Gas-Phase Reaction of Ozone with *Trans*-2-Hexenal, *Trans*-2-Hexenyl Acetate, Ethylvinyl Ketone, and 6-Methyl-5-Hepten-2-One

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ABSTRACT

The gas-phase reaction of ozone with the unsaturated oxygenates *trans*-2-hexenal, *trans*-2-hexenyl acetate, ethylvinyl ketone, and 6-methyl-5-hepten-2-one, which are components of biogenic emissions and/or close structural homologues thereof, has been investigated at atmospheric pressure and ambient temperature (286–291 K) and humidity (RH = 55 ± 10%). Reaction rate constants, in units of 10^{-18} cm^3 $molecule^{-1}$ s^{-1}, are 1.28 ± 0.28 for *trans*-2-hexenal, 21.8 ± 2.8 for *trans*-2-hexenyl acetate, and 394 ± 40 for 6-methyl-5-hepten-2-one. Carbonyl product formation yields, measured with sufficient cyclohexane added to scavenge the hydroxyl radical, are 0.53 ± 0.06 for *n*-butanal and 0.56 ± 0.04 for glyoxal from *trans*-2-hexenal, 0.47 ± 0.02 for *n*-butanal and 0.58 ± 0.14 for 1-oxoethyl acetate from *trans*-2-hexenyl acetate, 0.55 ± 0.07 for formaldehyde and 0.44 ± 0.03 for 2-oxobutanal from ethylvinyl ketone, and 0.28 ± 0.02 for acetone from 6-methyl-5-hepten-2-one. Reaction mechanisms are outlined and the atmospheric persistence of the compounds studied is briefly discussed.

INTRODUCTION

Biogenic hydrocarbons play a major role in the chemistry of the atmosphere [1–3]. Isoprene and terpenes have long been recognized as abundant components of biogenic emissions [4–6]. More recently, other unsaturated aliphatic compounds including unsaturated

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alcohols, aldehydes, ketones, and esters have been identified as important biogenic emissions [7–18]. As more information becomes available concerning the nature and abundance of these compounds, it is necessary to obtain the kinetic and product data that are needed to assess their persistence and fate in the atmosphere. Kinetic data have recently been reported for the reaction of ozone with unsaturated alcohols and with other unsaturated oxygenates [19–21]. Carbonyl products of the ozone-unsaturated alcohol reaction have been identified [22] and carbonyl and peroxyacyl nitrate ($RC(O)OONO_2$) products have been characterized in sunlight-irradiated mixtures of unsaturated alcohols and oxides of nitrogen [23,24].

In this work, we have studied the reaction of ozone, under conditions relevant to the atmosphere, with the unsaturated aliphatic oxygenates, *trans*-2-hexenal ($CH_3CH_2CH_2CH{=}CHCHO$), *trans*-2-hexenyl acetate ($CH_3C(O)OCH_2CH = CHCH_2CH_2CH_3$), ethylvinyl ketone (1-penten-3-one, $CH_2{=}CHC(O)CH_2CH_3$), and 6-methyl-5-hepten-2-one ($CH_3C(O)CH_2CH_2CH{=}C(CH_3)_2$). Reaction rate constants have been measured and carbonyl products have been identified with sufficient cyclohexane added to scavenge the hydroxyl radical, which forms as a product of the reaction of ozone with alkenes [25] and with other unsaturated aliphatic compounds [21,22].

The four unsaturated oxygenates studied were selected as abundant components of biogenic emissions and/or as close structural homologues thereof [7–18]. *Trans*-2-hexenal and 6-methyl-5-hepten-2-one have been the object of several reports [13,15–18]. *Trans*-2-hexenyl acetate and ethylvinyl ketone are representative of unsaturated esters and unsaturated ketones, respectively, that have been identified in biogenic emissions to the atmosphere [7–18]. Ethylvinyl ketone is also a close structural homologue of methylvinyl ketone, which forms as a major product in the atmospheric oxidation of the important biogenic hydrocarbon isoprene (26–29, and references therein].

While the compounds studied in this work were selected for their perceived importance as biogenic emissions to the atmosphere, unsaturated oxygenates are also relevant to other areas of environmental chemistry. Unsaturated carbonyls have received attention as toxic air contaminants [32,33] and as major reaction products in the atmospheric oxidation of aromatic hydrocarbons [34,35]. Unsaturated esters are of concern in indoor air quality [36] and as emissions from industrial cleaning and painting operations [37].

Products of the gas-phase reaction of ozone with unsaturated carbonyls have received scant attention [27,30,31] and are reported here for the first time for *trans*-2-hexenal, ethylvinyl ketone, and 6-methyl-5-hepten-2-one. To our knowledge, products of the gas-phase reaction of ozone with unsaturated esters have not been studied prior to this work.

EXPERIMENTAL METHODS

Trans-2-hexenal, *trans*-2-hexenyl acetate, ethylvinyl ketone, 6-methyl-5-hepten-2-one, and cyclohexane were obtained from Aldrich (stated purities 99, 98, 97, 99 and >99%, respectively) and were used without further purification.

Kinetic Measurements

The experimental protocol employed in this study was similar to that previously described [19,20]. Ozone was produced by the built-in generator of a continuous ozone analyzer (Dasibi 1108 ultraviolet photometer) and was introduced in 3.7 m^3 all-Teflon collapsible chambers constructed from 200 A FEP film and covered with black plastic. The continuous analyzer is periodically calibrated according to the procedures recommended by the U.S. Environmental Protection Agency. The precision of the ozone measurements in the concentration range relevant to this study was $\pm 1-2$ ppb. Temperature inside the chamber was recorded using a calibrated thermocouple. The matrix air, purified by passing ambient air through large sorbent cartridges containing activated carbon, molecular sieves, and silica gel, contained no detectable concentrations of ozone, oxides of nitrogen, reactive hydrocarbons, and carbonyls ($<1-2$ ppb, 1 ppb $= 2.5 \times 10^{10}$ molecule cm^{-3} at 760 torr and 298 K). The relative humidity was 55 $\pm$ 10%. Cyclohexane and the unsaturated oxygenate, in that order, were introduced in the chamber by injecting aliquots of the liquid into a 200 cm^3 glass bulb and by flushing the contents of the glass bulb into the chamber using purified air as the carrier gas. The initial concentration of the unsaturated oxygenate was calculated from the amount injected and the chamber volume.

The rate of loss of ozone by diffusion to the chamber walls was measured in a separate experiment involving 134 ppb of ozone in purified air ($T = 291 \pm 1$ K, RH $= 55 \pm 10\%$) and was $(2.10 \pm 0.04) \times 10^{-6}$ s^{-1} ($R = 0.999$). This value is consistent with those obtained in earlier measurements made in this laboratory [19,20]. The absence of ozone-consuming impurities in cyclohexane was verified in two experiments involving mixtures of cyclohexane (400 ppm) and ozone (175 and 245 ppb) in purified air (T = 288 ± 2 K, RH = 55 ± 10%). The loss rates of ozone in these experiments, (1.61 ± 0.41) × 10^{-6} s^{-1} (R = 0.941) and (1.64 ± 0.04) × 10^{-6} s^{-1} (R = 0.997) were essentially the same as that measured for loss of ozone alone in pure air. These results show that the ozone-cyclohexane reaction is negligibly slow at the ozone and cyclohexane concentrations employed in this study.

Under the conditions of this study, ca. 99% of the hydroxyl radical formed as a product of the ozone-unsaturated oxygenate reaction is consumed by its reaction with cyclohexane [19,38]. In the absence of cyclohexane, the OH radicals formed react with the unsaturated oxygenate but this has little effect on the ozone decay rate. Therefore the addition of cyclohexane is not important for the kinetic measurements but is obviously required to characterize the ozone-unsaturated oxygenate reaction products. Accordingly, cyclohexane was present in all experiments that involved the identification of carbonyl products and the determination of their formation yields.

The reaction was followed under pseudo-first order conditions, with initial concentrations of 0.5–4.0 ppm for the unsaturated oxygenates, 73–244 ppb for ozone, and 400 ppm for cyclohexane when added (Table I). Ozone was measured by ultraviolet photometry. Plots of ($[O_3]_0/[O_3]_t$) vs. time were constructed, where $[O_3]_0$ and $[O_3]_t$ are the initial ozone concentration and the ozone concentration at time t, respectively. Examples of these plots are shown in Figure 1. Linear regression of the data (unit-weighted least squares, not forced through the origin) yielded high correlation coefficients ($R \geq 0.984$), near-zero intercepts and slopes, which, after a small correction for the measured rate of ozone loss to the chamber walls (the correction required was one percent or less), yielded the corresponding pseudo first-order reaction rate constants (Table I).

The unsaturated carbonyls *trans*-2-hexenal and 6-methyl-5-hepten-2-one (but not ethylvinyl ketone) contributed a negative interference to the ozone concentrations measured by ultraviolet photometry. Control experiments carried out with about 2 ppm unsaturated carbonyl in purified air (RH = 55 ± 10%) indicated that the ozone analyzer signal decreased upon injection of the carbonyl and then slowly increased back to its initial value, a pattern consistent with retention and desorption of the unsaturated carbonyl on the instrument's scrubber. The rate of signal increase as a function of time was measured and was (7.6 ± 0.2) × 10^{-6} s^{-1}. This value was used to correct the ozone concentration data in the unsaturated carbonyl-ozone experiments. The correction thus applied was 8.7, 7.7, and 15.7% in the three experiments with *trans*-2-hexenal and was negligible (less than 1%) in the case of 6-methyl-5-hepten-2-one. A control experiment with ca. 2 ppm *trans*-2-hexenyl acetate in pure air (RH = 55 ± 10%)

Table I Summary of Kinetic Data

Initial Concentrations[a]						
Unsaturated Oxygenate, ppm	Ozone, ppb	T, K	10^4 × slope, s^{-1} [b]	10^3 × intercept[b]	R	Reaction Rate Constant, 10^{-18} cm^3 molecule^{-1} s^{-1}
trans-2-hexenal:						
2.6	73	288.7 ± 0.3	0.874 ± 0.008	3 ± 5	0.998	1.51
3.5[c]	114	287.7 ± 0.6	0.990 ± 0.009	−31 ± 6	0.999	1.37
2.34	100	285.9 ± 2.2	0.485 ± 0.005	−55 ± 6	0.996	0.97
trans-2-hexenyl acetate:						
4.0[c]	207	288.5 ± 0.2	19.0 ± 0.3	−36 ± 38	0.998	19.3
3.45	233	288.4 ± 0.2	21.1 ± 0.3	−66 ± 38	0.998	24.8
2.0	201	287.4 ± 0.2	10.4 ± 0.1	123 ± 11	0.999	21.2
6-methyl-5-hepten-2-one:						
1.51	152	287.0 ± 0.1	125 ± 2	9 ± 200	0.999	336
1.25	244	288.5 ± 0.1	131 ± 5	79 ± 37	0.995	424
0.49	118	291.5 ± 0.1	48.3 ± 0.7	81 ± 22	0.997	403
0.64	142	290.1 ± 0.1	65.1 ± 2.6	−12 ± 64	0.984	414

[a] 400 ppm cyclohexane in all experiments unless otherwise indicated by footnote [c].

[b] Least-squares linear repression of experimental data, ± one standard deviation.

[c] No cyclohexane added.

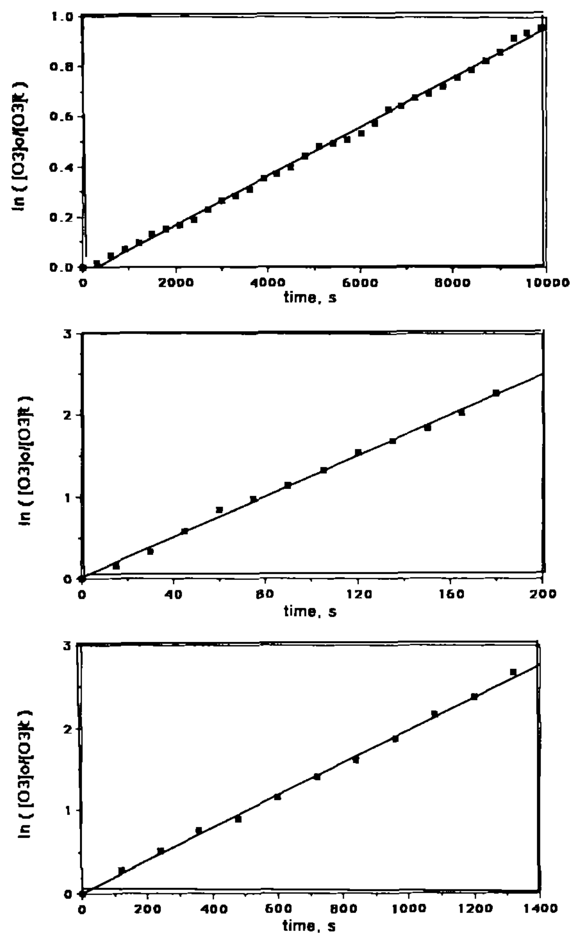

Figure 1 Examples of scatter plots of pseudo-first-order rate constants, $\ln([O_3]_0/[O_3]_t)$ vs. reaction time for *trans*-2-hexenal (top), 6-methyl-5-hepten-2-one (middle), and *trans*-2-hexenyl acetate (bottom). See Table I for least-squares linear regression parameters.

indicated no interference from this compound when measuring ozone by ultraviolet photometry.

Carbonyl Measurements

Carbonyl products were measured as their 2,4-dinitrophenylhydrazine (DNPH) derivatives by liquid chromatography following collection on DNPH-coated C_{18} cartridges. The experimental protocol has been described in detail elsewhere [39,40] and only a brief summary is given here. Samples of 30–60 min. duration were collected at a flow rate of 0.7 L/min. To minimize possible negative interference from ozone, the samples were collected after ozone had been consumed. Following sample collection, the cartridges were eluted with 2 mL acetonitrile and aliquots of the acetonitrile solution were analyzed by liquid chromatography (LC) with uv-visible detection [39,40]. Several samples were also analyzed by chemical ionization mass spectrometry [39], see example in Figure 2. Confirmation of the carbonyl structure in the samples collected in the ozone-unsaturated oxygenate-cyclohexane experiments involved the comparison of retention times, 430/360 nm absorbance ratios and chemical ionization mass spectra to those of data libraries constructed in our laboratory using carbonyl-DNPH standards [39].

Quantitative analysis involved the use of external standards synthesized in our laboratory. Calibration curves, i.e., plots of absorbance at a given detection wavelength vs. concentration, were constructed as described previously. The slopes of these calibration curves, i.e., response factors, were used to calculate carbonyl concentrations in the samples collected in the alkene-ozone-cyclohexane experiments. To verify day to day consistency in retention times and response factors, calibration standards were analyzed along with each batch of samples. Calibration standards employed in this study included two mixtures of carbonyl-DNPH derivatives, one prepared in our laboratory and the other obtained from a commercial

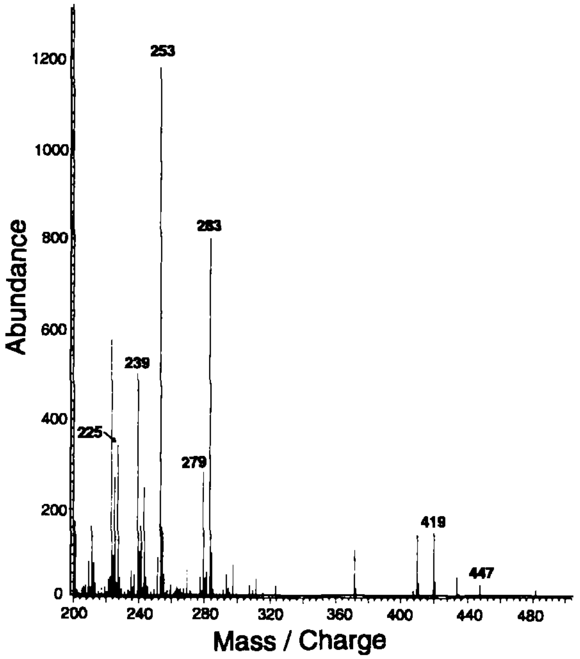

Figure 2 Chemical ionization mass spectrum of a sample collected in a *trans*-2-hexenyl acetate-ozone-cyclohexane experiment. Major peaks in this spectrum are the protonated molecular ions MH of the DNPH derivatives of butanal (MH = 253), 1-oxoethyl acetate (MH = 283), acetaldehyde (MH = 225), propanal (MH = 239), glyoxal (MH = 239, mono-DNPH derivative, and MH = 419, di-DNPH derivative), 2-oxo butanal (MH = 447, di-DNPH derivative), and cyclohexanone (MH = 279).

supplier. Response factors measured for the thirteen carbonyl-DNPH derivatives present in the two mixtures have been shown in previous work to agree within ±4 percent [39].

Carbonyl impurities in the unsaturated oxygenates were characterized in control experiments involving ca. 2 ppm of the unsaturated oxygenate in purified air (no ozone or cyclohexane present). The concentrations of the carbonyls reported as reaction products were corrected when appropriate. The loss of carbonyls to the chamber walls was measured for about 15 carbonyls including those relevant to this study. Carbonyl loss rates were comparable in magnitude to those for ozone and, when compared to the duration of the ozone-unsaturated oxygenate-cyclohexane experiments, made a negligible contribution to the measured carbonyl concentrations.

Carbonyl yields were calculated from the measured carbonyl concentration and the amount of ozone reacted, i.e., assuming a 1:1 stoichiometry for the ozone-unsaturated oxygenate reaction. This assumption appears reasonable since under the conditions of our study essentially all of the OH formed reacts with cyclohexane and the reactions of OH with the unsaturated oxygenate and with the carbonyl products of the ozone-unsaturated oxygenate reaction are of negligible importance.

A limitation of the liquid chromatography method employed in this study is that β-hydroxycarbonyls yield the DNPH derivatives of the corresponding α-dicarbonyls [39]. Thus, β-hydroxycarbonyls and the corresponding α-dicarbonyls could not be resolved when both carbonyls were formed in the same experiment. As a result, we could not distinguish between hydroxyacetone (CH_3COCH_2OH) and methylglyoxal (CH_3COCHO) in the 6-methyl-5-hepten-2-one experiments and between 2-hydroxybutanal ($CH_3CH_2CHOHCHO$) and 2-oxobutanal (CH_3CH_2COCHO) in the *trans*-2-hexenal and *trans*-2-hexenyl acetate experiments.

Two of the carbonyl products for which no standards are available were tentatively identified on the basis of retention, absorption, and mass spectrometry data: 2-oxobutanal (CH_3CH_2COCHO) from ethylvinyl ketone, *trans*-2-hexenal and *trans*-2-hexenylacetate and 1-oxoethyl acetate ($CH_3C(O)OCH_2CHO$) from *trans*-2-hexenyl acetate. The dicarbonyl 4-oxopentanal ($CH_3COCH_2CH_2CHO$) which may form from 6-methyl-5-hepten-2-one (see Results and Discussion) could not be conclusively identified.

The α-dicarbonyl 2-oxobutanal forms as a major product in the reaction of ozone with ethylvinyl ketone. Retention time, 430/360 nm absorbance ratio, and uv-visible absorption spectrum of the DNPH derivative of 2-oxobutanal have been reported in previous work [41]. The chemical ionization mass spectrum includes a peak at $m/e = 447$, which is the protonated molecular ion of the di-DNPH derivative [39]. Retention time, absorption, and mass spectrometry data also indicated that 2-oxobutanal formed as a minor product in the *trans*-2-hexenal and *trans*-2-hexenyl acetate experiments. The concentrations of 2-oxobutanal was calculated using a response factor estimated from data for other α-dicarbonyls for which reference standards are available, i.e., glyoxal, methyl glyoxal, and biacetyl [39]. The uncertainty on the response factor thus estimated is ca. ± 20 percent.

The carbonyl 1-oxoethyl acetate, $CH_3C(O)OCH_2CHO$, was tentatively identified as follows: the retention time of its DNPH derivative was consistent with those for DNPH derivatives of oxygenated structural homologues (e.g., δ-hydroxycarbonyls such as 5-hydroxy-2-pentanone and ether-carbonyls such as methoxyacetone and 2-furaldehyde); the chemical ionization mass spectrum of its DNPH derivative included an abundant fragment at $m/e = 283$ that corresponds to the protonated molecular ion (MW = 282). The concentration of 1-oxoethyl acetate was calculated using a response factor estimated from response factor vs. retention time relationships [37]. The uncertainty on the response factor thus estimated is ca. ±25 percent.

RESULTS AND DISCUSSION

Reaction Rate Constants

Second-order rate constants for the gas-phase reaction of ozone with *trans*-2-hexenal, *trans*-2-hexenyl acetate, and 6-methyl-5-hepten-2-one are listed in Table I. The rate constant for the reaction of ozone with ethylvinyl ketone has been measured in previous work [19]. Neglecting in first approximation the small differences in temperature from one experiment to the next (≤ 4.5 K), the rate constants given in Table I were averaged; these averages are, in units of 10^{-18} cm^3 $molecule^{-1}$ s^{-1}, 1.28 ± 0.28 for *trans*-2-hexenal (at $T = 287.3 \pm 2.3$ K), 21.8 ± 2.8 for *trans*-2-hexenyl acetate (at $T = 288.1 \pm 0.4$ K), and 394 ± 40 for 6-methyl-5-hepten-2-one (at $T = 289.3 \pm 2.0$ K).

These rate constants are consistent with considerations of substituent effects on reactivity of the unsaturated oxygenates toward ozone. For *trans*-2-hexenal, the measured rate constant reflects the strong electron-withdrawing effect of the —CHO group, e.g., replacing R = H (1-pentene [42]) by R = —CHO in $CH_3CH_2CH_2CH = CHR$ results in a ca. seven-fold decrease in reactivity. The ozone-*trans*-2-hexenal reaction rate constant is similar in magnitude to those for other unsaturated aldehydes including crontonaldehyde, methacrolein, and 2-ethylacrolein [19,42,43]. Our value of $(1.28 \pm 0.28) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} also agrees, within the stated uncertainties, with that of $(2.0 \pm 1.0) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} reported in recent work [21]. For *trans*-2-hexenyl acetate, the reaction rate constant measured in this study compares to values for other substituted unsaturated esters of (in units of 10^{-18} cm^3 molecule^{-1} s^{-1}) 4.4 ± 0.3 for methyl crotonate [19], 7.5 ± 0.9 for methyl methacrylate [19], and 54 ± 14 for the close structural homologue *cis*-3-hexenyl acetate [21]. For 6-methyl-5-hepten-2-one, the CH_3CO substituent at the delta carbon is not expected to have a large influence on reactivity, and indeed the rate constant $k = (394 \pm 40) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} is comparable in magnitude to those of (in units of 10^{-18} cm^3 molecule^{-1} s^{-1}) 425, 456, and 563 for the trisubstituted alkenes 2-methyl-2-butene [44], *cis*-3-methyl-2-pentene [45] and *trans*-3-methyl-2-pentene [45], respectively.

Carbonyl Products

Carbonyl products and their yields are listed in Table II. Major carbonyl products identified in the ozone-unsaturated oxygenate-cyclohexane experiments included butanal and glyoxal from *trans*-2-hexenal, butanal, and 1-oxoethyl acetate from *trans*-2-hexenyl acetate, formaldehyde, and 2-oxobutanal from ethylvinyl ketone, and acetone and methylglyoxal from 6-methyl-5-hepten-2-one. Cyclohexanone was observed in all experiments, thus providing evidence for the formation of the hydroxyl radical as a product of the ozone-unsaturated oxygenate reaction.

Table II Carbonyl Products and Yields in Ozone-Unsaturated Oxygenate-Cyclohexane Experiments

Carbonyl Product	Formation Yield[a]	Carbonyl Product	Formation Yield[a]
trans-2-hexenal:		*trans*-2-hexenyl acetate:	
butanal	0.527 ± 0.055	butanal	0.473 ± 0.023
glyoxal	0.559 ± 0.037	1-oxoethyl acetate[b]	0.583 ± 0.141
2-oxobutanal[b]	0.074 ± 0.006	glyoxal	0.209 ± 0.004
acetaldehyde	0.109 ± 0.020	propanal	0.102 ± 0.002
propanal	0.067 ± 0.008	2-oxobutanal[b]	0.091 ± 0.007
cyclohexanone	0.032 ± 0.003	acetaldehyde	0.039 ± 0.003
		cyclohexanone	0.090 ± 0.004
6-methyl-5-hepten-2-one:		ethyl vinyl ketone:	
acetone	0.282 ± 0.023	formaldehyde	0.548 ± 0.069[c]
methyl glyoxal	0.319 ± 0.037	2-oxobutanal[b]	0.444 ± 0.025[d]
formaldehyde	0.038 ± 0.032	acetaldehyde	0.097 ± 0.001[d]
cyclohexanone	0.229 ± 0.013	cyclohexanone	ND[e]

Unidentified Carbonyl Products

Unsaturated Oxygenate	Carbonyl-DNPH Derivative		
	Retention Time[f]	Peak Height	430/360 nm Absorbance Ratio
trans-2-hexenyl acetate	0.82	0.09[g]	0.22
	1.18	0.08[g]	0.23
6-methyl-5-hepten-2-one	1.56	5.0–12.0[h]	0.24

[a] ±One standard deviation.

[b] Tentative identification and estimated yields, see text.

[c] From data for four experiments. The formaldehyde yield for the two experiments in which 2-oxobutanal and acetaldehyde were measured was 0.555 ± 0.001.

[d] From data for two experiments.

[e] Not measured, coeluted with other compounds.

[f] Relative to that of formaldehyde-DNPH.

[g] Relative to that of butanal-DNPH.

[h] Relative to that of acetone-DNPH.

Unidentified carbonyls are also listed in Table II, which includes retention and absorption parameters that may be useful for identification in future work using relationships between carbonyl structure and retention and absorption of their DNPH derivatives [39]. The two minor unknowns in the *trans*-2-hexenal experiments were impurities as indicated by data from control experiments (no ozone present). The two minor unknowns in the *trans*-2-hexenyl acetate experiments were reaction products, probably ester-carbonyl products on account of their short retention times. The abundant unknown in the 6-methyl-5-hepten-2-one experiments could be the mono-DNPH derivative of 4-oxopentanal, but insufficient evidence was obtained for positive identification.

Primary Carbonyl Products of the Ozone-Unsaturated Oxygenate Reaction

The presently believed mechanism for the gas-phase reaction of ozone with alkenes involves electrophilic addition and subsequent decomposition of the 1,2,3-trioxolane adduct into two carbonyls (hereafter "primary" carbonyls) and two biradicals:

$$R_1R_2C = CR_3R_4 + O_3 \longrightarrow R_1COR_2 + R_3R_4COO \quad (1a)$$

$$\longrightarrow R_3COR_4 + R_1R_2COO \quad (1b)$$

followed by reactions of the two biradicals R_1R_2COO and R_3R_4COO as will be described later in this section. The mechanism summarized by reaction 1 implies that the sum of the formation yields of the two primary carbonyls R_1COR_2 and R_3COR_4 is 1.0. Recent experimental data for alkenes [46–48] and for unsaturated alcohols [20,24] are supportive of the simple mechanism given by reaction 1. Measured carbonyl formation yields (Table II) are consistent with the mechanism summarized by reaction 1 in the case of *trans*-2-hexenal, *trans*-2-hexenyl acetate, and ethylvinyl ketone, for which the sums of the primary carbonyl yields were 1.086 ± 0.066, 1.056 ± 0.143, and 0.992 ± 0.094, respectively (Fig. 3). The relevant reactions are, for *trans*-2-hexenal:

$$CH_3CH_2CH_2CH = CHCHO + O_3$$

$$\longrightarrow CH_3CH_2CH_2CHO + HC(O)CHOO \quad (2a)$$

$$\longrightarrow (CHO)_2 + CH_3CH_2CH_2CHOO \quad (2b)$$

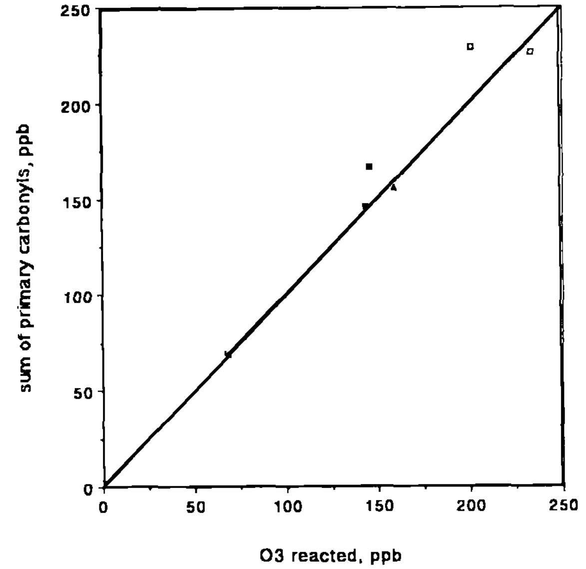

Figure 3 Scatter plot of sum of primary carbonyl concentrations, ppb, vs. reacted ozone, ppb, for butanal + glyoxal from *trans*-2-hexenal (solid squares), butanal + 1-oxoethyl acetate from *trans*-2-hexenyl acetate (open squares), and formaldehyde + 2-oxobutanal from ethyl vinyl ketone (solid triangles). The 1:1 line is included for comparison.

similarly for *trans*-2-hexenyl acetate:

$$CH_3CH_2CH_2CH = CHCH_2OC(O)CH_3 + O_3$$

$$\longrightarrow CH_3CH_2CH_2CHO + CH_3C(O)OCH_2CHOO \quad (3a)$$

$$\longrightarrow CH_3C(O)OCH_2CHO + CH_3CH_2CH_2CHOO \quad (3b)$$

and for ethylvinyl ketone:

$$CH_3CH_2C(O)CH = CH_2 + O_3$$

$$\longrightarrow HCHO + CH_3CH_2C(O)CHOO \quad (4a)$$

$$\longrightarrow CH_3CH_2C(O)CHO + H_2COO \quad (4b)$$

For 6-methyl-5-hepten-2-one, the predicted primary carbonyls are acetone, as observed, and 4-oxopentanal, which could not be measured:

$$CH_3C(O)CH_2CH_2CH = C(CH_3)_2 + O_3$$

$$\longrightarrow CH_3C(O)CH_3 + CH_3C(O)CH_2CH_2CHOO \quad (5a)$$

$$\longrightarrow (CH_3)_2COO + CH_3C(O)CH_2CH_2CHO \quad (5b)$$

The formation yields of the two primary carbonyls are also the formation yields of the corresponding biradicals, see reaction 1. From the data in Table II, we calculate formation yield ratios of 0.485 ± 0.059 for butanal/(butanal + glyoxal) from *trans*-2-hexenal, 0.448 ± 0.064 for butanal/(butanal + 1-oxoethyl acetate) from *trans*-2-hexenyl acetate, and 0.552 ± 0.094 for formaldehyde/(formaldehyde + 2-oxobutanal) from ethyl vinylketone. These ratios are close to the value of 0.50 that is consistent with a 50:50 split of the 1,2,3-trioxolane adduct, i.e., the experimental data do not indicate preferential formation of one of the two biradicals that are formed in reactions 2a vs. 2b, 3a vs. 3b, and 4a vs. 4b. For 6-methyl-5-hepten-2-one, the yield of acetone (0.28 ± 0.02) suggests preferential formation of the more substituted (and possibly more stable) biradical $(CH_3)_2COO$ i.e., reaction 5b, although no firm conclusion can be reached since the yield of the other primary carbonyl, 4-oxopentanal, could not be measured.

Carbonyl Formation From Biradicals

Several of the carbonyls (other than the primary carbonyls) that are listed in Table II can be accounted for by reactions of the biradicals: propanal and 2-oxobutanal from $CH_3CH_2CH_2CHOO$ (*trans*-2-hexenal and *trans*-2-hexenyl acetate) and formaldehyde and methylglyoxal from $(CH_3)_2COO$ (6-methyl-5-hepten-2-one). The relevant reactions have been described previously for the reaction of ozone with simple alkenes that lead to the same biradicals, i.e., $(CH_3)_2COO$ from 2-methylpropene, 2-methyl-2-butene and 2,3-dimethyl-2-butene [47], and $CH_3CH_2CH_2CHOO$ from 1-pentene [41] and from *trans*-4-octene (unpublished results from this laboratory, 1995). Formaldehyde and propanal may form from $(CH_3)_2COO$ and $CH_3CH_2CH_2CHOO$, respectively, via the biradical → unsaturated hydroperoxide → β-hydroxycarbonyl → α-hydroxyalkyl radical reaction sequence, followed by reaction of the α-hydroxyalkyl radical with O_2 [38,41,47]. This reaction sequence, which is consistent with data for simple alkenes [38,41,47], is assumed to apply to other unsaturated compounds as well. Thus, for $(CH_3)_2COO$:

$$(CH_3)_2COO \longrightarrow CH_2=C(CH_3)OOH \longrightarrow (CH_2OHCOCH_3)^* \qquad (6a)$$

$$(CH_2OHCOCH_3)^* \longrightarrow CH_3CO + CH_2OH \qquad (6b)$$

$$CH_2OH + O_2 \longrightarrow HO_2 + HCHO \qquad (6c)$$

and similarly for $CH_3CH_2CH_2CHOO$:

$$CH_3CH_2CH_2CHOO \longrightarrow CH_3CH_2CH=CH(OOH) \longrightarrow (CH_3CH_2CHOHCHO)^* \qquad (7a)$$

$$(CH_3CH_2CHOHCHO)^* \longrightarrow CH_3CH_2CHOH + HCO \qquad (7b)$$

$$CH_3CH_2CHOH + O_2 \longrightarrow HO_2 + CH_3CH_2CHO \qquad (7c)$$

The formation yields listed in Table II indicate that reaction 6 accounts for about four percent of the ozone-6-methyl-5-hepten-2-one reaction and that reaction 7 accounts for about seven percent of the ozone-*trans*-2-hexenal reaction and for about ten percent of the ozone-*trans*-2-hexenyl acetate reaction (reaction sequence 6, which involves H-atom abstraction in reaction 6a, is not possible for the $CH_3CH_2C(O)CHOO$ biradical from ethylvinyl ketone). Dividing the yield of propanal by the yield of the corresponding primary carbonyl (taken to be also the yield of the $CH_3CH_2CH_2CHOO$ biradical):

$$CH_3CH_2CH_2CHOO \longrightarrow \chi\, CH_3CH_2CHO \qquad (8)$$

gives $\chi = 0.120 \pm 0.016$ for *trans*-2-hexenal and $\chi = 0.175 \pm 0.042$ for *trans*-2-hexenyl acetate, which compare to $\chi = 0.232 \pm 0.046$ for 1-pentene [41] and $\chi = 0.133 \pm 0.006$ for *trans*-4-octene.

Since we were unable to resolve β-hydroxycarbonyls and the corresponding α-dicarbonyls, see Experimental Section, the yield listed in Table II for methylglyoxal from 6-methyl-5-hepten-2-one is in fact the sum of the yields of methyl glyoxal and hydroxyacetone which form from the biradical $(CH_3)_2COO$ via reaction 6a followed by [38,41,47]:

$$(CH_3COCH_2OH)^* \longrightarrow CH_3COCH_2OH \qquad (9a)$$

$$\longrightarrow H_2 + CH_3COCHO \qquad (9b)$$

$$\longrightarrow OH + CH_3COCH_2 \qquad (9c)$$

where the alkyl radical formed in reaction 9c may lead to products that include methyl glyoxal. Similarly, the measured yield for 2-oxobutanal is in fact the sum of the yields of 2-oxobutanal and 2-hydroxybutanal which form from the biradical $CH_3CH_2CH_2CHOO$ via reaction 7a followed by:

$$(CH_3CH_2CHOHCHO)^* \longrightarrow CH_3CH_2CHOHCHO \qquad (10a)$$

$$\longrightarrow H_2 + CH_3CH_2COCHO \qquad (10b)$$

$$\longrightarrow OH + CH_3CH_2CHCHO \qquad (10c)$$

where the alkyl radical formed in reaction 10c may lead to products that include 2-oxobutanal. The yields of 2-oxobutanal from the $CH_3CH_2CH_2CHOO$ biradical in the ozone-*trans*-2-hexenal and ozone-*trans*-2-hexenyl acetate reactions, see Table II, are consistent with that for 2-oxobutanal in the ozone-1-pentene reaction [48].

Other Carbonyl Products

In addition to the unidentified carbonyls listed in Table II, several carbonyls were observed to form in the following experiments: *trans*-2-hexenal: acetaldehyde; *trans*-2-hexenyl acetate: acetaldehyde and glyoxal; ethylvinyl ketone: acetaldehyde. Formation yields for these carbonyls are listed in Table II. These carbonyls may be carbonyl impurities in the starting materials, ozone reaction products of unsaturated oxygenate impurities, actual ozone-unsaturated oxygenate reaction products that form in pathways other than those discussed above, and/or products of the reaction of the unsaturated oxygenate with a small fraction of OH that was not scavenged by cyclohexane.

Atmospheric Implications

A kinetic and product study has been carried out of the gas-phase reaction of ozone with the unsaturated oxygenates *trans*-2-hexenal, *trans*-2-hexenyl acetate, ethylvinyl ketone, and 6-methyl-5-hepten-2-one, which are relevant to biogenic emissions to the atmosphere. Reaction rate constants have been measured, and their magnitude indicates that reaction with ozone is a major removal process for 6-methyl-5-hepten-2-one and, to a lesser extent, for *trans*-2-hexenyl acetate, with atmospheric lifetimes against removal by ozone of about 12 min and 3.5 h, respectively, when $[O_3] = 100$ ppb. Carbonyl products have been identified and their yields measured. Data for carbonyls indicate that the simple reaction mechanism: O_3 + unsaturated oxygenate $\rightarrow$ two carbonyls + two biradicals, which has recently received supportive evidence in the case of alkenes [46–48], appears to apply as well to the unsaturated ester *trans*-2-hexenyl-acetate, the unsaturated aldehyde *trans*-2-hexenal, and the unsaturated ketone ethylvinyl ketone (insufficient data were obtained in the case of 6-methyl-5-hepten-2-one). In turn, carbonyl products of the ozone-unsaturated oxygenate compound reaction are expected to be removed rapidly from the atmosphere by reaction with OH and by photolysis. Unsaturated carbonyls may also lead to unsaturated peroxyacyl nitrates, $RC(O)OONO_2$ [27,30,31,48,49].

As new information becomes available concerning biogenic emissions of unsaturated oxygenates, a topic currently receiving considerable attention [7–24], it will be necessary to continue to assess the fate and persistence of these compounds and of their carbonyl products in the atmosphere.

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