *et al.* (*26, 27*) found, adding NHCs to the anthropogenic emissions has a very small effect on O_3; 30 kg of NHCs per square kilometer caused only a 10% increase in O_3 in Fig. 1B. However, it would not be correct to conclude that NHCs can be neglected. For these high emission rates, there is an overabundance of hydrocarbons and, as a result, O_3 responds nonlinearly to any hydrocarbon addition. Thus increasing AHCs above present-day levels also has a very small effect on O_3. Note that NHCs can generate significant O_3 levels by themselves. In Fig. 1B, with AHCs set to 0, maximum O_3 levels of 0.08, 0.11, and 0.12 ppmv were obtained for NHC emission rates of 30, 40, and 50 kg km^{-2}, respectively.

Because of the nonlinear response to hydrocarbons of O_3, the presence of NHCs can exert a profound influence on the effectiveness of an O_3 abatement strategy based on AHC reductions. With no NHC emissions, the calculations imply that a 30% reduction in AHC emissions would be adequate to reduce O_3 to 0.12 ppmv. However, for an NHC emission rate of 30 kg km^{-2} [our estimate of the isoprene emission rate for the Atlanta area (*13*)], a 70% AHC reduction would be needed. For NHC emissions of 50 kg km^{-2} [our estimate of the total daytime NHC emission rate (*13*)], O_3 remains above the NAAQS even after AHC emissions are completely eliminated. We find that for NHC emissions of 30 kg km^{-2} or more, the percentage reduction in NO_x emissions needed to bring O_3 down to 0.12 ppmv is less than that required of AHC emissions.

Although our results should be viewed cautiously because of uncertainties in the chemical mechanism used in the model and in the AHC and NHC emission rates, a comparison of our results with the observations of Westberg and Lamb (*16*) suggests that the parameters used are not unreasonable. On 3 days in the summer of 1981 with winds out of the northwest, Westberg and Lamb measured hydrocarbon levels at Dekalb Community College, located approximately midway between downtown Atlanta and Conyers. The average midday levels of total nonmethane hydrocarbons and isoprene were 165 and 5 ppbv, respectively. In the model, with the use of present-day AHC levels and an NHC emission rate of 50 kg km^{-2}, the calculated, midday total hydrocarbon level was 173 ppbv and the NHC (as isoprene) level was 2.3 ppbv.

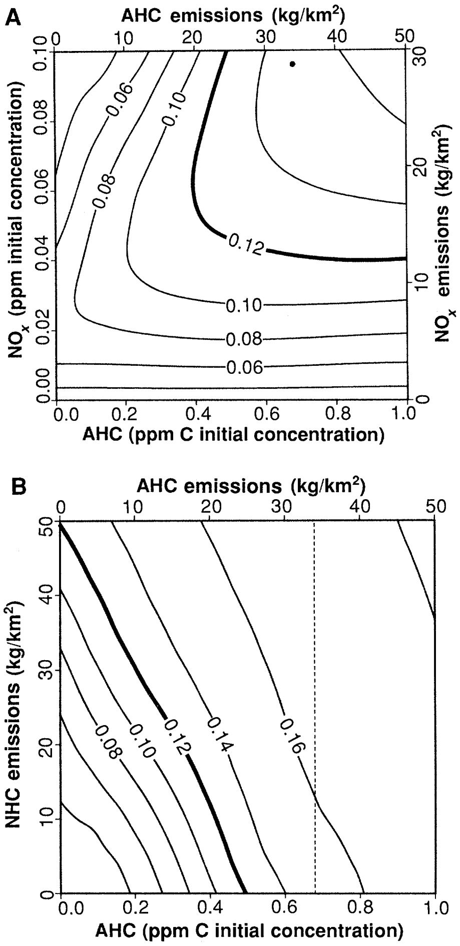

Fig. 1. Isopleths of the maximum, hourly O_3 levels (in parts per million by volume) calculated as a function of (**A**) NO_x and AHCs with NHC emissions set to 0 and (**B**) AHCs and NHCs (as isoprene) with NO_x set at present-day levels. The dot in (A) indicates the O_3 level obtained for present-day conditions (an initial AHC concentration of 0.68 ppmv, a total daytime AHC emission rate of 34 kg km^{-2}, an initial NO_x concentration of 0.096 ppmv, and a total daytime NO_x emission rate of 28 kg km^{-2}). EPA recommends that diagrams like this one be used by state agencies making emission control projections (*19*).

Our results indicate the potential importance of NHCs to urban photochemical smog and the errors that can be incurred by pursuing an O_3 abatement strategy that ignores their effect. Although uncertainties remain in the emission rates and atmospheric chemistry of NHCs, as they do in the case of AHCs, we believe that the effects of NHCs must be considered if we are to develop a reliable and effective strategy for controlling O_3.

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12. The importance of NHCs in O_3 episodes in rural forested areas has recently been pointed out by M. Trainer *et al.*, *Nature* **329**, 705 (1987).
13. An analysis of digitized LANDSAT data and information from the Atlanta Regional Commission indicates that about 57% of the 9000-km^2, 11-county, EPA-designated Atlanta nonattainment area was wooded in 1985; urban growth has caused these wooded areas to shrink at a rate of only about 2% per year (*14, 15*). Of this 57%, 23% was deciduous, 18% was mixed, and 16% was coniferous. Combining these data with Zimmerman's (*9*) biogenic emission factors at 30°C for the three forest types, we estimated Atlanta area–averaged, daytime emission rates of 2100 μg of carbon per square meter per hour for isoprene and 1400 μg m^{-2} $hour^{-1}$ of non-isoprene NHCs. Our isoprene emission estimate compares well with Westberg and Lamb's (*16*) estimate of 2500 μg m^{-2} $hour^{-1}$ for daytime isoprene emissions in Atlanta. At night, isoprene is not emitted and thus the total nighttime NHC emission rate is also ~1400 μg m^{-2} $hour^{-1}$. For 15 hours of daylight in the summer, the above results imply integrated daytime sources of about 30 kg km^{-2} for isoprene and 50 kg km^{-2} for all NHCs. Over a 24-hour period the integrated NHC source is about 65 kg km^{-2}. Although these NHC emission rates are small compared with the maximum AHC emission rate of 600 kg km^{-2} day^{-1} found in a 10-km^2 area of downtown Atlanta, they are equivalent to the averaged AHC emission rate for the 11-county area of about 30 kg km^{-2} day^{-1} (*5, 16*). Large NHC emissions are not unique to Atlanta. Independent estimates of the NHC emission rates in two other southern cities—Houston, TX (*17*), and Tampa Bay–St. Petersburg, FL (*9*)—are roughly equivalent to our estimate for Atlanta. Thus large sources of NHCs may be ubiquitous to cities in the South and possibly other regions of the country as well.
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19. *Guideline for Use of City-Specific EKMA in Preparing Post-1987 Ozone SIP's* (State Implementation Plans) (Environmental Protection Agency, Washington, DC, 1987), pp. 1–56.
20. Simulations were also performed with a photochemical box model that includes a more complete photochemical mechanism based on the work of F. W. Lurman, A. C. Lloyd, and R. Atkinson [*J. Geophys. Res.* **91**, 10905 (1986)]. The results of these calculations were similar to those presented here (*15*).
21. G. Whitten, H. Hugo, J. P. Killus, *Environ. Sci. Technol.* **14**, 690 (1980).
22. On 4 June 1984, temperatures in Atlanta during the daylight hours averaged 28°C and peaked at 32°C. The winds were out of the northwest, and by the end of the day O_3 at a DNR monitoring station in Conyers had peaked at 0.147 ppmv.
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24. To simulate present-day AHC and NO_x levels, the initial AHC and NO_x concentrations were set at 0.68 and 0.096 ppmv, respectively, in accordance with early morning observations from downtown Atlanta, and the total AHC and NO_x surface emissions from 0800 to 1900 LST were set at 34 and 28 kg km^{-2}, respectively. The emissions and their distribution as a function of time were chosen to correspond to the emissions an air column would encounter if it followed a trajectory from downtown Atlanta to Conyers. The chemical speciation of the initial mix of AHCs and NO_x and of the emissions was based on the apportioning factors or "reactivities" recommended by EPA (*19*).
25. Because all NHCs may not be as reactive and may not produce as much O_3 as isoprene, our treatment of all NHCs as isoprene may have caused us to overestimate the effect of NHCs on O_3 for a given NHC emission rate. However, even if isoprene were the only NHC species to produce O_3 [a very unlikely eventuality (*11*)], our conclusion regarding the importance of NHCs would still be valid; our calculations indicate that the daytime emission rate for isoprene alone [30 kg km^{-2} (*13*)] is sufficient to significantly affect urban O_3 levels.
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27. Lurman *et al.* (*26*) claimed to have shown that NHCs are unimportant through model simulations of the Tampa Bay–St. Petersburg area. Model simulations were reported with only AHC sources and with both AHC and NHC sources. Because the maximum O_3 level calculated with both sources was only about 10% larger than that calculated with only the AHC source, the authors concluded that NHCs were not important. However, as Trainer *et al.* (*12*) have shown, these results can be misleading; if the system is not limited by hydrocarbons, then the O_3 production rate will respond nonlinearly to the addition of AHCs as well as NHCs.

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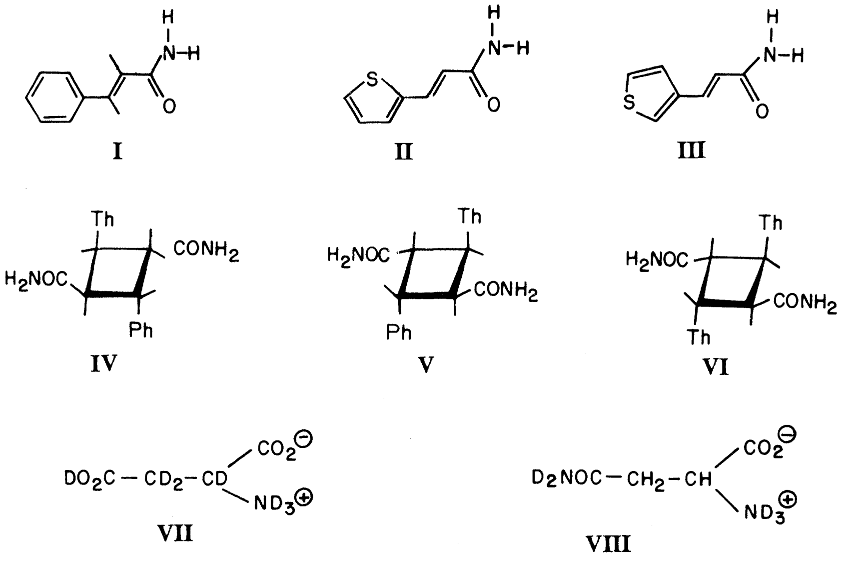
The Structure and Symmetry of Crystalline Solid Solutions: A General Revision

M. Vaida, L. J. W. Shimon, Y. Weisinger-Lewin, F. Frolow, M. Lahav, L. Leiserowitz, R. K. McMullan

Mixed single crystals composed of host and guest organic molecules of similar structures and shapes are shown to comprise sectors with different host-guest distributions and to have symmetries lower than that of the host crystal. These properties are determined by the structure of the guest and the surface structures of the crystal faces through which the guest molecules are occluded. This general concept is illustrated by studies of three mixed crystal systems, (*E*)-cinnamamide–(*E*)-2-thienylacrylamide, (*E*)-cinnamamide–(*E*)-3-thienylacrylamide, and (*S*)-asparagine–(*S*)-aspartic acid, with x-ray and neutron diffraction and solid-state photochemistry.

Mixed crystals composed of host and guest molecules of similar molecular structures and shapes have been generally observed to exhibit the same symmetries as those of the host crystals. Moreover, Kitaigorodsky proposed that guest molecules will occupy all symmetry-related sites with equal probability (*1*). These assumptions are the outcome of considerations of bulk thermodynamic properties, and, to our knowledge, no diffraction studies to the contrary have been reported.

We have shown that the adsorption and occlusion of minor amounts of additive during crystal growth are dictated by interactions between the additive and substrate molecules at the crystal surface (*2*). In cases where the additive is a substrate molecule with an altered moiety or functional group and these interactions are unfavorable, additive occlusion will be limited (0.01 to 1.0%). We show that for solid solutions, produced by the occlusion of large amounts of guest, the nature of the occlusion is also dictated by a mechanism dependent on surface symmetry and structural considerations. Thus the guest may be adsorbed and preferentially occluded at different subsets of surface sites on the various faces, leading to a mixed crystal composed of distinct sectors coherently compounded together. Each sector exposes to solution its bounding crystal face. By our proposed mechanism, we anticipate that the symmetry of each sector will, in general, be lower than that of the host crystal, as illustrated here by low-temperature diffraction studies of three mixed-crystal systems (see scheme 1), (*E*)-cinnamamide (**I**)–(*E*)-2-thienylacrylamide (**II**), (*E*)-cinnamamide–(*E*)-3-thienylacrylamide (**III**), and the amide-acid system (*S*)-asparagine (**VII**)–(*S*)-aspartic acid (**VIII**), and by studies of the photochemical behavior of the first system. With these examples we show that



Scheme 1

M. Vaida, L. J. W. Shimon, Y. Weisinger-Lewin, F. Frolow, M. Lahav, L. Leiserowitz, Department of Structural Chemistry, Weizmann Institute of Science, Rehovot 76100, Israel.
R. K. McMullan, Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973.