Ozone Formation in Coastal Urban Atmospheres:
The Role of Anthropogenic Sources of Chlorine

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In this communication, we present experimental results from our environmental chamber studies to suggest that anthropogenic sources of molecular chlorine (Cl_2), a photolytic source of Cl·, may contribute significantly to ozone formation in some urban environments. Many studies have focused on the sources and chemistry of halogen atoms in pristine marine environments[1-3], often attributing a net consumption of ground-level ozone to reactions with halogen atoms, primarily bromine and to a lesser extent, chlorine[4-7]. However, little attention has been directed at determining the effect of Cl· on ozone formation in urban environments, where oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) are ubiquitous and there exist many anthropogenic sources of Cl_2. Large anthropogenic sources of Cl_2 emissions include chemical production facilities, water treatment plants, and paper production operations. Chlorine atoms, formed by the photolysis of Cl_2, react with alkanes at up to two orders of magnitude faster than do hydroxyl radicals and can promote the formation of O_3 in the presence of VOCs and NO_x[2,3].

To understand how chlorine promotes ozone formation in a mixture of VOCs and NO_x representative of the coastal urban troposphere, we performed experiments in outdoor Teflon environmental chambers. The chambers were approximately 2 m³ in volume with internal volume to surface ratios of approximately 0.13 m when fully inflated. The chambers were conditioned[8,9] and subsequently prepared by flushing with zero air overnight. A commercially available mixture of 56 hydrocarbons (Matheson "Enviro-Mat" Ozone Precursor), as well as individual hydrocarbon reactants were used in the experiments. NO_x (Praxair- NO/NO_2 at a ratio

of 200:1) was also injected into the chamber while the chamber was covered with an opaque tarp. After these reactants were allowed sufficient time to mix, Cl_2 (Air Products and Chemicals) was injected, the tarp removed, and gas sampling begun. Gas withdrawn from the chamber was delivered to O_3 (Dasibi 1008AH or 1003PC) and NO_x (Monitor Laboratories 9841 or Columbia Scientific Industries 1600) analyzers. These continuous measurements were collected as 5-minute averages by Climatronics Corporation IMP 850 microloggers. Air samples for hydrocarbon analysis were collected in 6-liter stainless steel Summa® canisters and analyzed by a HP 5890A gas chromatograph (GC) equipped with a flame ionization detector (FID) and/or a HP 6890 GC with a HP 5972 mass selective detector and Entech 7000 preconcentrator/cryofocuser.

A first set of chamber experiments was directed at showing whether the addition of Cl_2 to a mixture of VOCs and NO_x representative of conditions found in Houston, TX would promote the formation of O_3. Initial reactants included a mixture of 56 hydrocarbons with a total hydrocarbon concentration of approximately 1 part per million carbon (ppm_c). Sufficient NO_x was injected to yield an initial VOC/NO_x ratio of 10 ppb_c/ppb_v. Initial Cl_2 concentrations were between 0 and 47 ppb_v. Each run was conducted under conditions of similar solar flux and temperature. The data summarized in Table 1 show that the peak O_3 concentration ($[O_3]_{peak}$) increases by up to a factor of six with the addition of Cl_2, and the time required to reach $0.63*[O_3]_{peak}$ was reduced by up to a factor of 3.5. In addition, experiments that included injections of Cl_2 showed significant losses of alkanes, specifically substituted alkanes. The loss of alkanes increased from less than 10 percent in experiments without added Cl_2 to greater than 60 percent for hexane, 2,3-dimethylpentane, and octane in experiments with added Cl_2. Losses of alkenes and aromatic compounds were similar between runs with and without added Cl_2 (Table 2). If the chemistry in these experiments were dominated by the reactions of hydroxyl

radical, loss of alkenes and substituted aromatics would be expected, but the C_{6+} alkanes would be relatively unreactive[10-15] and contribute little to the formation of ozone[16]. What was observed, however, was a depletion of alkanes and an increase in ozone concentrations. This is consistent with chlorine radical initiated oxidation chemistry.

A second set of chamber experiments were run to identify which classes of hydrocarbons were most significantly affecting O_3 production associated with the addition of Cl_2. During these experiments n-pentane (EM Omnisolv), propene (Matheson-C.P. grade), and benzene (EM-reagent grade) were used to represent each of the major classes (alkanes, alkenes, and aromatics) of hydrocarbons found in the urban troposphere.

In runs with approximately equal concentrations (in ppb_c) of benzene, pentane, and propene, no significant changes in peak O_3 concentration or rate of formation were observed with the addition of Cl_2. However, for runs containing only pentane in air, a significant increase in peak O_3 concentration was observed and the activation time for significant ozone production decreased by a factor of 2.

To a first approximation, these results can be explained by comparing the rates of reaction of OH· and Cl· with each of the reactant hydrocarbon species (Table 3). The reaction rate constant of OH· with propene is approximately an order of magnitude greater than the reaction rate constants of OH· with pentane or benzene. However, the reaction of Cl· with pentane and propene proceed with similar rate constants at 298K. Benzene reacts even more slowly with Cl· than OH· at this temperature. Because anthropogenic O_3 formation in the presence of VOCs and NO_x is initiated by reactions of free radicals with hydrocarbons and subsequent conversion of NO to NO_2, Cl· appears to have a pronounced effect on O_3 production

and peak concentrations when there exists significant Cl· activation of alkanes relative to alkene oxidation by OH· and Cl·.

Our initial findings are presented as evidence to suggest that Cl_2 can significantly contribute to ozone formation in urban areas. By adding Cl_2 to a mixture of VOCs and NO_x in air typical of urban atmospheres, we show that the rate of formation and peak concentrations of ozone significantly increase relative to control runs without added molecular chlorine. In addition to an increase in O_3 formation, Cl· dominated chemistry is evidenced by the significant loss of alkanes, typically not observed for chemistry dominated by OH·. Further environmental chamber studies will be performed to determine whether these phenomena occur at various VOC/NO_x ratios and with different VOC compositions.

Acknowledgements

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Table 1 Ozone Data Summary

Hydrocarbon (HC) Mixture	HC/NO_x (ppb_c/ppb_v)	$[Cl_2]_o$ (ppb_v)	$[O_3]_{Peak}$ (ppb_v)	Time to reach $0.63*[O_3]_{Peak}$ (min.)	$\dfrac{\Delta(O_3\text{-NO})}{Cl_2}$
O_3 Precursor	10	0	37	95	na
O_3 Precursor	10	14	85	41	4.5
O_3 Precursor	10	20	120	52	5.0
O_3 Precursor	10	47	262	27	5.1
				Average:	**4.9**
PBP[*]	20	0	312	165	na
PBP[*]	20	5	305	137	*
Pentane	5	0	90	227	na
Pentane	5	5	138	197	9.6

*   PBP – Pentane, benzene, and propene.
**   No increase in peak ozone concentration observed.

Table 2 Fractional Losses of VOCs: Experiments with O_3 Precursor

Compound	Fraction Lost $[Cl_2]_o$= 0 ppb$_v$	Fraction Lost $[Cl_2]_o$= 14 ppb$_v$	Fraction Lost $[Cl_2]_o$= 20 ppb$_v$	Fraction Lost $[Cl_2]_o$= 47 ppb$_v$
Alkanes				
2,3-Dimethylpentane	0.13	0.30	0.62	0.63
n-Hexane	0.02	0.39	0.37	0.60
n-Octane	0.06	0.32	0.55	0.76
n-Nonane	0.01	0.52	0.43	0.43
Alkenes				
1-Pentene	0.31	0.24	0.32	0.32
2-Methyl, 1-3-Butadiene	0.88	1.00	1.00	1.00
Aromatics				
Benzene	0.17	0.01	0.01	0.11
Toluene	0.18	0.10	0.01	0.21

Table 3 Rate Constants

Compound	k_{OH} $(10^{-14}$ cm^3 molecule^{-1} s^{-1})	k_{Cl} $(10^{-14}$ cm^3 molecule^{-1} s^{-1})
Alkanes		
Methane[10]	0.64	10
Ethane[10]	25	5,900
Propane[10]	110	14,000
n-Butane	244[11]	22,000[10]
n-Pentane[11]	400	28,000
n-hexane[11]	545	34,000
Alkenes		
Ethene	900[10]	10,700[11]
Propene	3,000[10]	28,000[11]
Aromatics		
Benzene	111[12]	0.9[13]
Toluene	5,960[12]	5,890[14]