P1.17 ATOMIC CHLORINE IS AN OXIDANT IN HOUSTON TEXAS

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1. INTRODUCTION

Atomic chlorine (Cl) has been identified as an important component of the atmospheric oxidation cycle in the marine boundary layer [*Finlayson-Pitts*, 1993] and has been implicated in tropospheric ozone formation in certain urban areas such as Houston, Texas [*Tanaka et al*., 2000]. In Harris County, Texas yearly emissions of Cl_2 have ranged from a high of 329,000 kg in 1988 to a low of 67,000 kg in 1996. The last year for which there are data shows emissions of 132,000 kg in 1999 [http://epa.gov/tri].

To determine the presence and extent of Cl chemistry in the Houston area, we measured specific tracers from isoprene oxidation by Cl. Isoprene is a highly reactive nonmethane hydrocarbon (NMHC) that is emitted by vegetation, and to a lesser degree, by anthropogenic activities. Laboratory studies have shown that the reaction of isoprene with Cl forms several unique tracers which could be used as evidence for Cl chemistry [*Nordmeyer et al*., 1997]. We investigated the isoprene oxidation process under ambient conditions at the LaPorte airport experimental site, and were able to characterize the different oxidation processes that were occuring. Our results confirm that Cl is indeed an oxidant in the Houston urban area. Unfortunately, the extent to which Cl serves as the major contributor to the persistent ozone problems in Houston is yet to be determined.

Isoprene oxidation chemistry is driven primarily by OH and O_3 with additional oxidation by NO_3 during the nighttime. In Houston oxidation by Cl also occurs. Isoprene oxidation by OH and O_3 results in the formation of methacrolein (MACR), methyl vinyl ketone (MVK) and formaldehyde (CH_2O). Isoprene oxidation by Cl addition forms the unique reaction products1-chloro-3-methyl-3-butene-2-one (CMBO) and several isomers of chloromethylbutenal (CMBA). 2-methylene-3-butenal (MBA) is formed as a result of H-abstraction by Cl. CMBO and CMBA serve as robust tracers of Cl chemistry. Rate coefficients for the isoprene oxidation reactions are shown in Table 1. Isoprene lifetimes with respect to the different oxidation processes are presented for ranges or medians of oxidation potential observed or estimated for Houston.

As part of TexAQS 2000, we completed an investigation to determine the presence and extent of Cl chemistry in the Houston urban area. This consisted of a field study at the LaPorte municipal airport, where we made ambient measurements of isoprene, methacrolein, methyl vinyl ketone and two products specific to the reaction of isoprene + Cl, CMBO and CMBA.

Table 1. Lifetime of isoprene relative to the oxidation processes found in the Houston, Texas area.

Oxidant Concentration	$k_{oxidant}$ (cm^3 mol^{-1} s^{-1})	Isoprene Lifetime (τ_{ox})(Min.)*
OH (mol cm^{-3})		
[a]2.46×10^6	[b]101×10^{-12}	67
O_3 (ppb)		
[c]below detection limit-212	[d]12.8×10^{-18}	>280
Cl (mol cm^{-3})		
[e]below detection limit-10^5	[f]460×10^{-12}	35-360

[a]Median OH concentration for LaPorte Airport (data source - W. Brune, Penn. State University); [b]*Atkinson*, 1994. [c]Range O_3 concentration for LaPorte Airport (data source - E.Williams, NOAA-AL); [d]*Atkinson*, 1994; [e]This work; [f]Ragains et al.,1997 and J. Orlando (in prep); *Lifetimes calculated as 1/([oxidant] x $k_{oxidant}$)

2. FIELD STUDY - LAPORTE MUNICIPAL AIRPORT

We conducted our experiment at the LaPorte Municipal Airport (29.699 °N, 95.064 °W) which is located southeast of the Houston Ship Channel area. The site is located in an ideal location to investigate Cl chemistry due to its proximity to the ship channel and the prevailing wind patterns. While the bulk of Cl_2 emissions occur in the Ship Channel, there are additional emission sources to the southeast of the LaPorte site (Figure 1). Biogenic isoprene emissions that are in close proximity to the field site are located predominantly to the north-northwest and adjacent to the Ship Channel. Under wind regimes from the northwest, freshly emitted isoprene will pass through the Ship Channel. We also observed anthropogenic sources of isoprene under certain circumstances. Chlorine atom chemistry is likely to occur when molecular chlorine is emitted from anthropogenic sources and is photolyzed forming atomic chlorine, which then reacts with hydrocarbons.

The principal goal of our field study was to determine if Cl chemistry is occurring in the Houston area and to what degree it serves as a precursor to the numerous ozone exceedences in that region. We made measurements over the period August 12, 2000 to September 12, 2000. During this period, we made measurements almost continuously, except for instances of instrument failure. At several times during the measurement campaign we observed the compounds CMBO and CMBA giving evidence for the presence of chlorine atom chemistry in Houston, Texas.

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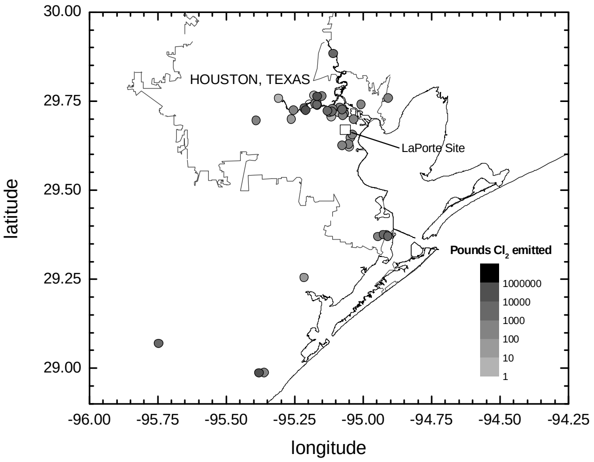

Figure 1. Cl_2 emission map for the Houston, Texas region showing the locations and magnitude of the emissions. Scale is in pounds of Cl_2 emitted (Data source - http://epa.gov/tri).

3. EXPERIMENTAL METHODS

As part of the TexAQS 2000 program, we developed a concentration technique, which allowed for the enrichment of approximately 0.5 liters of ambient air and consequently, the analysis of a series of compounds specific to isoprene chemistry. We focused on the following compounds: isoprene, methacrolein (MACR), methyl vinyl ketone (MVK), chloromethylbutenone (CMBO) and chloromethylbutenal (CMBA). The last two compounds are produced exclusively from the reaction of isoprene + Cl. We quantified all the compounds with mass spectrometry.

The analytical system was contained within a small trailer adjacent to a walk-up platform with a glass manifold. The analytical system was a two-trap design and was custom fabricated. The trapping system used glass beads and carbon sorbents in consecutive traps, and an open tubular cryofocusing trap. All traps and sample lines internal to the concentration system were constructed of fused-silica lined stainless steel (Restek Corporation or Entech Instruments).

Ambient air samples were initially drawn from a continuously flushed glass manifold into the concentration system through the sample trap which was held at 20 ^{o}C. Sample flow rate through the sample trap was 100 mL min^{-1} and was measured by a mass flow controller. Sampling time was approximately 5 minutes. The trap was then warmed to 250 ^{o}C and backflushed with helium onto a cryofocusing trap where the compounds were trapped at -165 ^{o}C. Injection onto the chromatographic column was done by rapidly heating the cryofocuser to 100 ^{o}C.

The sample trap consisted of a 25 cm x 0.3175 cm o.d. silcosteel tube packed with 70/80 glass beads, Carbopack C, Carbopack B, and Carboxen 1000 (Supelco, Inc.). The cryofocusing trap was constructed of an open section of 0.74 mm o.d. fused silica lined stainless steel capillary tubing. Transfer lines between the traps and the packed column were 0.159 cm o.d. fused silica lined stainless steel.

Chromatography was performed on a Hewlett-Packard 5890 Series II gas chromatograph. A 60 meter HP-624 column, 0.25 mm i.d. and 1.4 mm phase thickness (Agilent Technologies) was used for compound separation. The temperature program consisted of 35 ^{o}C for 5 minutes followed by a temperature ramp of 10 ^{o}C min^{-1} to 200 ^{o}C and held at that temperature for 3.5 minutes. Carrier gas was ultra high purity helium passed through a conditioning trap to remove residual moisture, oxygen, hydrocarbons and carbon dioxide impurities. Carrier flow was 2.7 mL min^{-1} controlled by a Tylan 280 mass flow controller.

Detection was by mass spectrometry used in single ion monitoring mode which allowed very low detection limits. The following ions were detected and used for quantification: 67, isoprene; 70, methacrolein; 55, methyl vinyl ketone; 69, CMBO; and 118, CMBA (Figure 2).

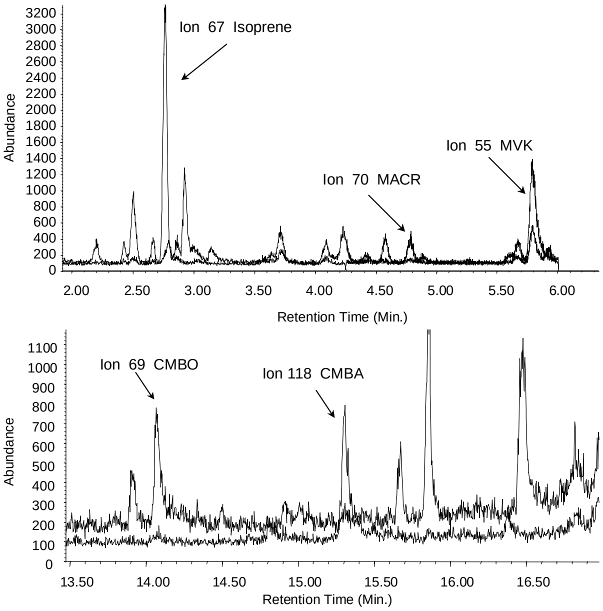

Figure 2. Representative ion chromatograms showing the compounds of interest during the current study.

Known mixtures were prepared to calibrate the analytical system. Due to the reactivity of several of the compounds, it was imperative that standardization took place through the entire system. The standards consisted of a high pressure gravimetrically prepared mixes for isoprene, methacrolein and methyl vinyl ketone. Calibration gases for CMBO and CMBA were prepared in a laboratory chamber by reacting Cl atoms with isoprene. The contents of the chamber were drawn into an evacuated, cleaned and passivated aluminum cylinder with a stainless steel valve. The cylinder was filled with high purity nitrogen to a pressure of 1800 psi. The resulting mix was then calibrated through effective carbon number techniques. Estimated accuracy of the calibration gases is ±2-3% for isoprene and ±<5% for methacrolein and methyl vinyl ketone. The estimated accuracy for CMBO and CMBA is higher at ±20-25% based on comparisons of other halogenated compounds and the effective carbon number technique. Calibration gases were diluted into humidified zero air that was produced by passing ambient air over a platinum on alumina catalyst bed at 350 °C. The diluted standard was passed through the entire sampling and analytical system except for the glass manifold. The standards were diluted to the concentration ranges present in the atmosphere. Detection limits for isoprene was less than 1 ppt; methacrolein and methyl vinyl ketone, 5-9 ppt; CMBO, approximately 1-3 ppt; and CMBA, approximately 1 ppt. Slight variations did occur because of changing noise levels of the system.

4. RESULTS AND DISCUSSION

Time series for two multi-day periods during the study are shown in Figure 3. A total of sixteen observable chlorine chemistry episodes occurred during the field experiment. Generally, we observed evidence of active chlorine oxidation on days when the winds were from the north and north-northwest or directly from the Houston Ship Channel. During these episodes, winds were usually less than 2-3 meters sec^{-1}. Episodes also occurred under other circumstances with winds from the east and south. During elevated wind velocities, the Cl chemistry tracers were usually not observed. This is likely due to more rapid mixing and dilution of the oxidant plumes compared to more stagnant conditions.

Each of the episodes was characterized in terms of its Cl concentration using steady state calculations. We used the concentrations of isoprene, CMBO, CMBA, and OH to determine the Cl concentrations for each of the Cl chemistry episodes. The results are shown in Table 2. The range of Cl concentrations calculated from our observed CMBO and CMBA concentrations varied from below our detection limit, which is approximately 1-5 x 10^3 Cl atoms cm^{-3}, to 3.3 x 10^5 Cl atoms cm^{-3}. While several ozone exceedences were preceded by Cl chemistry events, there were also chlorine events that occurred during periods without elevated ozone levels.

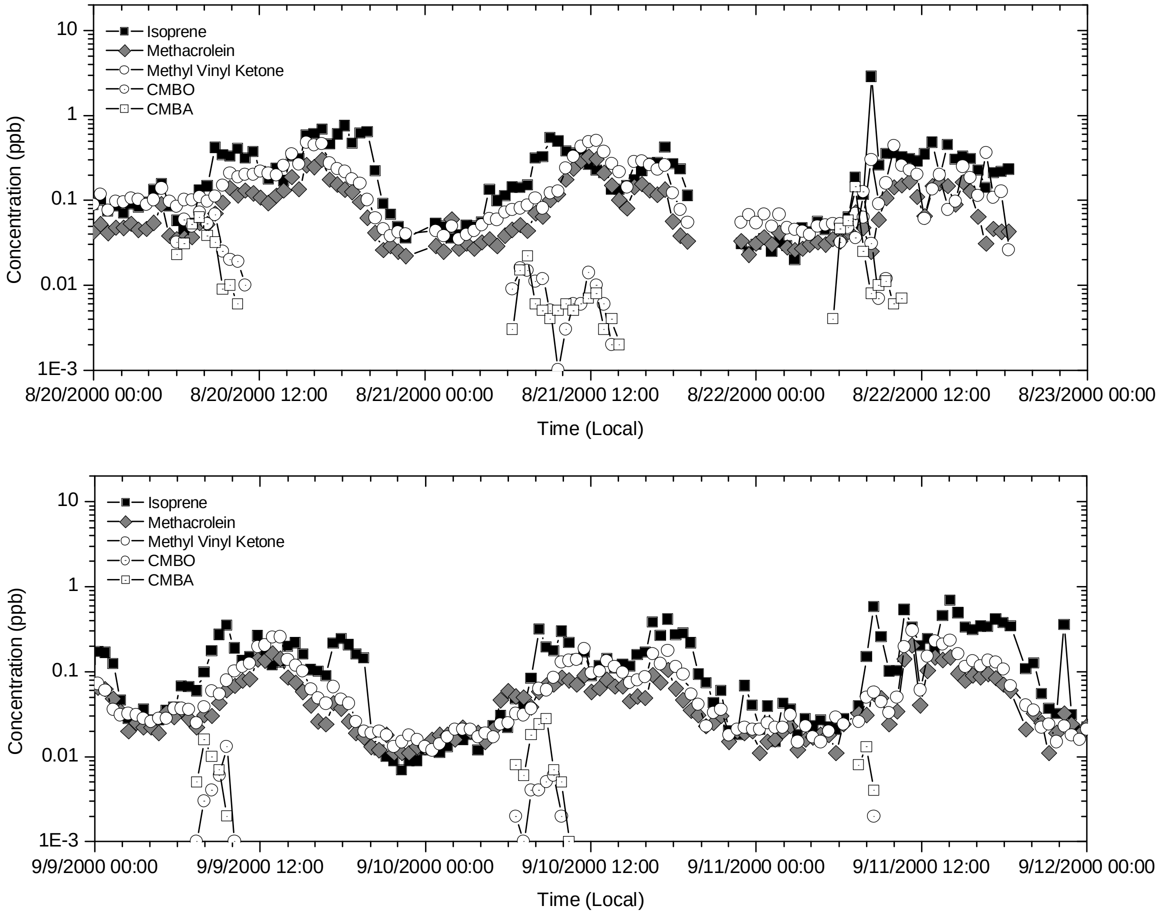

Figure 3. Time series data for (a) August 20, 2000 00:00 - August 23, 2000 00:00 for isoprene and isoprene oxidation products where three episodes of active Cl chemistry are apparent and (b) September 9, 2000 00:00 - September 12, 2000 00:00 where an additional three episodes of active Cl chemistry were observed.

Table 2. Periods of observable Cl chemistry and the calculated Cl concentrations during those periods

Date/Time local	[Isoprene] ppb median	[CMBO] ppb median	[CMBA] ppb median	[OH] 10^6 mol cm^{-3} median	[Cl] 10^5 atoms cm^{-3} median*	
8/20 06:02-11:00	0.224	0.041	0.026	3.98	2.2	3.3
8/21 06:21-14:05	0.279	0.008	0.006	4.25	0.82	1.2
8/22 05:34-10:34	0.464	0.029	0.032	2.90	0.96	1.9
8/23 08:10-11:29	5.32	0.008	0.007	2.78	0.04	0.06
8/25 07:06-09:18	0.437	0.052	0.028	2.47	1.1	1.5
8/29 18:09-19:48	0.607	0.005	0.010	2.87	0.19	0.65
8/30 06:19-15:42	0.430	0.028	0.032	3.83	1.3	2.6
8/31 08:24-15:03	0.569	0.024	0.037	4.34	1.2	2.7
9/1 07:43-11:03	0.664	0.016	0.012	2.52	0.42	0.62
9/5 06:52-10:43	0.546	0.017	0.014	2.90	0.60	0.94
9/6 06:04-08:49	0.267	bdl	0.008	2.53	bdl	0.93
9/7 06:54-07:27	0.026	bdl	0.0015	1.45	bdl	0.80
9/8 07:09-11:33	0.237	0.001	0.007	2.87	0.10	1.0
9/9 07:24-10:09	0.191	0.005	0.007	2.83	0.51	1.2
9/10 06:35-10:26	0.172	0.003	0.012	3.38	0.44	0.37
9/11 07:27-08:33	0.254	0.0006	0.008	1.51	0.03	0.60

bdl - below detection limit; *first column is calculated from the median CMBO concentration and the second is calculated from the CMBA concentration. [Cl] is calculated using steady state relationships. Rate coefficients are from *Atkinson* [1994] and *Orlando et al*., [in preparation, and references therein]; OH data is from B. Brune et al. Pennsylvania State University.

5. REFERENCES

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