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Carbonyl Products of the Gas-Phase Reaction of Ozone with Simple Alkenes

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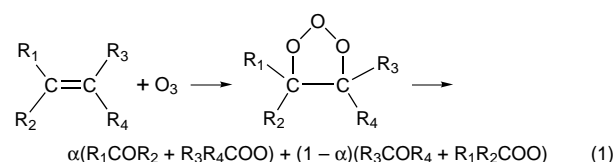
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Carbonyl products have been identified and their yields measured in experiments involving the gas-phase reaction of ozone with eight simple alkenes in purified air. Sufficient cyclohexane was added to scavenge the hydroxyl radical (OH) in order to minimize the reaction of OH with the alkenes and with their carbonyl products. Formation yields of primary carbonyls (carbonyl formed/ozone reacted) were 1.060 ± 0.071 (one standard deviation) for formaldehyde from ethylene, 1.150 ± 0.104 for acetaldehyde from 2-butene (ca. 40% cis and 60% trans isomers), 1.011 ± 0.049 for propanal from *trans*-3-hexene, 1.006 ± 0.049 for acetone from 2,3-dimethyl-2-butene, 0.980 ± 0.036 for formaldehyde + propanal from 1-butene, 0.987 ± 0.020 for acetaldehyde + acetone for 2-methyl-2-butene, 1.300 ± 0.030 for formaldehyde + acetaldehyde from propene, and 1.290 ± 0.103 for formaldehyde + acetone from 2-methylpropene. After correction for the estimated contribution of biradical reactions to formaldehyde, primary carbonyl yields were ca. 1.22 ± 0.03 for acetaldehyde + formaldehyde from propene and 1.08 ± 0.11 for acetone + formaldehyde from 2-methylpropene. These yields are consistent with the value of 1.0 for primary carbonyl yields according to the reaction mechanism: $O_3 + R_1R_2C = CR_3R_4 \rightarrow \alpha(R_1COR_2 + R_3R_4COO) + (1 - \alpha)(R_3COR_4 + R_1R_2COO)$ which, for symmetrical alkenes, reduces to $O_3 + R_1R_2C = CR_1R_2 \rightarrow$ one primary carbonyl ($R_1C(O)R_2$) + one biradical (R_1R_2COO). The results suggest modest preferential formation of the more substituted biradical for 1-butene (CH_3CH_2CHOO vs H_2COO , $\alpha = 0.643 \pm 0.039$), 2-methyl-2-butene [$(CH_3)_2COO$ vs CH_3CHOO , $\alpha = 0.694 \pm 0.024$], 2-methylpropene [$(CH_3)_2COO$ vs H_2COO , estimated $\alpha = 0.68 \pm 0.12$], and perhaps propene (CH_3CHOO vs H_2COO , estimated $\alpha = 0.57 \pm 0.03$). Reaction of the biradicals resulted in the formation of carbonyls and of hydroxycarbonyls and/or dicarbonyls, which together accounted for ca. 0.25, 0.31, and 0.57 of the biradical reactions for CH_3CHOO , CH_3CH_2CHOO , and $(CH_3)_2COO$, respectively. Carbonyls and

hydroxycarbonyls and/or dicarbonyls from propene, 2-methylpropene, 1-butene, and 2-methyl-2-butene were consistent in nature and yields with those that form from the symmetrical alkenes that lead to the same biradicals.

Introduction

The reaction of ozone with alkenes in the gas phase is of critical importance in atmospheric chemistry (1-5). The mechanism of the ozone-alkene reaction in the gas phase has received much attention (1-34) but is still poorly understood. The presently believed mechanism (1-7, 13-23, 27-31) involves electrophilic addition of ozone followed by decomposition of the 1,2,3-trioxolane adduct into two biradicals and two carbonyls, hereafter called "primary" carbonyls:



Major uncertainties in the reaction mechanism include the yields of the primary carbonyls formed in reaction 1 and the subsequent reactions of the corresponding biradicals (1-34). Contributing to these uncertainties in previous studies is the fact that the hydroxyl radical (OH) forms as a product of the ozone-alkene reaction and in high yields ranging from 0.12 for ethylene to 1.0 for 2,3-dimethyl-2-butene (5, 6). The hydroxyl radical reacts with alkenes some 5 orders of magnitude faster than ozone does (4) and also reacts rapidly with the carbonyl products of the ozone-alkene reaction, including the primary carbonyls formed in reaction 1. Therefore, a better understanding of the ozone-alkene reaction mechanism must involve experimental studies carried out under conditions that minimize the interferences that otherwise would result from the reactions of OH with the alkenes and with the carbonyl products of the ozone-alkene reaction.

We have investigated, under experimental conditions relevant to the atmosphere, the gas-phase reaction of ozone with eight alkenes: ethylene, propene, 2-butene (cis + trans), *trans*-3-hexene, 2,3-dimethyl-2-butene, 1-butene, 2-methylpropene and 2-methyl-2-butene. The objective of this study was to identify the major carbonyl reaction products and to measure their yields under conditions that minimize reactions of OH with the alkenes and with the carbonyl products of the ozone-alkene reaction. To this end, the ozone-alkene reaction was studied at room temperature and in 1 atm of air in the presence of sufficient cyclohexane to scavenge the hydroxyl radical.

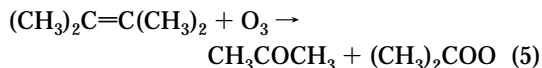
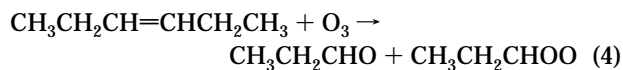
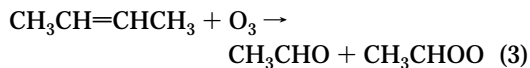
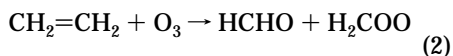
The eight alkenes studied were selected from structural considerations. The four symmetrical alkenes ethylene, 2-butene (cis + trans), *trans*-3-hexene, and 2,3-dimethyl-

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2-butene yield only one primary carbonyl and one biradical:



Therefore, carbonyl data for these alkenes provide information on biradical formation and biradical reactions as a function of the degree of substitution, i.e., H_2COO vs CH_3CHOO vs. $(\text{CH}_3)_2\text{COO}$ in reactions 2, 3, and 5, respectively, and as a function of the nature of the substituent, i.e., $\text{R} = \text{H}$ vs $\text{R} = \text{CH}_3$ vs $\text{R} = \text{C}_2\text{H}_5$ for the biradicals formed in reactions 2, 3–4, respectively.

The other four alkenes studied propene, 1-butene, 2-methylpropene, and 2-methyl-2-butene are structural "intermediates" between those listed above. Thus, propene is expected to yield the two carbonyls and two biradicals that form in reactions 2 and 3, 1-butene to yield those that form in reactions 2 and 4, 2-methylpropene to yield those that form in reactions 2 and 5, and 2-methyl-2-butene to yield those that form in reactions 3 and 5. Of interest in the case of the four alkenes of intermediate structures is the opportunity to examine possible preferential formation of the more substituted biradical, e.g., CH_3CHOO vs H_2COO for propene, $(\text{CH}_3)_2\text{COO}$ vs H_2COO for 2-methylpropene, $\text{CH}_3\text{CH}_2\text{CHOO}$ vs H_2COO for 1-butene, and $(\text{CH}_3)_2\text{COO}$ vs CH_3CHOO for 2-methyl-2-butene.

Five of the alkenes included in this study (ethylene, propene, 2-methylpropene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene) have been studied previously but without scavenging OH (15). We have studied previously, with cyclohexane added to scavenge OH, five of the alkenes that are included in this work: 2-methylpropene, 1-butene, *trans*-2-butene, 2-methyl-2-butene and 2,3-dimethyl-2-butene (15). However, our previous study was carried out in dry air ($\text{RH} = 3\text{--}7\%$), and because of incomplete recovery when sampling carbonyls in dry air using DNPH-coated C_{18} cartridges (35), the measured carbonyl yields were lower than actual yields, especially for formaldehyde. To our knowledge, carbonyl yields for ethylene, propene, and *trans*-3-hexene have not been measured before under conditions that minimize the OH-alkene and OH-carbonyl product reactions.

Information on carbonyl formation yields is important for at least three reasons. First, the mechanism outlined in reaction 1 implies primary carbonyl formation yields of 1.0. Therefore, the mechanism outlined in reaction 1 can be tested against experimental data for formation yields of primary carbonyls, e.g., formaldehyde in the ethylene-ozone reaction, the sum of formaldehyde and propanal in the ozone-1-butene reaction, and so on. Second, the relative abundances of the primary carbonyls provide information on the relative formation yields of the two biradicals. Third, experimental data on carbonyl products other than the primary carbonyls provide clues regarding the subsequent reactions of the biradicals. As noted above, there is considerable uncertainty regarding these three

aspects of the ozone-alkene reaction (1–34), and our objective was to obtain information on carbonyl products that could serve as a probe of the gas-phase ozone-alkene reaction mechanism.

Experimental Methods

Mixtures of alkene and ozone were allowed to react in the dark and under ambient conditions (1 atm of air, room temperature, relative humidity = $55 \pm 10\%$) in the presence of cyclohexane added to scavenge OH. Cyclohexane (Aldrich, stated purity $\geq 99.9\%$) and the alkenes (Aldrich, stated purity 95–99%) were used without further purification; 2-butene was studied as a mixture of ca. 60% *trans* isomer and ca. 40% *cis* isomer. *trans*-3-Hexene contained ca. 4% *trans*-2-hexene as an impurity. Butanal, a primary carbonyl product of the *trans*-2-hexene-ozone reaction, was measured, and its yield ($0.25 \pm 0.06\%$) was used to correct the acetaldehyde yield for the small contribution of *trans*-2-hexene to the production of acetaldehyde in the ozone-*trans*-3-hexene-cyclohexane experiments. The reactions were studied under first-order conditions, with initial ozone concentrations of 45–314 ppb and initial alkene-ozone concentration ratios ≥ 10 . The initial cyclohexane concentration was 400 ppm. From three to five experiments with different initial ozone concentrations and different initial ozone-alkene concentration ratios were carried out for each alkene.

The experiments were carried out in 3.7–3.9 m³ FEP Teflon film chambers covered with black plastic (15, 16). The concentration of ozone was monitored by ultraviolet photometry using a calibrated continuous ozone analyzer. Calibration of the ozone analyzer was carried out according to U.S. Environmental Protection Agency-prescribed procedures. Calibration data (instrument employed in this study vs Ventura County, CA, Air Pollution Control District "transfer standard" instrument) yielded a slope of 1.01 ± 0.01 , $R = 0.999$. The precision of ozone measurements in the range relevant to this study was $\pm 1\text{--}2$ ppb.

Once ozone had been consumed, samples were collected using C_{18} cartridges coated with 2,4-dinitrophenylhydrazine (DNPH), and the carbonyl products were analyzed as their carbonyl-DNPH derivatives by liquid chromatography with UV-visible detection (35–38). Validation aspects of the DNPH-coated C_{18} cartridge/liquid chromatography method have been the object of comprehensive studies (35–38). These studies included all carbonyls identified as reaction products in this work. For these carbonyls, detailed information is available regarding the corresponding carbonyl-DNPH derivatives including retention times, response factors for quantitative analysis, UV-visible absorption spectra recorded with diode array detection, and chemical ionization mass spectra (36, 38). Tests of carbonyl recovery in the cartridge elution step after sampling and tests carried out to verify the absence of breakthrough during sampling have been described (36, 37). For formaldehyde, acetaldehyde, propanal, acetone, glyoxal, methylglyoxal, and cyclohexanone, the average relative standard deviations were 3.0, 3.6, 4.2, 3.7, 4.0, 2.8, and 3.1%, respectively, for replicate analyses and were 5.8, 6.5, 8.7, 11.4, 9.8, 5.8, and 10.4%, respectively, for colocated cartridges (37). In this study, relative standard deviations for a set of three cartridges collected in one of the 2-methyl-2-butene-ozone-cyclohexane experiments were 3.0, 0.5, 1.5, 0.6, 8.4, and 4.7% for formaldehyde, acetaldehyde, acetone, cyclohexanone, glyoxal, and methylglyoxal, re-

TABLE 1

Carbonyl Products of Ozone–Alkene Reaction in Ozone–Alkene–Cyclohexane Experiments: Ethylene, 2-Butene (cis + trans), trans-3-hexene, and 2,3-Dimethyl-2-Butene^a

ozone (ppb) ^b	formaldehyde		Ethylene		glyoxal		cyclohexanone	
	ppb	yield	ppb	yield	ppb	yield	ppb	yield
77	82.4	1.07					0.7	0.0085
124	129.7	1.05	0.55	0.0044			0.7	0.0052
314	307.1	0.98					1.3	0.0041
110	126.5	1.15					1.0	0.0088
av ^c		1.060						0.0067
SD ^c		0.071						0.0023

ozone (ppb)	formaldehyde		2-Butene (cis + trans) acetaldehyde		glyoxal		cyclohexanone	
	ppb	yield	ppb	yield	ppb	yield	ppb	yield
240	36.0	0.15	285.7	1.19	39.2	0.163	11.9	0.049
66	8.5	0.13	83.6	1.27	11.5	0.175	3.7	0.056
114	12.6	0.11	116.3	1.02	17.2	0.151	4.9	0.043
107	14.1	0.13	120.8	1.13	16.1	0.151	4.7	0.044
av		0.126		1.150		0.160		0.048
SD		0.019		0.104		0.011		0.006

ozone (ppb)	acetaldehyde		trans-3-Hexene propanal		methylglyoxal		cyclohexanone	
	ppb	yield	ppb	yield	ppb	yield	ppb	yield
129	21.7	0.168	123.2	0.95	16.8	0.13	13.8	0.107
92	15.7	0.171	92.1	1.00	13.8	0.15	10.3	0.112
219	35.7	0.163	214.2	0.98	30.5	0.14	21.3	0.097
307	51.7	0.168	330.2	1.08	46.1	0.15	33.4	0.109
72	12.6	0.175	75.2	1.04	9.9	0.14	7.7	0.107
av		0.169		1.011		0.141		0.107
SD		0.004		0.049		0.009		0.005

ozone (ppb)	formaldehyde		2,3-Dimethyl-2-butene acetone		methylglyoxal		cyclohexanone	
	ppb	yield	ppb	yield	ppb	yield	ppb	yield
264	79.8	0.30	279.8	1.06	75.2	0.28	37.0	0.14
76	19.9	0.26	73.2	0.96	20.7	0.27	12.5	0.16
100	30.0	0.30	99.6	1.00	29.3	0.29	15.3	0.15
av		0.288		1.006		0.284		0.153
SD		0.023		0.049		0.010		0.012

^a In 1 atm of purified air at ambient temperature and humidity (RH = 55 ± 10%), 400 ppm of cyclohexane added to scavenge OH. ^b Ozone consumed, parts per billion. ^c Av = averaged yield, ppb of carbonyl formed/ppb of ozone reacted; SD = one standard deviation.

spectively, and relative standard deviations for a set of three cartridges collected in one of the 2,3-dimethyl-2-butene–ozone–cyclohexane experiments were 1.4, 3.4, 4.1, and 7.0% for formaldehydes, acetone, cyclohexanone, and methylglyoxal, respectively.

Quantitative analysis involved the use of external standards, i.e., carbonyl-DNPH derivatives synthesized in our laboratory (36). Calibration curves were constructed as described before (36, 38) and were used to measure the carbonyl concentrations in the samples collected in the ozone–alkene–cyclohexane experiments.

Control experiments involved ozone alone in purified air and ozone–cyclohexane mixtures in purified air (no alkene present). The measured loss of ozone in these experiments indicated that cyclohexane contained no ozone-consuming impurities and that loss of ozone to the chamber walls made a negligible contribution to the ozone concentration measured in the ozone–alkene–cyclohexane experiments (16). The loss of carbonyls to the chamber walls was measured for ca. 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–alkene–cyclohexane experiments, made a negligible contribution to the measured carbonyl concentrations. Thus, no correction was applied to the measured carbonyl yields. Samples collected with DNPH-coated C₁₈ cartridges in the control experiments indicated the presence of a small “system peak” with a retention time (relative to that of formaldehyde-DNPH) of 7.20 ± 0.07 and a 430/360 nm absorbance ratio of 0.15. Further analysis by chemical ionization mass spectrometry gave no additional clue regarding this system peak, which was also present in samples collected in the ozone–alkene–cyclohexane experiments.

A limitation of the method employed to measure carbonyls in this study involved β-hydroxycarbonyls, whose reaction with DNPH yielded the derivatives of the corresponding α-dicarbonyls (36). Thus, hydroxyacetaldehyde and glyoxal, hydroxyacetone and methylglyoxal, and 2-hydroxypropanal and methylglyoxal, respectively, could not

TABLE 2

Carbonyl Products of Ozone–Alkene Reaction in Ozone–Alkene–Cyclohexane Experiments: Propene, 1-Butene, 2-Methylpropene, and 2-Methyl-2-butene^a

ozone (ppb) ^b	formaldehyde		Propene acetaldehyde		glyoxal		cyclohexanone	
	ppb	yield	ppb	yield	ppb	yield	ppb	yield
96	75.1	0.78	49.7	0.52	8.4	0.087	1.6	0.016
45	34.4	0.77	25.0	0.56	3.9	0.087	1.6	0.035
213	170.6	0.80	109.2	0.51	15.7	0.074	5.0	0.024
88	68.0	0.77	43.5	0.49	7.4	0.085	1.9	0.022
av ^c		0.780		0.520		0.083		0.024
SD ^c		0.015		0.026		0.006		0.008

ozone (ppb)	formaldehyde		acetaldehyde		1-Butene propanal		methylglyoxal		cyclohexanone	
	ppb	yield	ppb	yield	ppb	yield	ppb	yield	ppb	yield
211	127.6	0.60	27.0	0.13	76.2	0.36	6.1	0.029	4.6	0.022
62	38.6	0.62	7.9	0.13	20.4	0.33	2.2	0.035	1.4	0.022
92	61.1	0.66	11.7	0.13	32.8	0.36	2.7	0.030	2.0	0.022
av		0.630		0.128		0.350		0.031		0.022
SD		0.031		0.001		0.018		0.003		0.000

ozone (ppb)	formaldehyde		2-Methylpropene acetone		methylglyoxal		cyclohexanone	
	ppb	yield	ppb	yield	ppb	yield	ppb	yield
291	265.9	0.91	105.9	0.36	58.0	0.20	16.3	0.056
137	119.5	0.87	42.2	0.31	27.3	0.20	9.0	0.066
253	268.0	1.06	90.8	0.36	43.6	0.17	14.3	0.056
av		0.950		0.340		0.190		0.059
SD		0.098		0.031		0.016		0.006

ozone (ppb)	formaldehyde		acetaldehyde		2-Methyl-2-butene acetone		glyoxal		methylglyoxal		cyclohexanone	
	ppb	yield	ppb	yield	ppb	yield	ppb	yield	ppb	yield	ppb	yield
201	49.6 (d)	0.25	137.6	0.68	61.9	0.31	10.9	0.054	49.9	0.25	25.1	0.125
154	36.2	0.23	102.6	0.67	46.1	0.30	10.1	0.066	37.8	0.25	15.8	0.10
146	37.5	0.26	102.8	0.70	43.5	0.30	8.8	0.060	35.8	0.24	16.2	0.11
av		0.246		0.685		0.302		0.060		0.246		0.013
SD		0.020		0.019		0.006		0.006		0.002		0.011

^a In 1 atm of purified air at ambient temperature and humidity (RH = 55 ± 10%), 400 ppm of cyclohexane added to scavenge OH. ^b Ozone consumed, parts per billion. ^c Av = average yield, ppb of carbonyl formed/ppb of ozone reacted; SD = one standard deviation. ^d Carbonyl concentrations for this experiment are the averages of data for three samples.

be resolved when both formed as reaction products from the same alkene.

At the ozone, alkene, and cyclohexane concentrations employed in this study, most (ca. 99%) of the hydroxyl radical formed as a product of the ozone–alkene reaction was scavenged by cyclohexane, leading to cyclohexanone (5, 6, 15), which we measured in all experiments. Under these conditions, the reaction of OH with alkenes and the reaction of OH with carbonyl products of the alkene–ozone reaction that react rapidly with OH, e.g., aldehydes, made negligible contributions to the observed carbonyl product distribution.

Results and Discussion

Carbonyl Products and Their Yields. Initial ozone concentrations and carbonyl product concentrations are listed in Table 1 for the four symmetrical alkenes [ethylene, 2-butene (cis + trans), *trans*-3-hexene, and 2,3-dimethyl-2-butene] and in Table 2 for the four alkenes of intermediate structures [propene, 1-butene, 2-methylpropene, and 2-methyl-2-butene].

Also listed in Tables 1 and 2 are the carbonyl formation yields, calculated as carbonyl formed (ppb)/reacted ozone

(ppb) and assuming a 1:1 stoichiometry for the alkene–ozone reaction. This assumption regarding the reaction stoichiometry appears reasonable under the conditions of this study, i.e., with initial alkene/ozone concentration ratios ≥ 10 and with sufficient cyclohexane added to scavenge OH. Examples of scatter plots of carbonyl concentration (ppb) vs reacted ozone (ppb) are given in Figure 1 for formaldehyde and acetaldehyde in the propene–ozone–cyclohexane experiments and for propanal and acetaldehyde in the *trans*-3-hexene–ozone–cyclohexane experiments. Tables 1 and 2 also include the concentrations and yields of cyclohexanone, which was observed to form from the eight alkenes studied, thus providing experimental evidence that the hydroxyl radical was formed as a reaction product.

Symmetrical Alkenes. Carbonyls identified as reaction products included formaldehyde from ethylene (glyoxal and/or hydroxyacetaldehyde was observed in one of the four experiments at the detection limit of 0.55 ppb, corresponding to a small yield of 0.44%), formaldehyde, acetaldehyde, and glyoxal and/or hydroxyacetaldehyde from 2-butene (cis + trans); propanal, acetaldehyde, and methylglyoxal and/or 2-hydroxypropanal from *trans*-3-

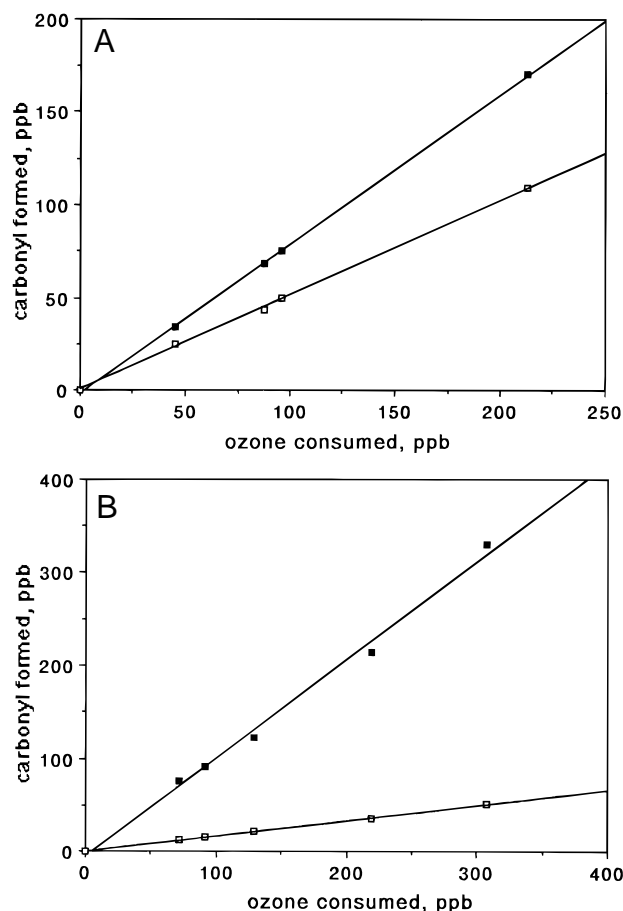


FIGURE 1. Carbonyl concentrations (ppb) versus ozone reacted (ppb) in ozone-alkene-cyclohexane experiments. (A) Formaldehyde (■) and acetaldehyde (□) from propene. (B) Propanal (■) and acetaldehyde (□) from *trans*-3-hexene.

hexene; and acetone, formaldehyde, and methylglyoxal and/or hydroxyacetone from 2, 3-dimethyl-2-butene.

Unidentified carbonyls observed to form in the ozone-symmetrical alkene experiments included one each for 2-butene, *trans*-3-hexene, and 2,3-dimethyl-2-butene (none was observed from ethylene). These unidentified carbonyls were minor products; the ratios of the peak heights of their DNPH derivatives to that of formaldehyde-DNPH were 0.13 ± 0.02 , 0.13 ± 0.04 , and 0.05 ± 0.01 in the experiments with 2-butene, *trans*-3-hexene and 2,3-dimethyl-2-butene, respectively. Retention times, absorption characteristics, and other parameters for the DNPH derivatives of these unidentified carbonyls are listed in Table 3. These parameters may be useful for the identification of the carbonyls in future work by use of relationships between carbonyl structure and carbonyl-DNPH retention and UV-visible absorption parameters (36, 38).

Yields of primary carbonyls for symmetrical alkenes were 1.060 ± 0.071 (one standard deviation) for formaldehyde from ethylene, 1.150 ± 0.104 for acetaldehyde from 2-butene (cis + trans), 1.011 ± 0.049 for propanal from *trans*-3-hexene, and 1.006 ± 0.049 for acetone from 2, 3-dimethyl-2-butene. As is shown in Figure 2, these yields are close to the value of 1.0, which is consistent with reactions 2-5 and with the simple overall reaction mechanism summarized by the following: symmetrical alkene + ozone \rightarrow 1.0 carbonyl + 1.0 biradical.

Carbonyl Products from Subsequent Reactions of Biradicals in the Reaction of Ozone with Symmetrical

TABLE 3

Summary of Data for Unidentified Carbonyls

alkene	retention time ^a	peak height ^a	carbonyl-DNPH derivatives	
			430/360 nm absorbance ratio ^b	comments
ethylene				
2-butene (cis + trans) ^e	0.85	0.132	0.21	c
<i>trans</i> -3-hexene	6.13	0.131	1.20	d
2,3-dimethyl-2-butene ^e	0.88	0.05	0.32	c
propene				
1-butene ^e				
2-methylpropene ^e	0.78	0.02	0.23	c
2-methyl-2-butene ^e	0.88	0.03	0.25	c
	6.43	0.03	1.00	d

^a Relative to that of formaldehyde-DNPH. ^b This ratio is used as a diagnostic test for DNPH derivatives of monofunctional carbonyls vs those of dicarbonyls (36). ^c Possible DNPH derivative of hydroxycarbonyl based on retention time and absorbance ratio. ^d Possible DNPH derivative of dicarbonyls based on 430/360 nm absorbance ratio. ^e Unidentified carbonyls for these alkenes are consistent with those previously observed to form in alkene-ozone-cyclohexane experiments in dry air (15).

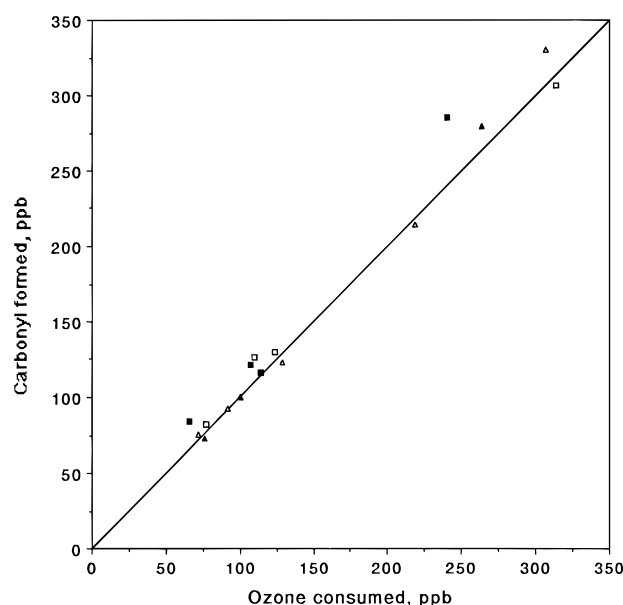
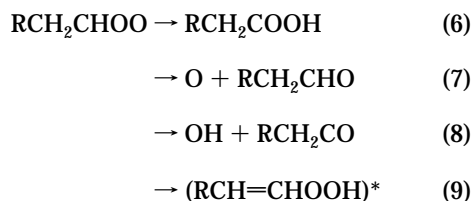


FIGURE 2. Scatter plot of primary carbonyl concentrations (ppb) versus ozone reacted (ppb) in alkene-ozone-cyclohexane experiments in humid air (RH = $55 \pm 10\%$). The line shown is the 1:1 line. Symbols: (□) formaldehyde from ethylene, (■) acetaldehyde from 2-butene (cis + trans), (Δ) propanal from *trans*-3-hexene, and (▲) acetone from 2,3-dimethyl-2-butene.

Alkenes. In addition to the primary carbonyls listed above, other carbonyls were observed to form from symmetrical alkenes as follows: ethylene: none; 2-butene (cis + trans): formaldehyde and glyoxal and/or hydroxyacetaldehyde; *trans*-3-hexene: acetaldehyde and methylglyoxal and/or 2-hydroxypropanal; 2,3-dimethyl-2-butene: formaldehyde and methylglyoxal and/or hydroxyacetone. These carbonyls are formed from the biradicals CH_3CHOO (2-butene), $\text{CH}_3\text{CH}_2\text{CHOO}$ (*trans*-3-hexene), and $(\text{CH}_3)_2\text{COO}$ (2,3-dimethyl-2-butene) as shown below.

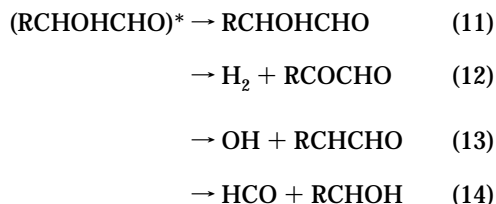
Reactions of the biradicals CH_3CHOO , $\text{CH}_3\text{CH}_2\text{CHOO}$, and $(\text{CH}_3)_2\text{COO}$ have been discussed before (1-34) and may include rearrangement to a carboxylic acid or ester, O-atom elimination, formation of $\text{OH} + \text{RCO}$, and formation of an unsaturated peroxide (15, 27-31):



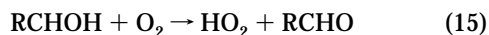
The unsaturated peroxide formed in reaction 9 leads to a hydroxycarbonyl:



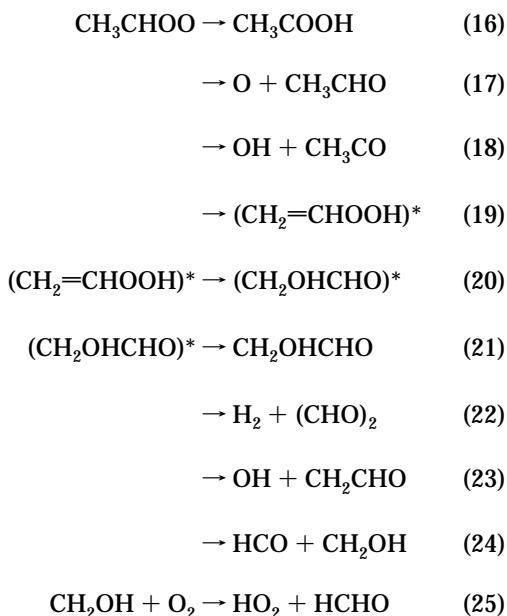
followed by the four pathways of stabilization, formation of H_2 + a dicarbonyl, formation of OH + a RCHCHO radical, and carbon-carbon bond scission leading to HCO + an α -hydroxyalkyl radical (15, 27–31):



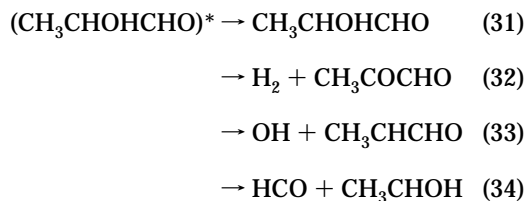
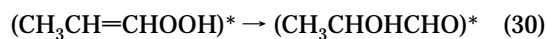
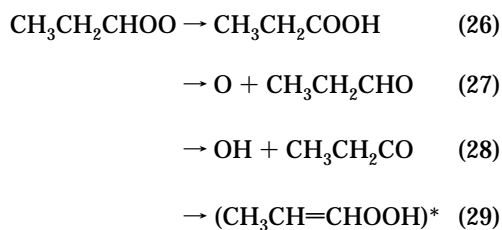
Under the conditions of our study, the α -hydroxyalkyl radical formed in reaction 14 reacts with oxygen by H-atom abstraction (3, 4):



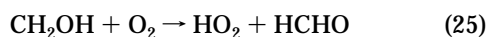
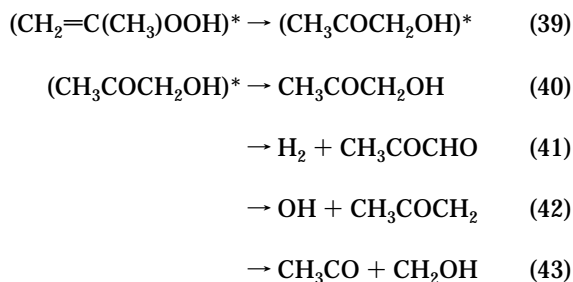
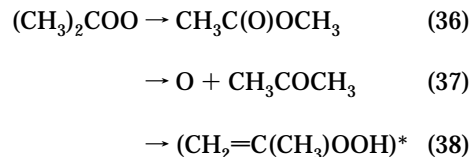
Reactions 6–15 are shown below for the methyl-substituted biradical CH_3CHOO :



Similarly for the ethyl-substituted biradical $\text{CH}_3\text{CH}_2\text{CHOO}$:



And, for the dimethyl-substituted biradical $(\text{CH}_3)_2\text{COO}$:



Carbonyls (other than primary carbonyls) measured in this study are consistent with three reaction sequences:

- (a) biradical \rightarrow (peroxide)* \rightarrow (hydroxycarbonyl)* \rightarrow carbon-carbon bond scission \rightarrow carbonyl + HO_2 (reactions 9, 10, 14, and 15)
- (b) biradical \rightarrow (peroxide)* \rightarrow hydroxycarbonyl (reactions 9, 10, and 11)
- (c) biradical \rightarrow (peroxide)* \rightarrow H_2 + dicarbonyl (reactions 9, 10, and 12)

Reaction sequence a is an important pathway for the biradicals CH_3CHOO , $\text{CH}_3\text{CH}_2\text{CHOO}$, and $(\text{CH}_3)_2\text{COO}$ with yields of 0.126 ± 0.019 for formaldehyde from 2-butene (reactions 19, 20, 24, and 25), 0.169 ± 0.004 for acetaldehyde from *trans*-3-hexene (reactions 29, 30, 34, and 35) and 0.288 ± 0.023 for formaldehyde from 2,3-dimethyl-2-butene (reactions 38, 39, 43, and 25). The apparent increase in carbonyl yield for $\text{CH}_3\text{CH}_2\text{CHOO}$ as compared to CH_3CHOO may reflect the fact that H-atom abstraction involves secondary C–H bonds in reaction 29 versus primary C–H bonds in reaction 19.

Since we could not resolve the hydroxycarbonyl formed in reaction 11 and the dicarbonyl formed in reaction 12 (hydroxyacetaldehyde and glyoxal from 2-butene, reactions 21 and 22; 2-hydroxypropanal and methylglyoxal from *trans*-3-hexene, reactions 31 and 32; and hydroxyacetone and methylglyoxal from 2,3-dimethyl-2-butene, reactions 40 and 41), we could not assess the relative importance of the two reaction sequences (b and c). These two sequences, taken together, were comparable in magnitude to reaction sequence a with hydroxycarbonyl and/or dicarbonyl yields

TABLE 4

Summary of Carbonyl Yields for Primary Carbonyls and for Products of Biradical Reactions in Alkene—Ozone—Cyclohexane Experiments

alkene	primary carbonyls ^a		biradical	biradical reactions					
	carbonyl	yield		decomposition ^b		dicarbonyl + hydroxycarbonyl ^c		carboxylic acid ^d	
				carbonyl	yield	carbonyl	yield	acid	yield ^d
ethylene	HCHO	1.06	H ₂ COO	none		none ^e		formic	0.16 ^f
2-butene (cis + trans)	CH ₃ CHO	1.15	CH ₃ CHOO	HCHO	0.13	glyoxal + hydroxy-acetaldehyde (G + HA)	0.16	acetic	0.10 ^g
<i>trans</i> -3-hexene	CH ₃ CH ₂ CHO	1.01	CH ₃ CH ₂ CHOO	CH ₃ CHO	0.17	methylglyoxal + 2-hydroxypropanal (MEG + 2HP)	0.14	propionic	<i>h</i>
2,3-dimethyl-2-butene	CH ₃ COCH ₃	1.01	(CH ₃) ₂ COO	HCHO	0.28	methylglyoxal + hydroxyacetone (MEG + HAC)	0.28	none	
propene	HCHO	0.70 ⁱ	CH ₃ CHOO	HCHO	0.11 ⁱ	G + HA	0.08	acetic	0.10 ^f
	CH ₃ CHO	0.52	H ₂ COO	none		none		formic	0.16 ^f
		1.22							
1-butene	HCHO	0.63	CH ₃ CH ₂ CHOO	CH ₃ CHO	0.13	MEG + 2HP	0.03	propionic	<i>h</i>
	CH ₃ CH ₂ CHO	0.35	H ₂ COO	none		none		formic	0.16
		0.98							
2-methylpropene	HCHO	0.74 ⁱ	(CH ₃) ₂ COO	HCHO	0.29 ⁱ	MEG + HAC	0.19	none	
	CH ₃ COCH ₃	0.34	H ₂ COO	none		none		formic	0.16
		1.08							
2-methyl-2-butene	CH ₃ COCH ₃	0.30	CH ₃ CHOO	HCHO	0.25	G + HA	0.06	acetic	0.06
	CH ₃ CHO	0.68	(CH ₃) ₂ COO	HCHO		MEG + HAC	0.25	none	
		0.98							

^a Those formed in reaction 1 along with the two biradicals. Standard deviations on yields are omitted for clarity and are given in Tables 1 and 2. ^b Decomposition denotes the biradical → hydroperoxide → hydroxycarbonyl → carbon-carbon bond scission → α-hydroxyalkyl radical → carbonyl sequence, see text. Standard deviations on yields are omitted for clarity and are given in Tables 1 and 2. ^c Sum of two pathways, see text. For clarity, yields have been rounded off, and standard deviations have been omitted, see Tables 1 and 2. ^d From ref 15, measured under similar experimental conditions but in dry air (RH = 3–7%) instead of humid air (this study, RH = 55%). Carboxylic acid yields have not been measured in humid air. ^e Glyoxal was observed at the detection limit corresponding to a small yield of 0.0044 in one experiment. ^f Not measured, estimated from data for other alkenes studied in ref 15 and that lead to the H₂COO biradical. ^g From *trans*-2-butene. ^h Yield not measured. ⁱ Estimated, see text. Formaldehyde forms as a primary carbonyl and in reactions of the CH₃CHOO and (CH₃)₂COO biradicals.

of 0.160 ± 0.011 for 2-butene (CH₃CHOO), 0.141 ± 0.009 for *trans*-3-hexene (CH₃CH₂CHOO), and 0.284 ± 0.010 for 2,3-dimethyl-2-butene [(CH₃)₂COO], see Table 4.

The data in Table 4 also indicate that carbonyl products (including hydroxycarbonyls and/or dicarbonyls) account for a significant fraction of the total biradical reactions, i.e., 0.249 ± 0.035 for CH₃CHOO, 0.306 ± 0.020 for CH₃CH₂CHOO and 0.568 ± 0.044 for (CH₃)₂COO. Carbonyl yields for the two monosubstituted biradicals CH₃CHOO and CH₃CH₂CHOO were lower than those for the disubstituted biradical (CH₃)₂COO. The possible relation between carbonyl yields and the degree of substitution of the biradical has been noted before (15) and will be examined further in future work.

Three additional observations can be drawn from the experimental data. First, the yields of the primary carbonyls were close to 1.0 for the four symmetrical alkenes studied. This implies that the formation of these carbonyls via the biradical → O-atom elimination pathway (reactions 7, 17, 27, and 37) is of minor importance, consistent with results from earlier studies carried out with and without scavenging OH (7, 27–29). Second, the radicals RCO formed in reaction 8 are expected to react with oxygen to form RCO₃ radicals (3, 4). While further reactions of the RCO₃ radicals may lead to products that include dicarbonyls, our data for biacetyl from 2-butene (none detected, yield <0.007) and for 3,4-hexanedione from *trans*-3-hexene (none detected, estimated yield ≤0.010) indicate that RCO radical reactions make a negligible contribution to dicarbonyl formation under the conditions of our study. Third, the HO₂ radical forms in reaction 24 followed by HCO + O₂ → HO₂ + CO and reaction 25 from 2-butene, in reaction 34 followed by HCO + O₂ → HO₂ + CO and reaction 35 from *trans*-3-hexene, and in reaction 25 from 2,3-dimethyl-2-butene.

Using the measured yields of formaldehyde and acetaldehyde, estimated HO₂ yields for these reactions are ca. 0.25 for the CH₃CHOO biradical (2-butene), 0.34 for the CH₃CH₂CHOO biradical (*trans*-3-hexene), and 0.29 for the (CH₃)₂COO biradical (2,3-dimethyl-2-butene).

Alkenes of Intermediate Structures. Of the four alkenes with intermediate structures, two (1-butene and 2-methyl-2-butene) lead to biradicals whose decomposition give carbonyls that are different from the primary carbonyls. These two alkenes will be discussed first. The other two alkenes (propene and 2-methylpropene) lead to biradicals whose decomposition lead to a carbonyl (formaldehyde) which is also formed as a primary carbonyl. For propene and 2-methylpropene, the sum of the primary carbonyl yields will be calculated by estimating the contribution of biradical reactions to the total measured formaldehyde. These two alkenes will be discussed last.

1-Butene and 2-Methyl-2-butene. Carbonyl products of the 1-butene–ozone reaction included formaldehyde, acetaldehyde, propanal, and methylglyoxal. Those of the 2-methyl-2-butene–ozone reaction included formaldehyde, acetaldehyde, acetone, glyoxal, and methylglyoxal. Two unidentified carbonyls formed as minor products in the 2-methyl-2-butene experiments, see Table 3; none was observed from 1-butene. The yields of the primary carbonyls were 0.980 ± 0.036 for formaldehyde + propanal from 1-butene and 0.987 ± 0.020 for acetaldehyde + acetone from 2-methyl-2-butene. As is shown in Figure 3, these yields are consistent with the reaction mechanism summarized by reaction 1.

Primary carbonyl yields for 1-butene and for 2-methyl-2-butene appear to be consistent with modest preferential formation of the more substituted biradical. Substituting α and (1 – α) in reaction 1 by the measured primary carbonyl

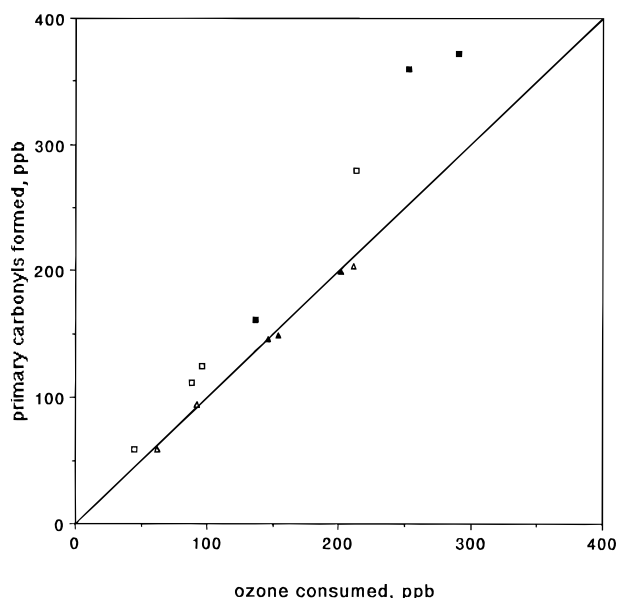
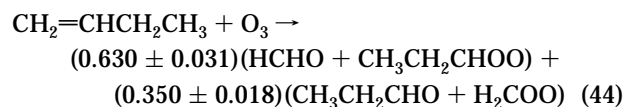
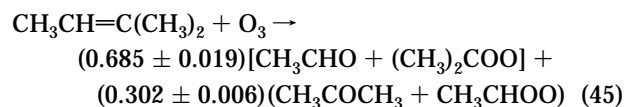


FIGURE 3. Scatter plot of primary carbonyl concentrations (ppb) versus ozone reacted (ppb) in alkene-ozone-cyclohexane experiments in humid air ($RH = 55 \pm 10\%$). The line shown is the 1:1 line. Symbols: (\square) for formaldehyde + acetaldehyde from propene, (\blacksquare) for formaldehyde + acetone from 2-methylpropene, (\triangle) for formaldehyde + propanal from 1-butene, and (\blacktriangle) for acetaldehyde + acetone from 2-methyl-2-butene. Data for propene and for 2-methylpropene are not corrected for the estimated contribution of the biradicals CH_3CHOO (propene) and $(\text{CH}_3)_2\text{COO}$ (methylpropene) to the measured formaldehyde concentrations, see text.

yields listed in Table 2 yields the following equation for 1-butene:



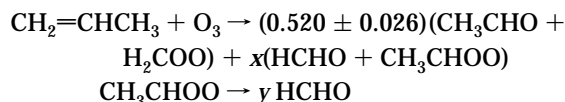
and similar for 2-methyl-2-butene:



Other carbonyl products of 1-butene and 2-methyl-2-butene and the formation yields of these carbonyls were consistent with those measured for their symmetrical structural homologues, i.e., ethylene and *trans*-3-hexene for 1-butene and 2-butene and 2,3-dimethyl-2-butene for 2-methyl-2-butene. For 1-butene, the two carbonyls acetaldehyde and methylglyoxal and/or 2-hydroxypropanal form from the biradical $\text{CH}_3\text{CH}_2\text{CHOO}$ as described above for *trans*-3-hexene. The measured yield of acetaldehyde, 0.128 ± 0.001 , compares to a value of 0.105 ± 0.006 calculated using the measured yield of acetaldehyde from *trans*-3-hexene and the fractional coefficient given in eq 44. For 2-methyl-2-butene, glyoxal forms from CH_3CHOO as described above for 2-butene; methylglyoxal and/or hydroxyacetone form from $(\text{CH}_3)_2\text{COO}$ as described above for 2,3-dimethyl-2-butene; and formaldehyde forms from both CH_3CHOO and $(\text{CH}_3)_2\text{COO}$. The measured yield for formaldehyde, 0.196 ± 0.010 , compares to a value of 0.208 ± 0.027 calculated using the measured yields of formaldehyde from CH_3CHOO (2-butene) and from $(\text{CH}_3)_2\text{CHOO}$ (2,3-dimethyl-2-butene) and the two fractional coefficients given in eq 45.

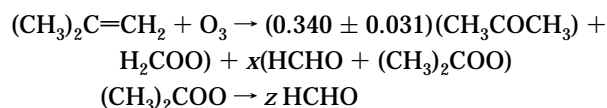
Propene and 2-Methylpropene. Carbonyl products of the propene-ozone reaction included formaldehyde, acetaldehyde, and glyoxal; those of the 2-methylpropene-ozone reaction included formaldehyde, acetone, and methylglyoxal. One unidentified carbonyl formed as a minor product from 2-methylpropene, see Table 3; none was observed from propene. Biacetyl was not observed to form from propene (yield <0.008), consistent with data for 2-butene as discussed above.

Apparent yields of primary carbonyls for propene and for 2-methylpropene were higher than those for the other six alkenes studied, i.e., 1.300 ± 0.030 for formaldehyde + acetaldehyde from propene and 1.290 ± 0.103 for formaldehyde + acetone from 2-methylpropene, see Figure 3. This is because formaldehyde forms not only as a primary carbonyl but also as a product of the biradicals CH_3CHOO (propene) and $(\text{CH}_3)_2\text{COO}$ (2-methylpropene). The contribution of biradical reactions to the measured formaldehyde yields can be estimated by comparison with data for the relevant symmetrical alkenes, i.e., 2-butene (CH_3CHOO) and 2,3-dimethyl-2-butene [$(\text{CH}_3)_2\text{COO}$]. Thus, for propene:



Matching formaldehyde data for propene and for 2-butene, for which $1.0\text{CH}_3\text{CHOO} \rightarrow (0.110 \pm 0.019) \text{HCHO}$, gives $x = 0.70 \pm 0.02$, from which the estimated sum of the primary carbonyls yields is 1.22 ± 0.03 and $\alpha = 0.57 \pm 0.03$ (matching glyoxal data for propene and 2-butene would lead to similar estimates, i.e., $x = 0.60$, sum of primary carbonyl yields = 1.12 and $\alpha = 0.54$).

Similarly for 2-methylpropene:



Matching formaldehyde data for 2-methylpropene and 2,3-dimethyl-2-butene, for which $1.0(\text{CH}_3)_2\text{COO} \rightarrow (0.286 \pm 0.027) \text{HCHO}$, gives $x = 0.74 \pm 0.10$, from which the sum of the primary carbonyl yields is 1.08 ± 0.11 and $\alpha = 0.68 \pm 0.12$ (matching methylglyoxal data for 2-methylpropene and 2,3-dimethyl-2-butene would lead to comparable estimates, i.e., $x = 0.67$, sum of primary carbonyl yields = 1.01 and $\alpha = 0.66$).

The above calculations lead to estimated sums of the primary carbonyl yields that are consistent with data for the other six alkenes studied, i.e., 1.22 ± 0.03 for propene and 1.08 ± 0.11 for 2-methylpropene. These calculations indicate modest preferential formation of the more substituted biradical for 2-methylpropene, $\alpha = (0.68 \pm 0.12)$ for $(\text{CH}_3)_2\text{COO}$ vs H_2COO , consistent with data for 1-butene and for 2-methyl-2-butene as discussed earlier, and perhaps also for propene, $\alpha = 0.57 \pm 0.03$ for CH_3CHOO vs H_2COO .

Other Minor Carbonyl Products. In addition to the minor unidentified carbonyls listed in Table 3, the carbonyls acetaldehyde and glyoxal were measured in low yields in experiments involving two of the eight alkenes studied: 1-butene [glyoxal, yield = $(0.87 \pm 0.14) \times 10^{-2}$] and 2-methylpropene [acetaldehyde, yield = $(2.0 \pm 0.7) \times 10^{-2}$; glyoxal, yield = $(0.56 \pm 0.10) \times 10^{-2}$]. Acetaldehyde and glyoxal in the experiments with these two alkenes may be

carbonyl impurities, ozone-alkene reaction products of alkene impurities, actual reaction products via pathways other than those discussed above, and/or products of the alkene reaction with a small fraction of OH that was not scavenged by cyclohexane.

Concluding Comments. The results obtained in this study provide useful information regarding the mechanism of the gas phase reaction of ozone with alkenes under conditions relevant to the atmosphere. For the eight alkenes studied under conditions that minimize the reaction of OH with alkenes and with the ozone-alkene carbonyl products, the sums of the formation yields of the primary carbonyls were close to the value of 1.0, which is consistent with the simple mechanism: $\text{ozone} + \text{alkene} \rightarrow 2 \text{ carbonyls} + 2 \text{ biradicals}$ (or $1 \text{ carbonyl} + 1 \text{ biradical}$ for the symmetrical alkenes).

Data for the symmetrical alkenes provided information on biradical reactions that lead to carbonyls (reaction sequence a) and to dicarbonyls and/or hydroxycarbonyls (reaction sequences b and c). Reaction sequence a leads to formaldehyde from CH_3CHOO (yield = 0.110 ± 0.019), acetaldehyde from $\text{CH}_3\text{CH}_2\text{CHOO}$ (yield = 0.167 ± 0.004), and formaldehyde from $(\text{CH}_3)_2\text{COO}$ (yield = 0.286 ± 0.027). Yields of dicarbonyls and/or hydroxycarbonyls [0.139 ± 0.016 for CH_3CHOO , (0.139 ± 0.011) for $\text{CH}_3\text{CH}_2\text{CHOO}$, and (0.282 ± 0.017) for $(\text{CH}_3)_2\text{COO}$] from reaction sequences b and c were comparable in magnitude to those for carbonyls from reaction sequence a. All together, carbonyl products accounted for ca. 0, 25, 31, and 57% of the reactions involving the biradicals H_2COO , CH_3CHOO , $\text{CH}_3\text{CH}_2\text{CHOO}$, and $(\text{CH}_3)_2\text{COO}$, respectively (Table 4).

Carbonyls accounted for ca. 0.16–0.45 of the biradical reactions for the four alkenes that lead to two of the biradicals listed above (Table 4). Measured carbonyl yields were consistent with modest preferential formation of the more substituted biradical for 1-butene, 2-methyl-2-butene, 2-methylpropene, and perhaps propene.

Adding the yields of carboxylic acids ($\text{RCHOO} \rightarrow \text{RC(O)OH}$) measured in previous work (15), see Table 4, results in an additional 6–10% (acetic acid) and 16% (formic acid) of the biradical reactions being accounted for in the case of those alkenes that lead to H_2COO and CH_3CHOO biradicals (Table 4). The information presented in this work contributes to a better understanding of the ozone-alkene reaction and may serve as input to computer kinetic models that attempt to describe urban and regional atmospheric photochemistry (1, 3).

Acknowledgments

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