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Atmospheric carbonyl compounds at a rural southeastern United States site

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Abstract. Atmospheric concentrations of a series of carbonyl compounds known as formaldehyde (FA), acetaldehyde (AC), acetone (AN), glycolaldehyde (GA), glyoxal (GL), methylglyoxal (MG), glyoxylic acid (GD), and pyruvic acid (PD) were measured at a rural site in Georgia in summers of 1991 and 1992. The midafternoon median concentrations, in parts per billion, determined for 1991–1992 were FA, 3.6/3.1; AC, 0.58/0.74; AN, 1.7/1.8; GA, 0.21/0.26; GL, 0.02/0.09; MG, 0.03/0.08; GD, 0.46; and PD, 0.11, the latter two for 1992 only. All of the carbonyls except AC and AN exhibited a strong diurnal dependence, with maxima in the midafternoon and minima during the night, consistent with a rapid in situ photochemical production in the daytime and a loss by dry deposition in a shallow inversion during the night. FA correlated well with O_3, GA and MG, consistent with their photochemical production near the surface at the measurement site. GL and MG showed the strongest correlation among all species, suggesting common origins as well as similar atmospheric lifetimes. The presence of GA, MG, and GL along with FA at the observed relative concentrations are consistent with laboratory developed isoprene oxidation mechanism and the expectation that isoprene represents a major reactive hydrocarbon in this rural region. At the concentrations observed, these carbonyls serve as important radical sources. The contribution of FA accounts for half of that by O_3 and the higher carbonyls approximates half of that by FA. With respect to production of peroxyacetyl nitrate, isoprene contributes as much as acetaldehyde. These results lend further credence to the notion that isoprene plays a pivotal role in photochemical processes, especially in rural environments.

Introduction

Atmospheric carbonyl compounds are intermediates produced from oxidation of hydrocarbons (HC) and, as such, offer important mechanistic insights into the oxidation processes [*Atkinson*, 1990; *Carter*, 1990]. Further, because carbonyls produce free radicals upon photolysis [e.g., *Pitts and Wan*, 1966; *Finlayson-Pitts and Pitts*, 1986], react rapidly with the OH radicals [*Atkinson et al.*, 1989], and serve as precursors of peroxyacyl nitrates, they play a crucial role in the formation of photooxidants such as ozone [*National Research Council* (*NRC*), 1991]. Consequently, the speciation and quantitation of atmospheric carbonyls is critical for gaining an understanding of HC oxidation and its contribution to photooxidant production.

For rural areas of the southeastern United States where biogenic HC may dominate their anthropogenic counterpart, formulation of sound O_3 mitigation strategies requires a quantitative understanding of the roles these biogenic HC play in ozone production [*Chameides et al.*, 1988]. Because isoprene, emitted from deciduous trees and many conifers, dominates biogenic HC in the southeastern United States [e.g., *Guenther et al.*, 1994a] and many other forested regions, its oxidation chemistry has been under intense investigation. As a result, a fairly coherent description of its oxidation mechanism and atmospheric fate has emerged [*Tuazon and Atkinson*, 1989, 1990a, b; *Carter*, 1990; *NRC*, 1991; *Paulson and Seinfeld*, 1992]; the OH initiated oxidation pathway under NO_x (= NO + NO_2) rich conditions produces methyl vinyl ketone (MVK), methacrolein (MACR), formaldehyde (FA), and 3-methylfuran as first stage products. The two unsaturated carbonyls, MVK and MACR, further react with OH to produce multi-oxygenated carbonyls: glycolaldehyde (GA), glyoxal (GL), methylglyoxal (MG), hydroxyacetone (HA), and two peroxy radicals: peroxyacetyl (PA) and peroxymethacryl (PM) radicals. The mechanism and reaction yields are shown in Figure 1.

In order to corroborate the laboratory established mechanistic data and to constrain model calculations concerning isoprene [e.g., *Lurmann et al.*, 1986; *Atkinson*, 1990; *Carter*, 1990], positive identification and quantitation in the field of key intermediates emanated from isoprene must be made. Toward this goal, MVK, MACR [*Pierotti et al.*, 1990; *Martin et al.*, 1991; *Montzka et al.*, 1993a; *Yokouchi*, 1994], peroxymethacryl nitrate (MPAN) [*Grosjean et al.*, 1993], and 3-methylfuran [*Montzka et al.*, 1993b; *Yokouchi*, 1994] have all been identified. However, the multi-oxygenated carbonyls, GA, GL, MG, and HA, are yet to be positively identified in the field.

As part of the Southern Oxidants Study (SOS) program to gain a fundamental understanding of O_3 production in the southeastern United States, Brookhaven National Laboratory (BNL) conducted two field measurement intensives at Metter, Georgia, during July–August 1991 and June 1992. In this paper we present the measurement results of formaldehyde (FA) and the multi-oxygenated carbonyls mentioned above that are im-

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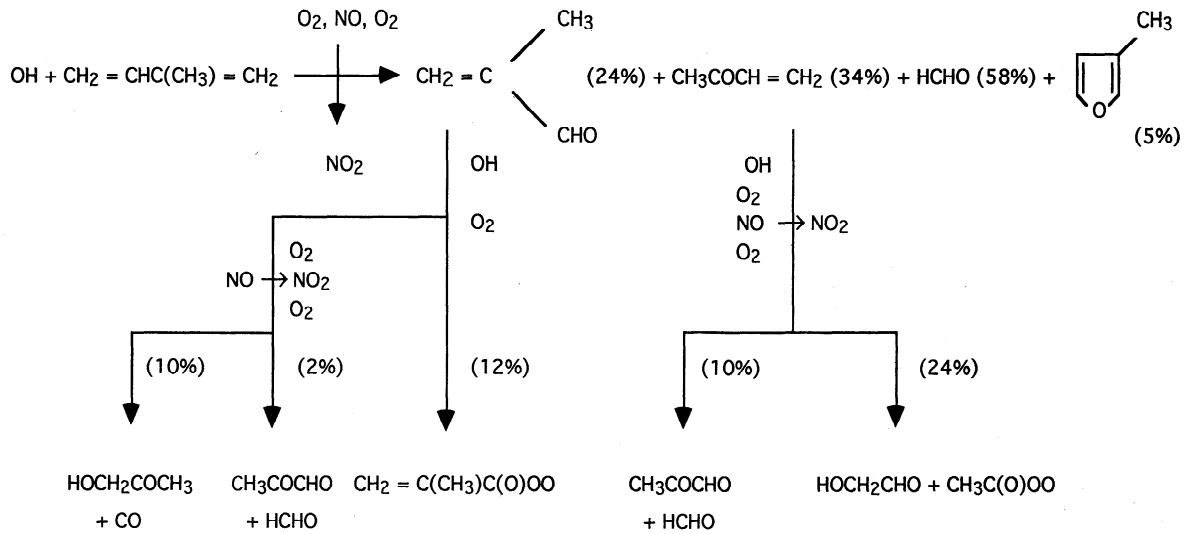


Figure 1. A simplified diagram of isoprene oxidation chemistry depicting the formation of first and second generation of carbonyl compounds produced.

portant signatures of isoprene oxidation. Acetaldehyde (AC) and pyruvic acid (PD) were also measured because the former competes with isoprene as a precursor for peroxyacetyl nitrate (PAN) and the latter has been purported to be a reaction product of isoprene. Acetone (AN) and glyoxylic acid (GD) were determined in this work mainly because they are feasible with the techniques employed. We examine the concentrations of and relationships among the relevant carbonyls in the context of isoprene oxidation mechanism and the contributions of these carbonyls to formation of free radicals, PAN, and carbon monoxide (CO). Some inferences are made on the rates of deposition of the multi-oxygenated carbonyls. The qualitative analysis represents an attempt to provide a framework with which model calculations can be more readily comprehended.

Experimental Section

General descriptions. The Metter measurement site is located in a cleared area inside of George Smith State Park (32°32′N, 82°08′W), Candler County, Georgia, ~100 km west by northwest of the coastal city of Savannah. The lightly traveled state route runs north-south approximately 4 km west of the state park. The clearing is covered by red clay with patchy low grass and approximates a 30-m radius circle. The site is surrounded by vegetation typical of the area, namely, mixed deciduous and conifers, with a canopy height of ~6 to 7 m. A. Guenther et al. (Estimates of regional natural volatile organic compound fluxes from enclosure and ambient concentration measurements, submitted to the *Journal of Geophysical Research*, 1994b) reports for this area a leaf biomass of the top five species of pine, gum, oak, sweetgum, and maple as ~170, 50, 50, 25, and 20 g m^{-2}, respectively, accounting for ~90% of the total. Isoprene was found to dominate the biogenic emission at an 8:1 ratio over terpenes. These characteristics are similar to those of another SOS measurement site, the ROSE site, in western Alabama [*Cantrell et al.*, 1992; *Goldan et al.*, 1995]. Regarding anthropogenic emissions, the National Acid Precipitation Assessment Program (NAPAP) emission inventory [*NAPAP*, 1989] indicates this region has a small vehicle source of NO_x (~0.1 ton km^{-2} yr^{-1}), with no major point sources (i.e., >100 t yr^{-1}) of SO_2 and NO_x within 50 km of Candler County.

The meteorological and chemical measurements included temperature, relative humidity, total UV irradiance, wind speed and direction, rainfall rate, and concentrations of CO, O_3, SO_2, NO, NO_2, NO_y, total NO_3^-, PAN, carbonyls, peroxides, and aerosol sulfate and nitrate (see *Kleinman et al.* [1994, 1995] for an overview). Nonmethane HC were measured by Rodgers and coworkers of the Georgia Institute of Technology (1991 and 1992) and Zimmerman and coworkers of the National Center for Atmospheric Research and Washington State University (1991). Carbonyl compounds were measured by two different techniques, both based on high performance liquid chromatography (HPLC) analysis following derivatization of the carbonyls with 2,4-dinitrophenylhydrazine (DNPH): a C_{18} cartridge trapping technique [*Zhou and Mopper*, 1990] for AC and AN and a coil technique [*Lee and Zhou*, 1993] for FA, GA, GL, MG, GD, and PD. All but GD and PD (1992 only) were measured during both intensives.

The cartridge technique. Pairs of new C_{18} cartridges, one for sampling and the other as a blank, were cleaned with acetonitrile (CH_3CN) and coated with a 20-mL DNPH solution (~0.1 mM at pH = 2.4) [*Kieber and Mopper*, 1990] immediately before use. Ambient air from a Teflon sampling mast (i.d. = 1 in, flow ~ 600 L min^{-1}, ~4 m above the ground) was drawn through the cartridge at 0.70 L min^{-1} controlled by a mass flow controller (Sierra, 0–2 SLM), the typical sampling time being 1 hour. Upon completion of sampling, the cartridge was immediately eluted with 1.8 mL of CH_3CN, the eluant being stored in a capped 5-mL Teflon vial. The unexposed blank cartridge was also eluted and analyzed in the same fashion. On a nearly daily basis, calibration was made by analyzing cartridges loaded with known amounts of aqueous carbonyl standards.

To examine possible effects of ambient O_3 on the cartridge technique, we conducted an experiment in an open field at BNL (Long Island, New York) in April 1992 in which simultaneous samples were drawn from a common manifold with and without connecting a KI cartridge to remove the ambient

O_3. The cartridge collection efficiencies were determined by connecting two cartridges in series and measuring the carbonyls collected by each cartridge. We attached a KI filter upstream of the cartridges to remove O_3 in the 1991 intensive, but eliminated the filter in 1992.

During 1991, the HPLC consisted of a pump (Spectra Physics, SP8800), a 25-cm C_{18} reverse phase column (Alltech, 5-μm Hypersil ODS), a UV-Vis detector (Spectra Physics, Spectra 200) equipped with a 6-mm pathlength optical cell, and a 6-port sample injector (Rheodyne, 7125) equipped with a 20-μL sample loop. The gradient elution used H_2O, CH_3OH, and CH_3CN at flow rate of 1.6 mL min^{-1}. The data were collected and analyzed using a digital integrator (Spectra Physics, Chrom-Jet). Since the configuration of the HPLC had to be rearranged daily to accommodate the two types of samples, the analysis of some cartridge eluants were delayed for up to 36 hours. However, the samples were found to be stable under refrigeration. During 1992, two HPLC systems were used (both Hitachi pumps, 6200A) and the cartridge samples were always analyzed on the day of collection. Also new in 1992 were a Radial-Pak C_{18} cartridge column (Waters, Novapak 4 μm, 8 mm $\times$ 100 mm) and a H_2O-CH_3CN gradient elution at 2.0 mL min^{-1}.

The coil technique. The soluble carbonyls were determined using a glass coil scrubber and HPLC analysis following DNPH derivatization [*Lee and Zhou*, 1993]. The coil assembly, protected from the sun under an inverted funnel, was also placed ~4 m above the ground. Typical conditions were gas and liquid flow rates of 2.3 L min^{-1} and 0.30 mL min^{-1}, respectively; derivatization time of ~24 hours at [DNPH] = 0.10 mM and pH = 2.4; sample injection volume 1.2 mL; 6-mm pathlength flow cell (360 nm for FA, GA, GD, and PD; 400 nm for GL and MG). The HPLC used in 1991 was described in the cartridge technique section. In 1992, a second UV-Vis detector (Spectra Physics, UV2000) equipped with a 10-mm flow cell was use. The gradient elution were H_2O-CH_3OH-CH_3CN and H_2O-CH_3OH in 1991 and 1992, respectively. In the manual batch mode, the number of samples taken was typically five a day, mainly during daytime hours, and the sample integration time was ~20 min. On the basis of liquid standards, scrubbing efficiencies, and chromatographic characteristics, the limits of detection (LOD) were typically ~0.005 ppb (parts per billion in the gas phase) for MG, ~0.01 ppb for GL, GD, and PD, and ~0.015 ppb for FA and GA. The uncertainties are estimated to be ±15% of the concentration + the respective LOD.

While most of the samples were collected in the batch mode, we also tested the on-line continuous sampling approach [*Zhou et al.*, 1994] during a portion of the 1992 intensive. This method incorporated an electrically actuated 6-port valve injector (VICI/Valco) equipped with a 1.2 mL sample loop through which sample liquid flowed continuously. A section of Teflon tubing (O.D. = 0.32 cm) with an ~18-mL hold-up volume was placed in between the coil and the injector to permit ~60-min derivatization time. The extents of derivatization for FA, GA, GL, and MG were 96, 82, 87, and 52%, respectively [*Lee and Zhou*, 1993], the uncertainties being ~5%. For GD and PD, the derivatization was 100%. Sample injection and chromatographic analysis were controlled by chromatography software (Rainin, MacIntegrator II) running on a Macintosh computer. The sampling frequency was every 40 min and the sample integration time was ~7 min, which was governed by the sample loop size and liquid flow rate.

Rainwater collection and analysis. Event rainwater samples were collected during the 1991 intensive using an automatic rainwater collector equipped with a protective cover. The samples were retrieved and analyzed at the end of each daytime event or the following morning of night events. A 5-mL portion of the rainwater sample was derivatized by adding 17.0 μL of a concentrated DNPH stock solution [*Lee and Zhou*, 1993], yielding identical final DNPH concentration as in the coil samples. Water was used as blanks.

Materials. FA (37% aqueous w/w), GL (40%), MG (40%), GA (dimer), GD, PD, AC, and AN were all obtained from Aldrich as the purest grade available. DNPH (Kodak) was purified according to *Kieber and Mopper* [1990]. HPLC grade CH_3CN, and CH_3OH were purchased from either Baker or Baxter. The C_{18} Sep-Pak cartridges were purchased from Waters. Ultrahigh purity He (Matheson) was used to degas the HPLC solvents in 1991. Water was purified using a Millipore Milli-Q filtering system.

Results and Discussions

Chromatography analysis. Representative HPLC chromatograms of cartridge and coil samples, along with their respective blanks, are shown in Figure 2. It is seen that while FA exhibited the largest blank values, the effect of the blanks on quantitation is unimportant because of the substantial ambient concentrations of this species. The blanks for the higher carbonyls were all nearly undetectable. The GA peak in the 1992 analysis was sometimes not baseline resolved from a background signal, resulting in a greater uncertainty, that is, ~25%.

The cartridge technique. The C_{18} cartridge technique we employed was found to be affected by O_3. In the case of AN, the ambient O_3 was found to give rise to a negative bias of ~20%. In contrast, AC did not show a systematic dependence on O_3, but rather exhibited a scatter (±15%), suggesting possible interferences that were not constant in time. By connecting two cartridges in series, we determined the collection efficiencies of AC and AN to be 84 ± 20% and 68 ± 8%, respectively, under the experimental conditions employed (e.g., sample flow rate = 0.70 L min^{-1}). The AN concentrations reported in this work have been corrected for its collection efficiency as well as for the O_3 induced bias (1992). Because of the scatter exhibited by AC both in collection efficiency and O_3 effect, no correction on its concentrations was made, yielding an uncertainty in the reported values of ~20%. An account of the study of the effects of O_3 on the cartridge technique will be reported elsewhere.

Speciation, concentration, and diurnal variations. A total of eight carbonyls were determined in the two intensives. They were FA, GA, GL, MG, GD, and PD by the coil technique and AC and AN by the cartridge method. The time series of the concentrations obtained during the 1991 and 1992 intensives are displayed in Figures 3 and 4, respectively. The mean, median, and maximum concentrations are summarized in Table 1.

The concentrations of the carbonyls are also plotted in Figures 5 (1991) and 6 (1992) as a function of time of day to show composite diurnal dependencies. The lines represent the smoothed values of the data as determined by a biweight algorithm which yielded values in close approximation with the median values [*Mosteller and Tukey*, 1977]; the midafternoon median concentrations thus determined are also listed in Table 2. Although the data were dominated by daytime measurements, it is possible to discern for the soluble carbonyls a

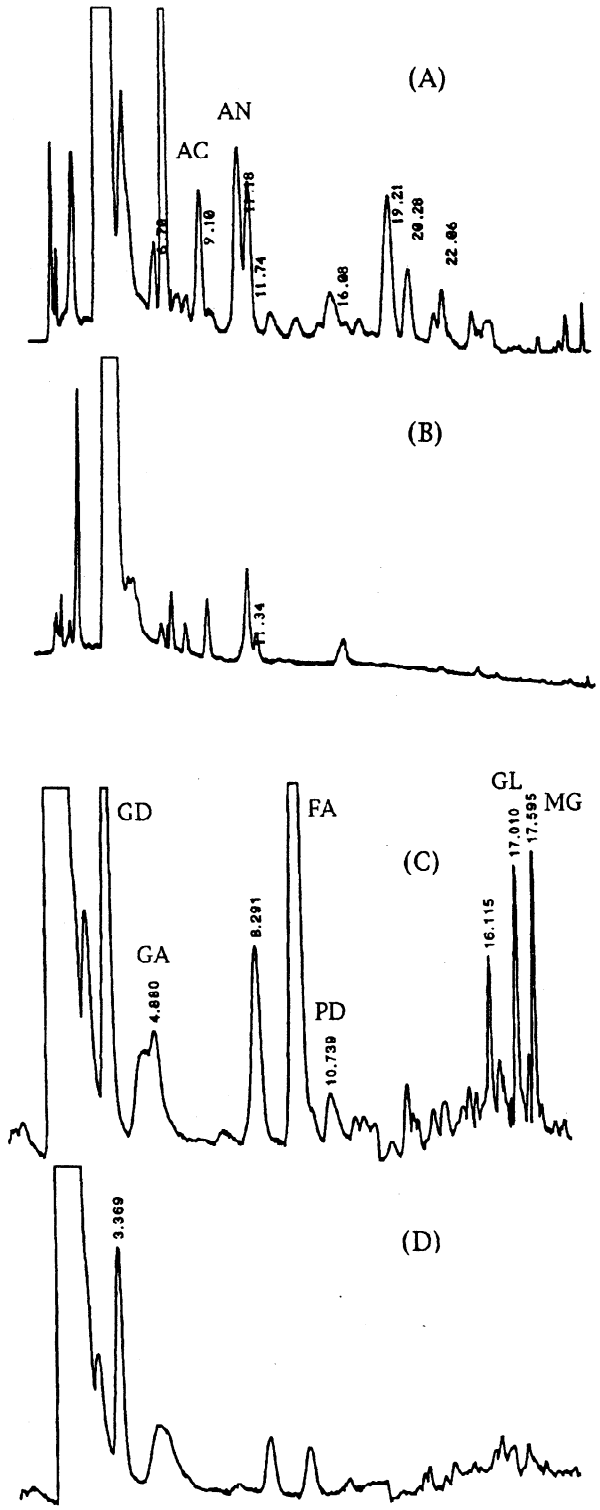


Figure 2. HPLC chromatograms of samples collected at the Metter, Georgia, site. A cartridge (a) sample of June 4, 1992 along with (b) a blank. (c) A coil sample collected on June 17, 1992 and a (d) blank.

diurnal pattern marked by a midafternoon maximum and nighttime minimum. Such pattern is consistent with a rapid in situ photochemical production in the daytime and a loss by dry deposition in a shallow inversion during the night [e.g., *Hastie et al.*, 1993]. We noted very low concentrations of the soluble carbonyls during a 5-day rainy period between July 29, 1991, and August 2, 1991 (Figure 3). However, reanalysis of the data with those 5 days excluded resulted only in a slight increase in the weighted smoothed values by ~10–15% over those given in Table 2, too small to alter any of the conclusions presented in this work. The concentrations of AC and AN obtained in 1991 exhibited little diurnal dependence, despite the fact that most of the nighttime determinations were made during the rainy period mentioned above. This observation suggests that AC and AN are not efficiently removed by wet scavenging processes, consistent with their low Henry's law solubilities. The 1992 data were difficult to judge because only daytime measurements were made.

Isoprene oxidation products. Isoprene is believed to be the dominant HC in rural southeastern United States, including the Metter site (A. Guenther et al., submitted manuscript, 1994b), for which a daytime median concentration was determined to be ~2 ppb for both 1991 and 1992. This notion was supported by a photochemical model analysis based on HC measured at the ROSE site [*Goldan et al.*, 1995]; [*Cantrell et al.*, 1992]. Since FA, GA, GL, and MG were shown to be produced from isoprene by way of MACR and MVK [*Tuazon and Atkinson*, 1989; 1990a, b; *Paulson and Seinfeld*, 1992], the identification of these multi-oxygenated carbonyls along with FA in an isoprene dominated environment is in qualitative agreement with the laboratory mechanistic data. Other pathways for the formation of GA, Gl, and MG are found to be much less important compared to isoprene, as shown below. It may be noted that the only carbonyl produced from isoprene yet to be identified in the field is HA. Despite its high solubility (X. Zhou and Y.-N. Lee, Henry's law solubility of some atmospheric carbonyl compounds, to be submitted to *Environmental Science and Technology*, 1995), HA could not be detected by our coil technique [*Lee and Zhou*, 1993] because of the low

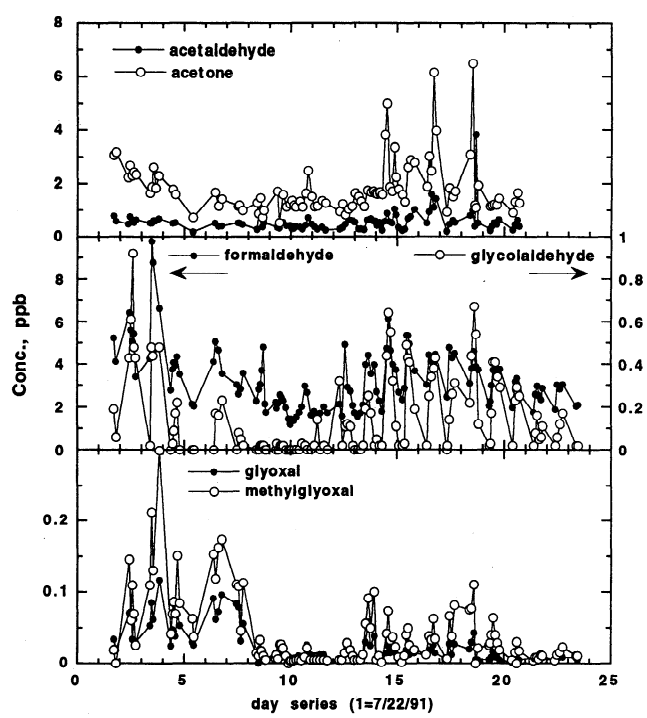


Figure 3. Series plot of concentrations of the carbonyl compounds determined during the 1991 intensive.

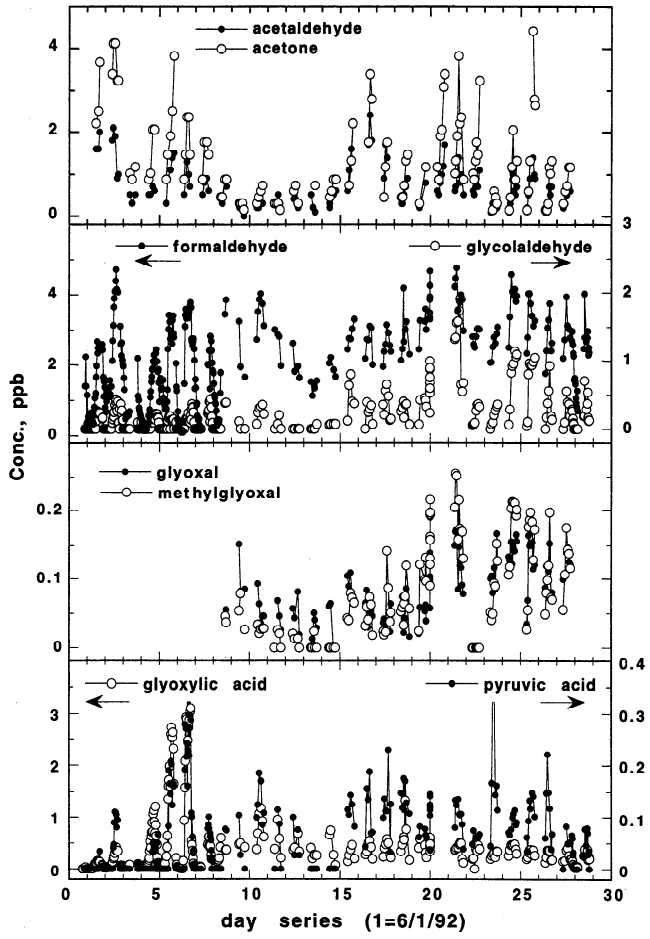


Figure 4. Series plot of the concentrations of the carbonyl compounds determined during the 1992 intensive.

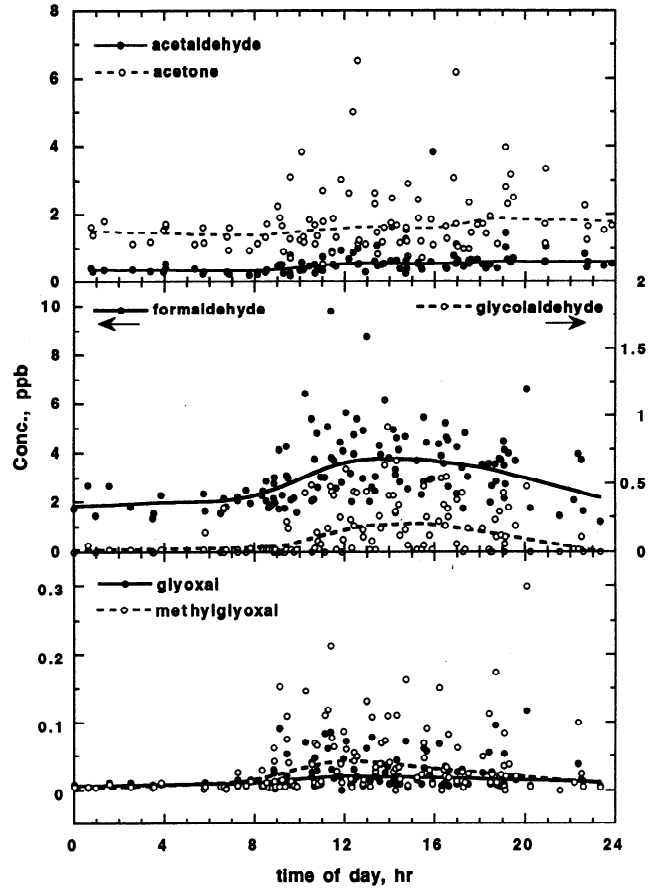


Figure 5. Composite diurnal dependences of the carbonyl compounds during the 1991 intensive.

sensitivity for ketones of the aqueous DNPH reaction system used in the coil technique.

Although the oxidation of aromatic HC also produces GL and MG [e.g., *Tuazon et al.*, 1986], its contribution is negligible due to the low concentrations of these precursors in rural environments. An analysis of the reactivities of the HC measured at the ROSE site showed that the sum of benzene, toluene, and xylenes only contributed to ~0.07% of the total OH reactivity [*Cantrell*, 1993]. The fact that the median concentrations (1991/1992, in ppb C) of benzene (0.6/1.0), toluene (1.6/3.0), and xylenes (0.6/1.6) measured at the Metter site were comparable to those of the ROSE site suggests that these HC should be similarly unimportant at the Metter site. The oxidation of C_2H_4 by OH [*Niki et al.*, 1981] as a source of GA is examined. Since the rate constant of OH-C_2H_4, 8×10^{-12} $cm^3\ mol^{-1}\ s^{-1}$ [*Atkinson and Lloyd*, 1984] is roughly a factor of 2 smaller than that of the OH-MVK [*Paulson and Seinfeld*, 1992], the importance of C_2H_4 will approximate MVK at $[C_2H_4] \sim 1.4[MVK]$. A noontime median C_2H_4 value of ~0.1 ppb for 1992 derived from a limited number of measurements suggests that C_2H_4 is unimportant if $[MVK] \geq 0.4$ ppb. Taking as surrogate the 1.5 ppb midafternoon average of MVK measured at the ROSE site [*Montzka et al.*, 1993a] for the Metter site, we conclude that C_2H_4 is unimportant as a precursor for GA.

Table 1. Statistical Summary

Compound	Mean	Median	Maximum	Cases
		1991		
AC	0.56	0.47	3.8	81
AN	1.8	1.5	6.7	81
FA	3.0	2.8	6.1	108
GA	0.13	0.033	0.67	108
GL	0.018	0.011	0.091	108
MG	0.031	0.016	0.16	108
		1992		
AC	0.74	0.61	2.4	120
AN	1.7	1.3	4.5	120
FA	2.1	2.1	4.8	359
GA	0.20	0.10	1.91	358
GL	0.083	0.081	0.19	116
MG	0.088	0.07	0.26	117
GD	0.41	0.21	3.53	357
PD	0.052	0	0.35	357

AC is acetaldehyde, AN is acetone, FA is formaldehyde, GA is glycolaldehyde, GL is glyoxal, MG is methylglyoxal, GD is glyoxylic acid, and PD is pyruvic acid.

Formaldehyde. The midafternoon median concentrations of FA during the 1991 and 1992 intensives were 3.6 and 3.1 ppb, respectively (Figures 5 and 6). The daytime average concentrations (0700–1700 LT) of 3.2 and 2.6 ppb for 1991 and 1992, respectively, were slightly lower than that measured at the ROSE site (1990): averages over the same time period were 5.3 ppb and 3.0 ppb for July 11 and July 14, respectively [*Cantrell et al.*, 1993]. From their measurement at Scotia, Penn-

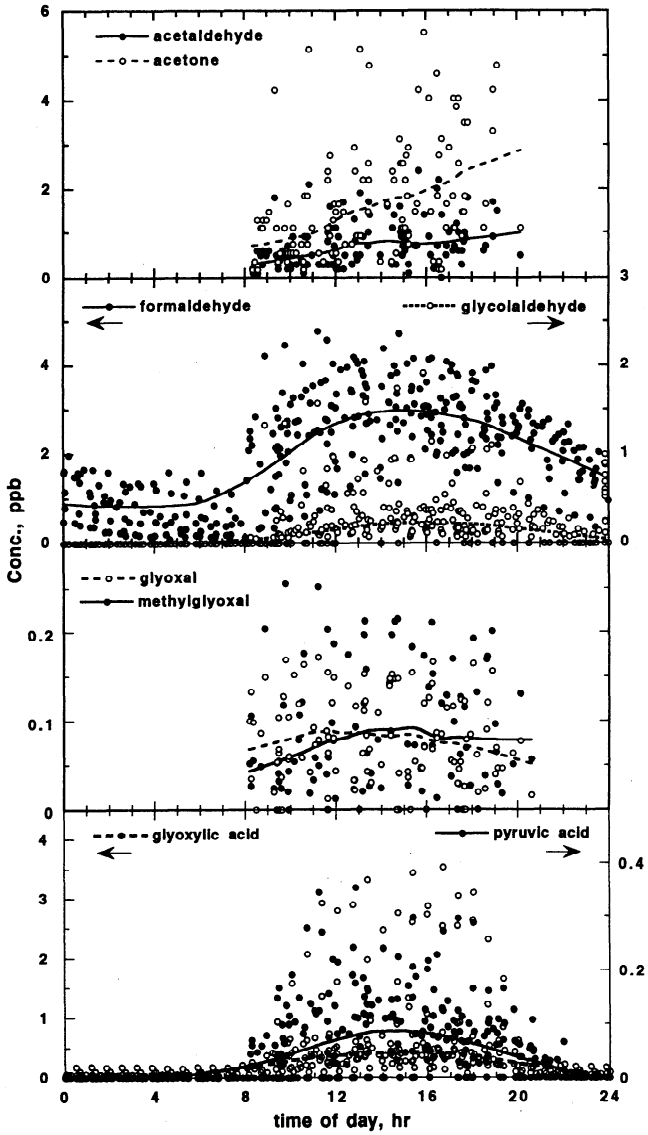


Figure 6. Composite diurnal dependences of the carbonyl compounds during the 1992 intensive.

sylvania, in July-August, 1988, a rural site occasionally impacted by man-made emissions, *Martin et al.* [1991] determined a midafternoon average FA of 4.4 ppb. This value is somewhat greater than that measured at the Metter site, qualitatively in line with a higher isoprene concentration, by a factor of ~2, observed at the Scotia site.

Since FA is produced from HC oxidation, which effects ozone formation via oxidizing NO to NO_2 by HO_2 and RO_2 [*NRC*, 1991], a positive correlation is expected between these two photochemical reaction products. A plot of O_3 versus FA indeed shows a positive correlation with $r = 0.6$ (the 1992 data shown in Figure 7). Considering the vastly different atmospheric lifetimes of O_3 and FA, by almost an order of magnitude, we take this correlation as evidence of in situ photochemical production of these species in the vicinity of this surface site. At this juncture, we point out that we qualify a correlation significant based on a statistical assessment of only a ~1% probability for two unrelated quantities to show a correlation of 0.3 ($N = 60$).

It is noted that the slopes of the O_3-FA correlation are essentially identical between the daytime (0900–1800 LT) and the nighttime (0200–0700 LT) data. If the daytime concentrations are not significantly affected by dry deposition, then this observation suggests that nighttime decay rates of these two species are comparable, thereby preserving the daytime established ratios. Since the nighttime removal of O_3 is effected by reaction with NO as well as by dry deposition, we surmise that the rate of nighttime dry deposition of FA is greater than that of O_3. Finally, the intercept of ~23 ppb O_3 (Figure 7) and ~17 ppb for 1991 during daytime are similar to the value ~25 ppb determined from an O_3 versus NO_y correlation [*Kleinman et al.*, 1994]. This value may be viewed as the background ozone in the absence of in situ photochemistry ozone and is attributable to transport, from either upper atmospheres [*Davies and Schuepbach*, 1994] or processed boundary air that contained little of the precursors and soluble products.

Relationships among the soluble carbonyls. The identification in the field of FA, GA, GL, and MG, where isoprene is believed to be the dominant HC, provided qualitative evidence to corroborate the laboratory established mechanism for the oxidation of isoprene. We further examine whether the ambi-

Table 2. Midafternoon Median Concentrations and Lifetimes of the Carbonyl Compounds

Species	Concentration, ppb 1991	Concentration, ppb 1992	j,[a] 10^5 s^{-1}	τ,[b] h	$k^c \times 10^{11}$	τ,[d] h	τ,[e] h
FA	3.6	3.1	3.2 (r)	8.7	1.1	5	3.5
FA			44 (m)	6.3			2.8
AC	0.58	0.74	0.62	45	1.6	3.5	3.3
AN	1.7	1.8	0.13	(9 d)	0.023	(10 d)	(5 d)
GA	0.21	0.26	~0.7	~40	1.0	~6	5.2
GL	0.016	0.085	6.0	4.6	1.1	5	2.4
MG	0.033	0.08	23	1.2	1.7	3.3	0.9
GD		0.46	?	~5	1.5	~5	~3
PD[f]		0.11	27	1	<0.05	long	1

FA is formaldehyde, AC is acetaldehyde, AN is acetone, GA is glycolaldehyde, GL is glyoxal, MG is methylglyoxal, GD is glyoxylic acid, and PD is pyruvic acid.

[a]Noon time maximum value (r, radical route; m, molecular route; d, day).

[b]Taken as the inverse of the rate constant.

[c]In units of cubic centimeters per mol per second [*Atkinson and Lloyd*, 1984; *Atkinson et al.*, 1989].

[d]At [OH] = 5×10^6 mol cm^{-3}.

[e]Total.

[f]*Grosjean* [1983].

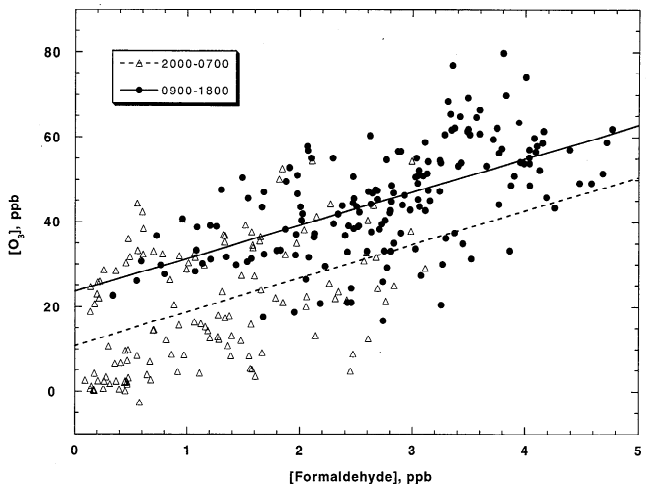


Figure 7. Correlation between O_3 and H_2CO measured during the 1992 intensive.

ent concentrations of these carbonyls exhibit relationships expected from this mechanism: the yields of GA, MG, and FA are 24, 10, and 70% under NO_x-rich conditions (Figure 1, NRC, 1991): if the atmospheric lifetimes of these carbonyls are

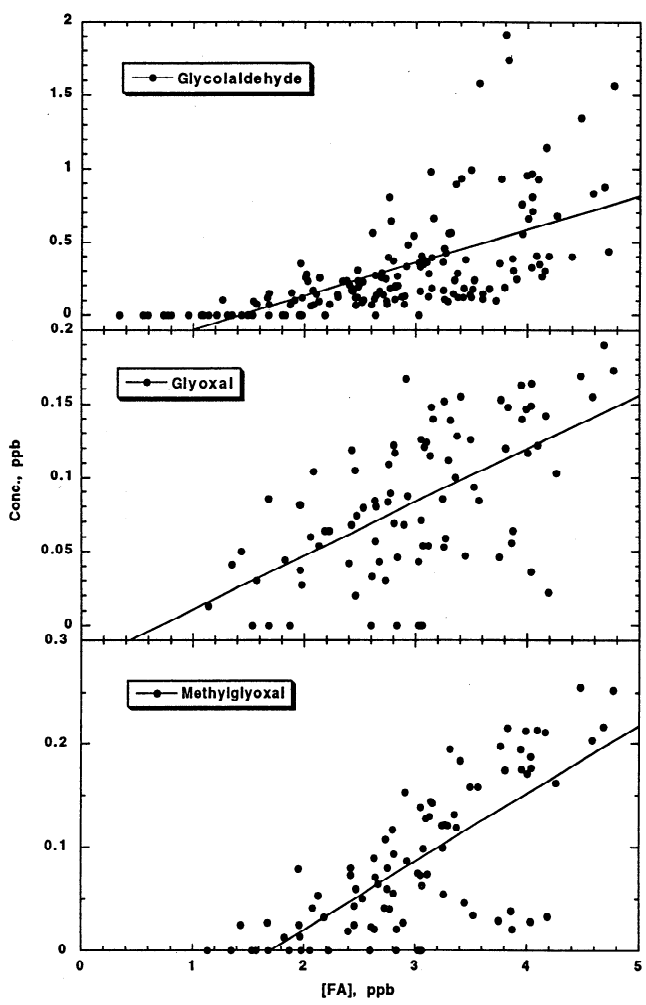


Figure 8. Correlations among various carbonyl compounds measured in the 1992 intensive. Time coverage: 0090 to 1800 LT.

Table 3. Comparison of the 1991 and 1992 Intensives at Metter, Georgia

Variables	1991	1992
Temperature, °C	33.4 (33.0)	28.6 (28.0)
Dew point, °C	22.9 (23.2)	19.3 (19.0)
Total UV, W/m^2	34.6 (33.2)	32.9 (31.7)
O_3, ppb	41 (42)	46 (46)
NO, ppb	0.057 (0.087)	0.092 (0.102)
NO_2, ppb	0.27 (0.41)	0.47 (0.56)
CO, ppb	198 (203)	233 (235)

Shown are average and median (in parenthesis) values for the hours 1000–1800 LT.

comparable, then their yields should be preserved and reflected in their ambient concentrations. Such an examination has been made for the reaction products of isoprene, MVK, and MACR; an observed ratio of ~2 for MVK/MACR in the midafternoon was found to be consistent with predictions of a one-dimensional chemical model [*Montzka et al.*, 1993a].

We note that the correlation between GA and FA was significant (r = 0.7, Figure 8). The slopes of this plot for the photochemical hours (0900–1800 LT), 0.17 ± 0.015 (1991) and 0.23 ± 0.022 (1992), however, are somewhat smaller than the value of 0.3 expected from isoprene oxidation yields, suggesting that either GA has a shorter lifetime than FA and/or that there are additional FA sources. Both scenarios are plausible as the surface concentration of GA is likely to be attenuated by dry deposition resulting from its high aqueous solubility, and other precursors for FA are present in the atmosphere, for example, propane and terpenes [e.g., *Atkinson*, 1990]. Furthermore, since the mechanism illustrated in Figure 1 is appropriate for NO_x-rich conditions, the higher NO_x concentration observed during 1992 (Table 3) might result in the apparently closer agreement between the 1992 field data and the laboratory observations. We thus conclude that the observed ratios of GA/FA are not inconsistent with the laboratory established isoprene oxidation mechanism.

The correlation of the daytime concentrations of GA and FA (Figure 8) indicated an intercept of ~1.4 ppb of FA, implying possibly a FA source that does not concomitantly produce GA. In view of the minor contribution of anthropogenic HC in rural areas [*Cantrell et al.*, 1992], this intercept may indicate that isoprene also dominates MACR and MVK in FA production. Although the O_3-monoterpene reactions are known to also produce FA [*NRC*, 1991], we estimated a fairly weak contribution from these reactions, namely, ~0.1 ppb h^{-1} at 50 ppb of O_3, using an 8 to 1 emission ratio between isoprene and monoterpenes (A. Guenther et al., submitted manuscript, 1994b) and a second-order rate constant of 1×10^{-16} cm^3 mol^{-1} s^{-1}. A similar rate, 0.16 ppb h^{-1}, is obtained using 50 ppb O_3 and the average concentrations of α-pinene, β-pinene, camphene, p-cymene, and myrcene measured at the ROSE site in 1990 [*Goldan et al.*, 1995], that is, 0.30, 0.17, 0.012, 0.008, and 0.015 ppb, respectively.

The correlations of daytime concentrations of GL and MG with FA are significant, r = 0.6 and 0.7, respectively (Figure 8). The ratio of the midafternoon medians of FA to MG, 15, is about a factor of 2 greater than that indicated by the reaction yield, 7. However, since the atmospheric lifetime of MG is at least a factor of 2 shorter than that of FA, the observed value is therefore in qualitative agreement with the mechanism. GL and MG are highly correlated (r = 0.9, Figure 9), indicating

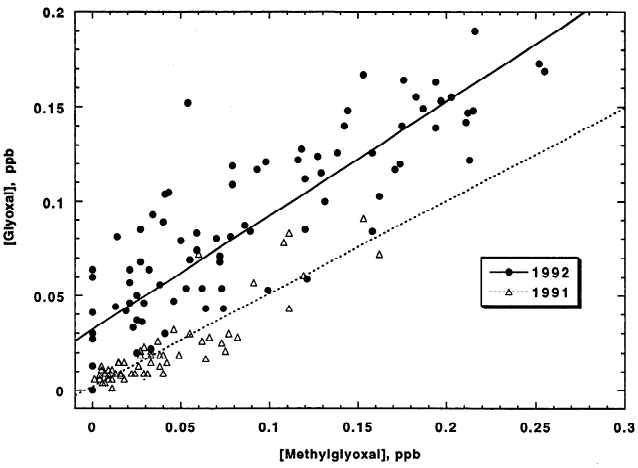


Figure 9. Correlation between the daytime concentrations (0900–1800 LT) of glyoxal and methylglyoxal.

possible common sources. However, a detailed isoprene oxidation mechanism by *Paulson and Seinfeld* [1992] showed that GL constitutes only a minor product, with a yield of ≤2%. On the other hand, the yield of MG is ≥12%. The expected concentration ratio of MG to GL therefore is ≥3, taking into account the roughly a factor of 2 shorter lifetime of MG compared to GL (Table 2). However, since the observed ratios of MG to GL, ~1 and ~2 for 1991 and 1992, respectively, are smaller than that predicted, additional sources of GL may exist.

Two potentially important GL sources are the OH-initiated oxidation of GA producing GL ($k = 1 \times 10^{-11}$ cm^3 mol^{-1} s^{-1}) at 22% yield [*Niki et al.*, 1987] and the OH-initiated oxidation of acetylene ($k = 7 \times 10^{-13}$ cm^3 mol^{-1} s^{-1}, [*Atkinson et al.*, 1989]). In order to contribute equally to the GA-OH reaction, C_2H_2 should be ≥15 [GA] or ~3 ppb. However, since the measured midafternoon median concentration of C_2H_2 during 1992 was ~1 ppb, C_2H_2 could at best only be a minor contributor to GL comparing to GA.

Finally, GL may be produced from the oxidation of less well understood initial products of isoprene, for example, organic nitrates and organic peroxides, which account for ~25% of the products under NO_x-dominated conditions [*Paulson and Seinfeld*, 1992]. Since the NO concentration at which the rate of NO-RO_2 reaction is comparable to that of the HO_2-RO_2 reaction is ~50 ppt [*Paulson and Seinfeld*, 1992], the mechanism developed for isoprene oxidation under NO_x-rich conditions is less applicable when [NO] falls below 50 ppt. The fact that the midafternoon median [NO] was ~60 and ~100 ppt in 1991 and 1992, respectively (Table 3), the data of 1992 perhaps should fit better than that of 1991 to the mechanism utlined in Figure 1. The higher ratio of MG to GL observed in 1992 relative to 1991 is also consistent with this argument.

The acid carbonyls. Pyruvic acid has been previously identified in nonurban environments [e.g., *Andreae et al.*, 1987], but to our knowledge gas phase glyoxylic acid is being reported for the first time. In spite of much research, the detailed mechanism responsible for atmospheric carboxylic acids have not been firmly established [*Keene and Galloway*, 1986; *Jacob and Wofsy*, 1988a; *Madronich et al.*, 1990; *Talbot et al.*, 1990]. While PD concentrations were typically very low, <0.4 ppb, with a midafternoon median of 0.1 ppb, GD reached as high as 3 ppb with a midafternoon median of 0.4 ppb. This fairly substantial concentration suggests that GD is relatively unreactive, resembling perhaps AC more so than PD. The large aqueous solubilities of these two acids, Henry's law constants ≥1 × 10^5 M atm^{-1} (X. Zhou and Y.-N. Lee, submitted manuscript, 1995), may result in a large dry deposition rate [e.g., *Grosjean*, 1989], consistent with the near zero concentrations of these compounds during nighttime (Figure 6).

As with previous studies [e.g., *Jacob and Wofsy*, 1988a], we found that PD to be correlated with FA (Table 4). However, since PD was not reported as a reaction product of isoprene by laboratory studies, we examine whether this correlation supports a precursor-product relationship. With regard to concentration, we noted (1) PD observed at the Metter site was similar to that observed and predicted at a remote forest in the Amazonia [*Andreae et al.*, 1987; *Jacob and Wofsy*, 1988a,b] despite the substantial difference in NO concentrations of these two sites (cf. 20 to 30 ppt at the Amazonia site), and (2) PD at the Metter site was slightly greater than that observed at the Scotia, Pennsylvania site which was marked by higher isoprene and NO_x levels [*Martin et al.*, 1991]. The lack of a dependence of PD on isoprene and NO_x seems to argue against a reactant-product relationship between isoprene and PD. In a recent field measurement in Nova Scotia, Canada, we found that while PD and GD were highly correlated with each other, they were at times decoupled from the photochemically produced FA [*Zhou and Lee*, 1994]. We therefore see further evidence for separate natural sources of PD and GD. Finally, from a structural point of view, GD could serve as a precursor for oxalic acid, which has been observed in aerosol and precipitation [*Norton et al.*, 1983; *Kawamura and Ikushima*, 1993], possible precursor-product relationship between these two species should be examined both in the laboratory and the field, to provide mechanistic insights for carboxylic acids formation.

Acetone and acetaldehyde. The atmospheric distribution of AN is expected to be more uniform than that of the reactive carbonyls as a result of its fairly long atmospheric lifetime [*Singh et al.*, 1994]. The observations that its diurnal variation was weak and the midafternoon median concentrations were essentially identical between the two intensives (Table 2) are consistent with that notion. These median concentrations are similar to those measured at Egbert and Dorset, two rural Ontario sites [*Shepson et al.*, 1991], that is, midafternoon average of 1.7 ppb and 2.8 ppb, respectively. All of these values, however, are significantly greater than the calculated surface concentration of ~0.3 ppb [*Singh et al.*, 1994] based on propane oxidation alone, thereby implicating other important precursors. In contrast, AC exhibited a somewhat greater median value in 1992 (0.75 ppb) than in 1991 (0.58 ppb). It is interest-

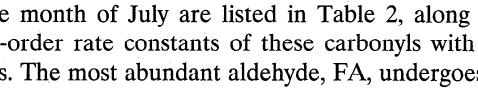
Table 4. Correlation Coefficients (r) Among the Carbonyls

Pairs	1991	1992
FA–GA	0.76	0.69
MG–GA	0.35	0.81
GL–MG	0.91	0.86
FA–MG	0.46	0.62
FA–GD		0.45
MG–GD		0.01
GD–PD		0.70
FA–PD		0.69

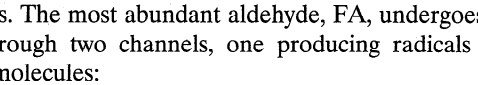
FA is formaldehyde, GA is glycolaldehyde, MG is methylglyoxal, GL is glyoxal, GD is glyoxylic acid, and PD is pyruvic acid.

ing to point out that a comparable relative increase was also observed for PAN between 1992 and 1991 [*Lee et al.*, 1993]. Noting that AC is an important precursor of PAN, we consider this corresponding increase in both species self consistent. *Shepson et al.* [1991] reported AC midafternoon averages of 0.7 and 0.9 ppb for Egbert and Dorset, respectively, again fairly similar to the values observed at the Metter site.

Carbonyls as radical sources. The photolysis rate constants of the carbonyl compounds calculated for the Metter site and the month of July are listed in Table 2, along with the second-order rate constants of these carbonyls with the OH radicals. The most abundant aldehyde, FA, undergoes photolysis through two channels, one producing radicals and the other molecules:



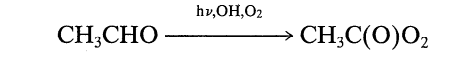
$$H_2CO \rightarrow 2HO_2 + CO \quad (1)$$



$$H_2CO \rightarrow H_2 + CO \quad (2)$$

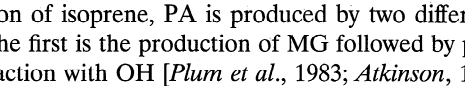
From the photolysis rate constants and the midafternoon median concentrations of the carbonyls, we estimated the contribution of FA to free radical production at midafternoon hours to be ~30% to ~50% of that by O_3 photolysis generating the OH radicals [*Kleinman et al.*, 1994, 1995]. The rest of the carbonyls measured in this work contributed up to ~50% of that by FA, or ~25% of that by O_3. Clearly, the carbonyls, the higher analogs as well as FA, as radical sources is an important consideration in photochemical model calculations. In addition, since the relative importance of aldehydes as radical sources compared to O_3 is greater in the morning and late afternoon hours [e.g., *Cantrell et al.*, 1992], information on diurnal variations of carbonyls is needed to further refine photochemical model calculations.

Isoprene oxidation and PAN production. PAN plays a pivotal role in photochemistry by sequestering NO_x in source regions and supplying radicals and NO_x in clean environments [*Singh and Hanst*, 1981]. In order to quantitatively determine the distribution of PAN and other reactive nitrogen compounds, detailed knowledge of the formation and destruction pathways of PAN must be available. Consequently, AC has been investigated as the main precursor of PAN through the production of the precursor, peroxyacetyl radical (PA):



$$CH_3CHO \xrightarrow{h\nu, OH, O_2} CH_3C(O)O_2 \quad (3)$$

especially in regions where anthropogenic emission is important. However, for rural and remote areas, it is necessary to also consider contributions from biogenic sources. From the oxidation of isoprene, PA is produced by two different pathways: the first is the production of MG followed by photolysis and reaction with OH [*Plum et al.*, 1983; *Atkinson*, 1990]



$$CH_3C(O)CHO \xrightarrow{h\nu, OH, O_2} CH_3C(O)O_2 + CO \quad (4)$$

The second is the direct production of PA from OH initiated oxidation of MVK (Figure 1, *Tuazon and Atkinson* [1989]).

We first examine the contribution of MG in relation to that of AC. Using the midafternoon median concentrations of these two carbonyls and their respective photolysis and OH reaction rates (Table 2), we determined the relative production rate (E) of PA from MG and AC as

$$E(MG)/E(AC) = (j_{(MG)} + k_{MG}[OH])[MG]/(j_{(AC)} + k_{AC}[OH])[AC] = 3.7 \times [MG]/[AC]$$

Thus MG constituted ~20% (1991) and ~50% (1992) of the PA produced from AC, indeed significant. The values are greater if we used [OH] ~ 2×10^6 mol cm^{-3} as calculated for the ROSE site [*Cantrell et al.*, 1992] instead of 5×10^6 mol cm^{-3}.

Table 5. Composition of Event Precipitation Samples Collected During the 1991 Intensive

Date	Rain Fall, cm	pH	FA	GA	GL	MG
July 25	3.30	4.29	8.2	3.0	0.6	1.3
July 27	0.38	4.30	9.3	4.4	0.9	2.1
July 29	1.78	4.08	6.7	3.7	0.5	0.9
July 30	0.89	4.26	4.0	1.9	0.2	0.3
July 31	1.24	4.50	2.6	0.8	0.1	0.1
Aug 02	7.11	4.73	2.1	0.6	0.0	0.1

Concentration units in micromolars. FA is formaldehyde, GA is glycolaldehyde, GL is glyoxal, and MG is methylglyoxal.

The contribution to PA from the MVK-OH reaction is estimated from the steady state concentration of the coproduced GA (Figure 1), whose formation is balanced by its destruction. Considering the OH-initiated decay of GA alone, we derive a PA production rate of $k_{OH}[OH][GA] = 1.1 \times 10^{-5}$ ppb s^{-1}. This represents ~25% of that from AC at the same OH concentration, a fairly significant contribution. Since dry deposition of GA is conceivably rapid arising from its high solubility, we estimate a removal rate of 1×10^{-5} s^{-1}, using deposition velocity of 1 cm s^{-1} and a mixing height of 1 km. This removal rate is comparable to that of the OH reaction, thereby increasing the contribution of the MVK-OH reaction as a source of PAN to ~50% of that by AC.

Being an analog of AC, GA is expected to serve as a precursor for a PAN analog, peroxyhydroxyacetyl nitrate (HO-PAN), sequestering NO_2. Consequently, this PAN type compound may contribute to the so-called missing NO_y, operationally defined as the difference between the total NO_y and the sum of total nitrate, NO, NO_2, and PAN [*Parrish et al.*, 1993]. The observed median concentrations of AC and GA (Table 2) indicate that HO-PAN could reach one third of PAN produced from AC.

Production of carbon monoxide. FA produces CO from all three reaction pathways mentioned above, namely, reaction (1), (2), and the reaction with OH:

$$d[CO]/dt = (j_1 + j_2 + k_{FA}[OH])[H_2CO]$$

Using the j values listed in Table 2 and an [OH] of 5×10^6 mol cm^{-3}, we estimated a CO production rate in the midafternoon of 1.4 ppb hr^{-1}. GL and MG contribute to CO production analogously at $k_{(GL)} = 1.2 \times 10^{-4}$ s^{-1} and $k_{(MG)} = 3.2 \times 10^{-4}$ s^{-1} [*Green et al.*, 1990]. The resulting rate of 0.16 ppb hr^{-1}, however, represents a much smaller contribution compared to FA. A 24-hour averaged CO production at the ground level from the three aldehydes is ~9 ppb d^{-1}. Since FA and its analogs at this rural site are believed to derive mainly from isoprene oxidation, the contribution to CO budget of this significant biogenic source must be further examined to better characterize the atmospheric distribution of this important photochemical species.

Carbonyls in precipitation samples. During the 1991 intensive we analyzed six event precipitation samples (Table 5). The processes by which the rainwater acquired the dissolved species include rain-out and wash-out. The observation of substantial amounts of soluble carbonyls in precipitation is ex-

pected from their large Henry's law constants and provides additional evidence for their presence in the gas phase. Using $H = 5 \times 10^3$ M atm^{-1} (22°C, X. Zhou and Y.-N. Lee, submitted manuscript, 1995) and the observed concentrations, we calculated gas phase concentrations of FA between 0.4 and 1.8 ppb. These values are similar to but somewhat smaller than the surface ambient concentrations, and indicate a vertical gradient in FA, decreasing with altitude and/or a diminished production of this compound under cloudy conditions. This procedure cannot be applied to evaluating the gas phase concentrations of the more soluble multi-oxygenated carbonyls as the liquid water concentration needed for these calculations is not available.

The aqueous concentrations of the soluble carbonyls are potentially useful for assessing wet deposition fluxes of these species provided that statistically meaningful precipitation rate and composition are established. Nonetheless, for the 9-day period listed in Table 5, we estimated a deposition flux of the four carbonyls of 0.08 mgC m^{-2} hr^{-1}. Since the isoprene flux is estimated to be ~1 mg C m^{-2} hr^{-1} for this locality (24-hour average based on a rate at 30°C and a photosynthetic active radiation of 1000 μmol m^{-2} s^{-1} [*Guenther et al.*, 1994a]), it appears for this period wet scavenging is only marginally important for removing the isoprene carbons from the atmosphere. We must point out that this analysis is valid only if the dissolved carbonyls did not undergo significant aqueous transformation (see below). Concerning dry deposition, we estimated a flux of ~0.05 mg C m^{-2} hr^{-1} for the three multi-oxygenated carbonyls for the midafternoon hours using the median concentrations given in Table 2 and an upper limit deposition velocity of 4 cm s^{-1}. In view of the rather large midday isoprene flux, that is, ~3 mg C m^{-2} hr^{-1}, it appears that dry deposition of the multi-oxygenated carbonyls constitutes only a minor removal pathway for the isoprene carbons.

With the limited precipitation data, we note that all the carbonyls were highly correlated, $r \sim 0.9$, in contrast to those measured in the gas phase. In addition, the observed GA/MG ratio of 2 in precipitation is in excellent agreement with that expected from gas phase isoprene oxidation [*Paulson and Seinfeld*, 1992]. One rationale for the preserved relationships may be a reduced photolysis rate of the secondary products under cloudy conditions. One might also argue that because of the rapid in-cloud gas liquid mass transfer [*Schwartz*, 1986], soluble products are scavenged before much gas phase reaction can occur, thereby retaining the gas phase reaction stoichiometry. In any case, it may be pointed out that the retention of the product yields suggests slow aqueous phase decay of these species. Also, dry deposition which is an important consideration for surface concentrations plays a much reduced role for air masses aloft in or near clouds.

Some contrast between the two intensives. We briefly compare the results obtained in the two intensives for possible insights into the chemistry of isoprene. Since the median temperature, humidity, and total UV irradiance in the midafternoon were all greater in 1991 than 1992 (Table 3), we expect isoprene emission to be stronger in 1991 as well [*Lamb et al.*, 1986; *Guenther et al.*, 1993]. Following that, we may also expect greater concentrations of the downstream products of isoprene in 1991 than in 1992. Although FA seemed to fit this expectation, the other three soluble carbonyls exhibited the opposite behavior, greater in 1992 than in 1991. Consequently, it appears that higher isoprene concentrations do not necessarily lead to higher concentrations of the downstream products. This behavior has also been observed at the ROSE site. Comparing July 11 to July 14 for which isoprene concentrations were 5.6 and 1.9 ppb, respectively, *Cantrell et al.* [1993] reported a smaller MVK level but a slightly higher concentration for MACR for July 14, despite the similar NO and UV irradiance levels of these two days. For the Metter site, the weaker UV irradiance of 1992 may be partially responsible for the increased atmospheric lifetimes and therefore the steady state concentrations of the soluble carbonyls. As mentioned earlier, the levels of NO_x could also influence the product distribution: the ~50% increase of NO_x in 1992 over 1991 (Table 3) would favor the production of the carbonyls from RO_2 radicals at the expense of organic peroxides. Modeling work by *Cantrell et al.* [1992] also showed that at ~70 to 80 ppt of NO, RO_2 reaction is dominated by NO, leading to greater concentrations of the carbonyl compounds. The higher level of carbonyls in response to increased NO_x levels may offer a mechanistic understanding of the greater O_3 concentration observed in 1992 over 1991.

Conclusion

A series of carbonyl compounds known as formaldehyde (FA), acetaldehyde (AC), acetone (AN), glycolaldehyde (GA), glyoxal (GL), methylglyoxal (MG), glyoxylic acid (GD), and pyruvic acid (PD) were measured at a rural site in Georgia during two field intensives in summers of 1991 and 1992 as part of the Southern Oxidants Study (SOS) aiming at gaining understanding of hydrocarbon oxidation and ozone production in the southeastern United States. We conclude based on the following measurement results: (1) The identification of GA, GL, MG along with FA at this rural site where isoprene is expected to be the dominant hydrocarbon provided corroborative evidence for the laboratory developed isoprene oxidation mechanism. (2) The concentration ratios of these carbonyls are in qualitative agreement with the yields of the mechanism, consistent with the notion that isoprene is the dominant HC. (3) The contribution to radical formation from FA and the higher carbonyls is highly important and accounts for ~70% of that by O_3. (4) Concerning the formation of PAN, it was found that MG and methyl vinyl ketone derived from isoprene oxidation is equal to or more important than AC as a precursor of the peroxyacetyl radicals. (5) FA is a major source of CO over other carbonyls with a CO production rate of ~9 ppb d^{-1}. (6) Wet scavenging of the soluble carbonyls, that is, GA, GL, and MG, appears to only play a minor role in removing the isoprene carbons from the atmosphere.

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