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Rate Constants for the Gas-Phase Reactions of OH Radicals with a Series of Hydroxyaldehydes at 296 ± 2 K

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Using a relative rate method with in situ generation of the hydroxyaldehydes, rate constants for the reactions of the OH radical with 2-hydroxybutanal [$CH_3CH_2CH(OH)CHO$], 3-hydroxybutanal [$CH_3CH(OH)CH_2CHO$], 2-hydroxypropanal [$CH_3CH(OH)CHO$], 2-hydroxy-2-methylpropanal [$(CH_3)_2C(OH)CHO$], and 3-hydroxypropanal [$HOCH_2CH_2CHO$] have been measured at atmospheric pressure and 296 ± 2 K. The hydroxyaldehydes were generated in situ from the OH radical-initiated reactions of precursor compounds (1,2- and 1,3-butanediol, 2-methyl-2,4-pentanediol, 2-methyl-3-buten-2-ol, and *cis*-3-hexen-1-ol) and the rate constants for the reaction of OH radicals with the hydroxyaldehydes were determined relative to those for reaction of OH radicals with the precursor compound. The rate constants obtained (in units of 10^{-11} cm^3 molecule^{-1} s^{-1}) were $CH_3CH_2CH(OH)CHO$, 2.37 ± 0.23; $CH_3CH(OH)CH_2CHO$, 2.95 ± 0.24; $CH_3CH(OH)CHO$, 1.70 ± 0.20; $(CH_3)_2C(OH)CHO$, 1.40 ± 0.25; and $HOCH_2CH_2CHO$, 1.99 ± 0.29.

Introduction

The atmospheric photooxidations of volatile organic compounds (VOCs) lead to the formation of organic nitrates and oxygenated products.[1] Among these oxygenated products, hydroxycarbonyls are formed from the OH radical-initiated reactions of alkanes,[1−4] diols,[5] and certain oxygenated VOCs, including some unsaturated aldehydes (for example, acrolein[6,7] and methacrolein[8,9]) and biogenically emitted oxygenates (for example, 2-methyl-3-buten-2-ol[10−13] and *cis*-3-hexen-1-ol[13,14]). Glycolaldehyde [$HOCH_2CHO$] appears to be the only commercially available hydroxyaldehyde, and hydroxyaldehydes do not appear to elute from gas chromatographic columns without prior derivatization.[2,4,5,11−14] It is, hence, not surprising that the only hydroxyaldehyde which has been the subject of kinetic and product studies is glycolaldehyde.[15−17]

In this work, we have generated a series of hydroxyaldehydes in situ from the OH radical-initiated reactions of their parent diols or unsaturated alcohols (referred to hereafter as alcohols) and determined their OH radical reaction rate constants by monitoring the hydroxyaldehyde concentrations during these experiments. Previous studies have shown that the OH radical-initiated reactions of 1,2-butanediol, 1,3-butanediol, 2-methyl-2,4-pentanediol, 2-methyl-3-buten-2-ol, and *cis*-3-hexen-1-ol lead to the formation of the following carbonyl-containing products: $CH_3CH_2C(O)CH_2OH$ (66%), $CH_3CH_2CH(OH)CHO$ (∼27%), and $HOCH_2CHO$ (10%) from 1,2-butanediol;[5,18] $CH_3C(O)CH_2CH_2OH$ (50%), $CH_3CH(OH)CH_2CHO$ (∼15%), $CH_3CH(OH)CHO$ (∼0.7%), and $HOCH_2CHO$ (10%) from 1,3-butanediol;[5,18] $(CH_3)_2C(OH)CH_2C(O)CH_3$ (47%) and $CH_3CH(OH)CHO$ (∼24%) from 2-methyl-2,4-pentanediol;[5,18] $(CH_3)_2C(OH)CHO$ (∼31%), HCHO (29−35%), $HOCH_2CHO$ (50−61%), and $CH_3C(O)CH_3$ (52−58%) from 2-methyl-3-buten-2-ol;[10,11,13] and CH_3CH_2CHO (75%) and $HOCH_2CH_2CHO$ (∼101%) from *cis*-3-hexen-1-ol,[13,14] where the reported yields are in parentheses. In this work, we have used Solid-Phase Micro Extraction (SPME) with on-fiber derivatization of carbonyl-containing compounds[5,13,18] to monitor the concentrations of the above carbonyl compounds during the OH radical-initiated reactions of 1,2- and 1,3-butanediol, 2-methyl-2,4-pentanediol, 2-methyl-3-buten-2-ol, and *cis*-3-hexene-1-ol. This has allowed us to determine rate constants for the reactions of OH radicals with the hydroxyaldehdyes $CH_3CH_2CH(OH)CHO$, $HOCH_2CHO$, $CH_3CH(OH)CH_2CHO$, $CH_3CH(OH)CHO$, $(CH_3)_2C(OH)CHO$, and $HOCH_2CH_2CHO$.

Experimental Section

For the reactions,

$$\text{OH} + \text{alcohol} \rightarrow \alpha\ \text{hydroxycarbonyl} \qquad (1)$$

$$\text{OH} + \text{hydroxycarbonyl} \rightarrow \text{products} \qquad (2)$$

where α is the hydroxycarbonyl yield from reaction 1 and k_1 and k_2 are the rate constants for reactions 1 and 2, respectively, then the variation of the hydroxycarbonyl concentration with time is given by[19,20]

$$[\text{hydroxycarbonyl}]_t = \frac{\alpha[\text{alcohol}]_{to}\, k_1}{(k_2 - k_1)} \left(e^{-k_1[\text{OH}]t} - e^{-k_2[\text{OH}]t}\right) \qquad \text{(I)}$$

where $[\text{hydroxycarbonyl}]_t$ is the hydroxycarbonyl concentration at time t, $[\text{alcohol}]_{to}$ is the initial alcohol concentration, k_1 and k_2 are the rate constants for reactions 1 and 2, respectively, and [OH] is the OH radical concentration. Computer calculations carried out previously,[20] as well as in this study, show that eq I holds even if the OH radical concentration is not constant (in which case $[\text{OH}]t$ is replaced by $\int[\text{OH}]dt$). The sole assumption for formulating eq I is that reactions 1 and 2 are the only loss processes for the alcohol and the hydroxycarbonyl, respectively. In a rearranged form, equations derived from eq I and appropriate for the reactions occurring and the reactant and product involved have been used for many years to correct measured

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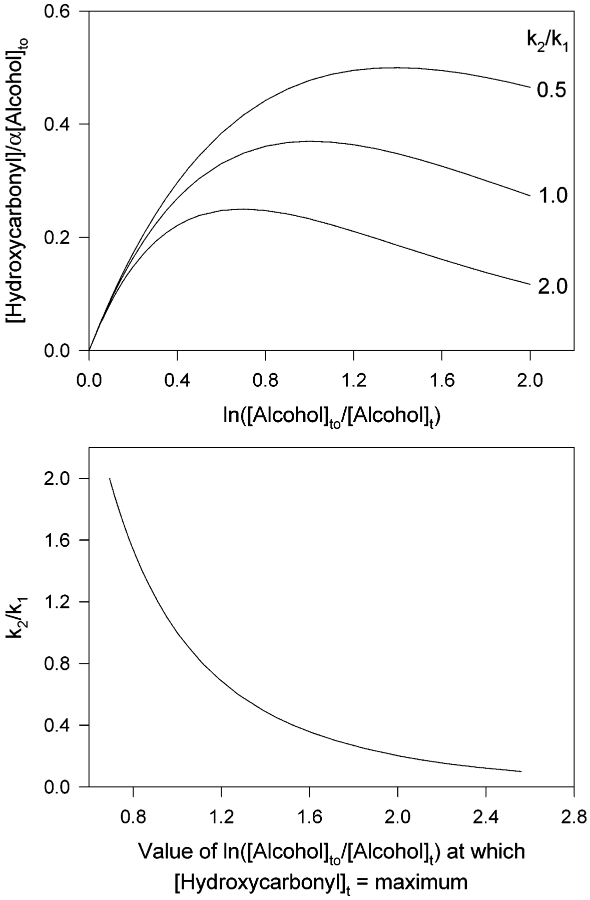

Figure 1. Top: calculated plots of eq II for values of $k_2/k_1 = 0.5$, 1.0, and 2.0. Bottom: plots of values of $\ln([\mathrm{alcohol}]_{to}/[\mathrm{alcohol}]_t)$ at which $[\mathrm{hydroxycarbonyl}]_t$ is a maximum against the rate constant ratio k_2/k_1.

product concentrations for secondary reactions (see, for example, refs 4, 20, and 21). Because $\ln([\mathrm{alcohol}]_{to}/[\mathrm{alcohol}]_t) = k_1\int[\mathrm{OH}]t$ (or $k_1[\mathrm{OH}]t$ if the OH radical concentration is constant), eq I then becomes

$$[\mathrm{hydroxycarbonyl}]_t = A(\mathrm{e}^{-x} - \mathrm{e}^{-Bx}) \qquad \text{(II)}$$

where $A = \alpha[\mathrm{alcohol}]_{to}k_1/(k_2 - k_1)$, $B = k_2/k_1$, and $x = \ln([\mathrm{alcohol}]_{to}/[\mathrm{alcohol}]_t)$. For a given experiment, or a series of experiments with the same initial concentration of the same alcohol, A is therefore constant, and the hydroxycarbonyl concentration at time t depends on the values of x and B.

The variation of the hydroxycarbonyl concentration with extent of reaction, defined as $\ln([\mathrm{alcohol}]_{to}/[\mathrm{alcohol}]_t)$, as a function of the rate constant ratio k_2/k_1 is shown by the calculated plots of eq II in Figure 1 (top) for three different values of k_2/k_1. The value of $\ln([\mathrm{alcohol}]_{to}/[\mathrm{alcohol}]_t)$ at which the hydroxycarbonyl concentration is a maximum, $[\mathrm{hydroxycarbonyl}]_{\mathrm{max}}$, depends only on the rate constant ratio k_2/k_1, as shown in Figure 1 (bottom), being given by $\ln(k_2/k_1)/[(k_2/k_1) - 1] = \ln B/(B - 1)$. Measurement of the hydroxycarbonyl concentration as a function of the extent of reaction during OH radical-initiated reactions of the precursor alcohols therefore allows the rate constant ratio k_2/k_1 and, hence, the rate constant k_2 to be determined.

All experiments were carried out in a 7500 L Teflon chamber, equipped with two parallel banks of blacklamps for irradiation, at 296 ± 2 K and 740 Torr total pressure of purified air at ~5% relative humidity. This chamber is fitted with a Teflon-coated fan to ensure the rapid mixing of reactants during their introduction into the chamber. OH radicals were generated by the photolysis of methyl nitrite (CH_3ONO) in air at wavelengths >300 nm,[5,13] and NO was added to the reactant mixtures to suppress the formation of O_3 and, hence, of NO_3 radicals. The initial reactant concentrations (molecule cm^{-3}) were: CH_3ONO, $\sim 4.8 \times 10^{13}$; NO, $\sim 4.8 \times 10^{13}$; and alcohol, $\sim 1.1 \times 10^{13}$. 3-Pentanone ($\sim 4.6 \times 10^{12}$ molecule cm^{-3}) was also included in the reactant mixtures to check the reproducibility of the analyses of the SPME fibers during the experiments (3-pentanone is a factor of 10−50 less reactive than the diols and unsaturated alcohols,[1,22] and hence, its concentration which was measured (see below) decreased only slightly during the reactions). Irradiations were carried out at 20% of the maximum light intensity for 10−40 min (1,2-butanediol), 3−40 min (1,3-butanediol), 5−40 min (2-methyl-2,4-pentanediol), 3−40 min (2-methyl-3-buten-2-ol), and 3−15 min (*cis*-3-hexen-1-ol), resulting in up to 84−89% consumption of the initially present diols and up to 97.5−98.5% consumption of the initially present unsaturated alcohols.

The concentrations of the alcohols and 3-pentanone were measured during the experiments by gas chromatography with flame ionization detection (GC-FID).[5,11,13,14,18] Gas samples of 100 cm^3 volume were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ~225 °C onto a 30 m DB-1701 megabore column held at 0 °C and then temperature programmed to 200 °C at 8 °C min^{-1}. Based on replicate analyses in the dark, the GC-FID measurement uncertainties were ≤3% (and typically <2%) for 3-pentanone, 1−4% for 1,2-butanediol, 1−5% for 1,3-butanediol, ≤3% (and typically <2%) for 2-methyl-2,3-pentanediol, and 1−2% for 2-methyl-3-buten-2-ol and *cis*-3-hexen-1-ol. The hydroxyaldehyde and hydroxyketone products (and 3-pentanone) were sampled using a 65 μm poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) "StableFlex" SPME fiber. The fiber was coated prior to use with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) for on-fiber derivatization of carbonyl compounds.[5,13] The derivatization reagent was loaded onto the SPME fiber for 30 min using headspace extraction from a 17 mg ml^{-1} PFBHA hydrochloride solution immediately before sampling in the chamber. The coated fiber was inserted into the chamber and exposed to the chamber contents for 5 min with the chamber mixing fan on. The fiber was then removed and introduced into the inlet port of the GC-FID with subsequent thermal desorption at 250 °C onto a 30 m DB-1701 megabore column held at 40 °C and then temperature programmed to 260 °C at 8 °C min^{-1}. Previous work has shown that these SPME/GC-FID analyses of the oximes are linear with hydroxycarbonyl concentration under the conditions used here.[13,23] The products of these reactions have previously been identified by gas chromatography−mass spectrometry (GC-MS), using a Varian 2000 MS/MS with isobutane chemical ionization and equipped with a DB-1701 column.[5,13] NO concentrations and the initial NO_2 concentration were measured during the experiments by a Thermo Environmental Instruments, Inc. Model 42 chemiluminescence $NO-NO_2-NO_x$ analyzer (CH_3ONO is measured as "NO_2" by commercial $NO-NO_2-NO_x$ analyzers).

The chemicals used and their stated purities were 1,2-butanediol (99%), 1,3-butanediol (99+%), *cis*-3-hexen-1-ol (95%), 2-methyl-3-buten-2-ol (98%), 2-methyl-2,4-pentanediol (99%), 3-pentanone (99+%), and *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (98+%), Aldrich Chemical Co. and NO (≥ 99.0%), Matheson Gas Products. Methyl nitrite was prepared as described by Taylor et al.[24] and stored at 77 K under vacuum.

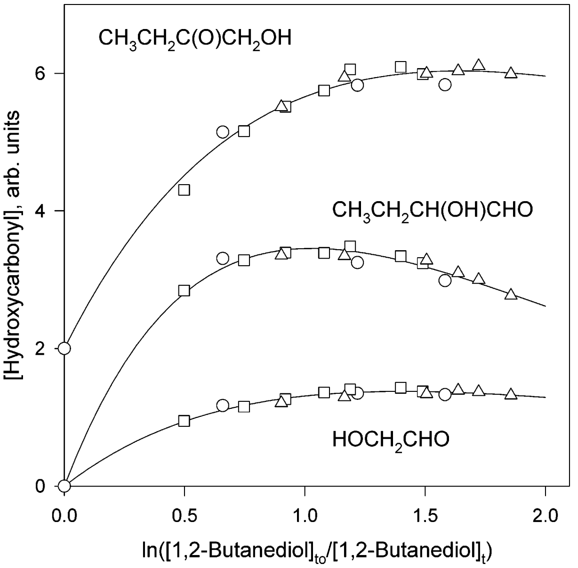

Figure 2. Plots of eq II for the formation of $CH_3CH_2C(O)CH_2OH$, $CH_3CH_2CH(OH)CHO$, and $HOCH_2CHO$ from the OH radical-initiated reaction of 1,2-butanediol, together with the nonlinear least-squares fits of the data to eq II. The different symbols denote different experiments, and the hydroxycarbonyl concentrations are in arbitrary units based on the GC peak areas. The data for $CH_3CH_2C(O)CH_2OH$ have been offset vertically by 2.0 units for clarity.

Results

GC-FID analyses of the coated SPME fibers after irradiations of CH_3ONO−NO−diol (or unsaturated alcohol)−3-pentanone−air mixtures showed the presence of GC peaks at the same retention times and with the same intensity profiles as those observed in our previous studies of the OH radical-initiated reactions of 1,2- and 1,3-butanediol and 2-methyl-2,4-pentanonediol[5] and of 2-methyl-3-buten-2-ol and *cis*-3-hexen-1-ol.[13] The hydroxycarbonyl products were, hence, assigned on the basis of our recent identifications[5,13] (note that to minimize secondary reactions of the products, these previous studies[5,13] to determine the product identifications and yields utilized significantly lower extents of reaction, with a maximum consumption of the diols of 61% and of the unsaturated alcohols of 41%). The hydroxycarbonyls and carbonyl products which were formed in sufficiently high yield that the GC-FID peak areas of their oximes were high enough to allow accurate peak area integration free from other interfering peaks were $CH_3CH_2C(O)CH_2OH$, $CH_3CH_2CH(OH)CHO$, and $HOCH_2CHO$ from 1,2-butanediol; $CH_3C(O)CH_2CH_2OH$ and $CH_3CH(OH)CH_2CHO$ from 1,3-butanediol; $(CH_3)_2C(OH)CH_2C(O)CH_3$ and $CH_3CH(OH)CHO$ from 2-methyl-2,4-pentanediol; $(CH_3)_2C(OH)CHO$ and $HOCH_2CHO$ from 2-methyl-3-buten-2-ol; and CH_3CH_2CHO and $HOCH_2CH_2CHO$ from *cis*-3-hexen-1-ol. While $HOCH_2CHO$ and $CH_3CH(OH)CHO$ were formed from the 1,3-butanediol reaction (the latter in low yield[5]), these hydroxyaldehydes can also be formed as second-generation products from the OH radical-initiated reactions of the first-generation products $CH_3C(O)CH_2CH_2OH$ and $CH_3CH(OH)CH_2CHO$, respectively, and our data suggested that this was the case because the concentrations of $HOCH_2CHO$ and $CH_3CH(OH)CHO$ increased monotonically with increasing extent of reaction. Secondary formation of the other hydroxycarbonyls (and propanal), for which data are reported here, is not expected.

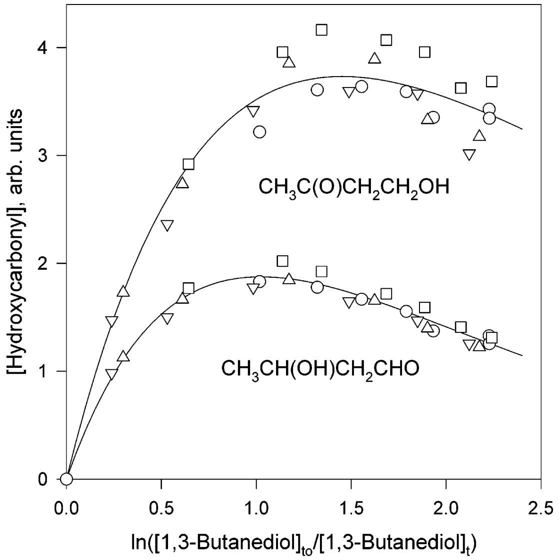

Figure 3. Plots of eq II for the formation of $CH_3C(O)CH_2CH_2OH$ and $CH_3CH(OH)CH_2CHO$ from the OH radical-initiated reaction of 1,3-butanediol, together with the nonlinear least-squares fits of the data to eq II. The different symbols denote different experiments, and the hydroxycarbonyl concentrations are in arbitrary units based on the GC peak areas.

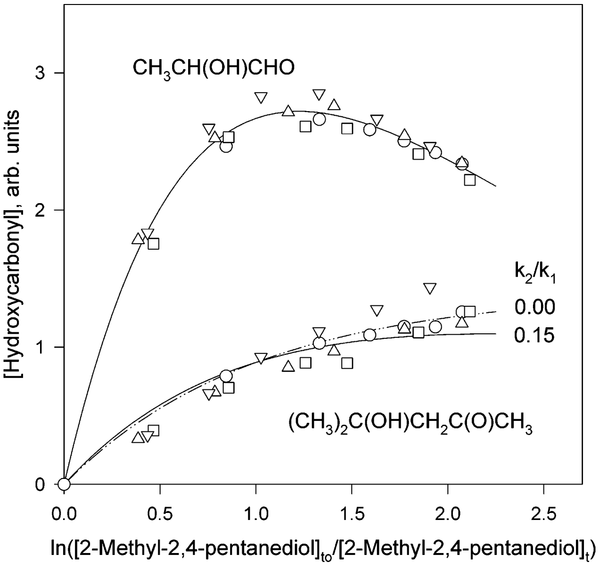

Figure 4. Plots of eq II for the formation of $(CH_3)_2C(OH)CH_2C(O)CH_3$ and $CH_3CH(OH)CHO$ from the OH radical-initiated reaction of 2-methyl-2,4-pentanediol, together with the nonlinear least-squares fit of the data for $CH_3CH(OH)CHO$ to eq II and two calculated profiles for $(CH_3)_2C(OH)CH_2C(O)CH_3$ for differing values of k_2/k_1. The different symbols denote different experiments, and the hydroxycarbonyl concentrations are in arbitrary units based on the GC peak areas.

Figures 2−6 show plots of the GC-FID peak areas (in arbitrary units) of the hydroxycarbonyls against the extent of reaction, ln([alcohol]$_{to}$/[alcohol]$_t$), for the reactions of OH radicals with 1,2-butanediol, 1,3-butanediol, 2-methyl-2,4-pentanediol, 2-methyl-3-buten-2-ol, and *cis*-3-hexen-1-ol, respectively. In all cases, the GC-FID peak areas of the oximes have been scaled to a constant initial concentration of the alcohol being studied (the measured initial concentrations of the alcohols varied by 6−17%, depending on the alcohol). While, for each alcohol, there is some run-to-run variability, this being more so for the 1,3-butanediol reactions for which the GC-FID analyses of 1,3-butanediol had the worst reproducibility (see Experimental Section above), the shape of the plots for the individual runs for a given alcohol are similar with similar values of ln([alcohol]$_{to}$/[alcohol]$_t$) at which [hydroxycarbonyl]$_t$ is a maximum. The rate constant ratios, k_2/k_1, were derived from nonlinear least-squares fits of the experimental data to eq II

TABLE 1: Rate Constant Ratios k_2/k_1 and Rate Constants k_2 at 296 ± 2 K, Together with Literature Data

			$10^{12} \times k_2$ (cm^3 molecule^{-1} s^{-1})	
alcohol	product	$k_2/k_1{}^{a}$	this work^{b}	literature
1,2-butanediol	$CH_3CH_2C(O)CH_2OH$	0.337 ± 0.069	8.5 ± 1.8	7.2 ± 0.7^{c}[29]
	$CH_3CH_2CH(OH)CHO$	0.944 ± 0.074	23.7 ± 2.3	
	$HOCH_2CHO$	0.485 ± 0.073	12.2 ± 2.0	9.4 ± 0.9^{d}[15]
				15.5 ± 2.0^{d}[16]
				12.9 ± 0.8^{e}[16]
1,3-butanediol	$CH_3C(O)CH_2CH_2OH$	0.450 ± 0.087	13.9 ± 2.8	7.6 ± 0.7^{c}[29]
	$CH_3CH(OH)CH_2CHO$	0.956 ± 0.068	29.5 ± 2.4	
2-methyl-2,4-pentanediol	$(CH_3)_2C(OH)CH_2C(O)CH_3$	≤ 0.15	<4.2	3.7 ± 0.8^{f}[30]
				3.6 ± 0.6 [21]
	$CH_3CH(OH)CHO$	0.657 ± 0.050	17.0 ± 2.0	
2-methyl-3-buten-2-ol	$(CH_3)_2C(OH)CHO$	0.234 ± 0.033	14.0 ± 2.5	
	$HOCH_2CHO$	0.124 ± 0.025	7.4 ± 1.7	9.4 ± 0.9^{d}[15]
				15.5 ± 2.0^{d}[16]
				12.9 ± 0.8^{e}[16]
cis−3-hexen-1-ol	$HOCH_2CH_2CHO$	0.184 ± 0.025	19.9 ± 2.9	
	CH_3CH_2CHO	0.157 ± 0.033	17.0 ± 3.7	17.1 ± 2.4 [31]
				20 ± 3 [32]
				22.2 ± 0.9^{g}[33]
				19.4 ± 1.5^{g}[34]
				20.2 ± 1.4^{h}[35]
				18.9 ± 1.6^{e}[36]

[a] From nonlinear least-squares fits of the data to eq II, as shown in Figures 2−6, apart from the formation of $(CH_3)_2C(OH)CH_2C(O)CH_3$ from 2-methyl-2,4-pentanediol, where the upper limit was estimated by inspection (see Figure 4). The cited error limits are the approximate 95% confidence limits obtained from the nonlinear least squares analyses. [b] The rate constant ratios have been placed on an absolute basis by use of rate constants (in units of 10^{-12} cm^3 molecule^{-1} s^{-1}) at 296 K of 1,2-butanediol, 25.1 ± 1.3;[18] 1,3-butanediol, 30.9 ± 1.0;[18] and 2-methyl-2,4-pentanediol, 25.8 ± 2.2[18] (all three being re-evaluated with $k(OH + n\text{-octane}) = 8.07 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K[25]); 2-methyl-3-buten-2-ol, 60 ± 6;[26,27] and *cis*-3-hexen-1-ol, 108 ± 4.[28] The cited uncertainties include the uncertainties in the rate constants k_1. [c] Relative to $k(OH + n\text{-octane}) = 8.07 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K.[25] [d] Relative to $k(OH + CH_3CHO) = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.[17] [e] Relative to $k(OH + \text{propene}) = 2.63 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.[37] [f] Relative to $k(OH + n\text{-butane}) = 2.33 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K.[25] [g] Relative to $k(OH + \text{ethene}) = 8.52 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[37] [h] Relative to $k(OH + \text{methyl vinyl ketone}) = 2.06 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 296 K.[35]

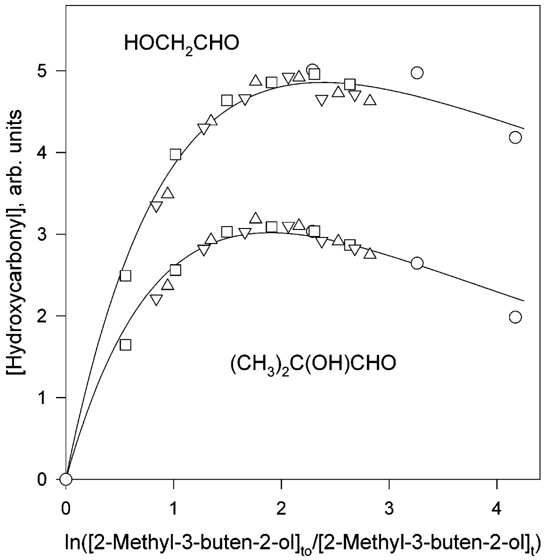

Figure 5. Plots of eq II for the formation of $(CH_3)_2C(OH)CHO$ and $HOCH_2CHO$ from the OH radical-initiated reaction of 2-methyl-3-buten-2-ol, together with the nonlinear least-squares fits of the data to eq II. The different symbols denote different experiments, and the hydroxycarbonyl concentrations are in arbitrary units based on the GC peak areas.

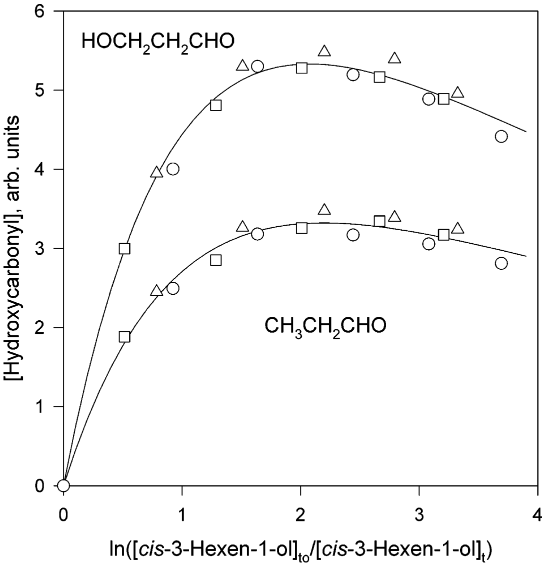

Figure 6. Plots of eq II for the formation of CH_3CH_2CHO and $HOCH_2CH_2CHO$ from the OH radical-initiated reaction of *cis*-3-hexen-1-ol, together with the nonlinear least-squares fits of the data to eq II. The different symbols denote different experiments, and the hydroxycarbonyl concentrations are in arbitrary units based on the GC peak areas.

using the value of ln([alcohol]$_{to}$/[alcohol]$_t$) at which the hydroxycarbonyl concentration maximized to provide an initial value for k_2/k_1. The lines in Figures 2−6 (except for the formation of $(CH_3)_2C(OH)CH_2C(O)CH_3$ from 2-methyl-2,4-pentanediol in Figure 4) are the nonlinear least-squares fits of the experimental data to eq II for each hydroxycarbonyl (and for propanal from *cis*-3-hexen-1-ol). For the formation of $(CH_3)_2C(OH)CH_2C(O)CH_3$ from 2-methyl-2,4-pentanediol, an upper limit to the rate constant ratio k_2/k_1 was obtained from visual inspection of calculated profiles, as shown in Figure 4, and this upper limit corresponds to approximately the upper four standard deviations of the nonlinear least-squares fit. The rate constant ratios, k_2/k_1, obtained from the nonlinear least-squares analyses and the upper limit to the rate constant ratio for $(CH_3)_2C(OH)CH_2C(O)CH_3$ are given in Table 1.

As evident from the calculated profiles shown in Figure 1 (top and bottom), the profiles are increasingly insensitive to the rate constant ratio k_2/k_1 as k_2/k_1 decreases below ~0.5, with the maximum sensitivity occurring when $k_2/k_1 \approx 1.0$. While measurements of the absolute concentrations of the hydroxycarbonyls would provide additional data concerning the rate constant ratios k_2/k_1 [see Figure 1 (top)], the uncertainties in the hydroxyaldehyde concentrations arising from the estimated SPME/GC-FID analysis response factors[5,13] preclude this. Hence, while the nonlinear least-squares fits lead to values of A in eq II, these are in arbitrary units and give no information concerning the values of $\alpha k_1/(k_2 - k_1)$.

The rate constant ratios, k_2/k_1, given in Table 1 are placed on an absolute basis by use of rate constants k_1 (in units of 10^{-12} cm^3 molecule^{-1} s^{-1}) for the precursor alcohol at 296 K of 1,2-butanediol, 25.1 ± 1.3;[18] 1,3-butanediol, 30.9 ± 1.0;[18] and 2-methyl-2,4-pentanediol, 25.8 ± 2.2[18] (all three being reevaluated with $k(\mathrm{OH} + n\text{-octane}) = 8.07 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K[25]); 2-methyl-3-buten-2-ol, 60 ± 6;[26,27] and *cis*-3-hexen-1-ol, 108 ± 4,[28] and the resulting rate constants, k_2, are also given in Table 1.

Discussion

Dark losses of 1,2- and 1,3-butanediol, 2-methyl-2,4-pentanediol, 2-methyl-3-buten-2-ol, and *cis*-3-hexen-1-ol in the Teflon chamber have been shown in recent studies conducted in this laboratory[13,18,26] to be of no importance, being <5% over periods of 1.5−4.5 h, time periods comparable to those between the first sample being collected for analysis and the last sample collection which averaged 3.9 h and had a range of 2.0−5.1 h (except for one experiment in which this time was 6.5 h). Aliphatic alcohols do not absorb below ~200 nm,[38] and hence, photolysis by blacklamps at >300 nm was of no importance, as we have previously verified for 2-methyl-3-buten-2-ol[26] for light intensities and irradiation times comparable to those employed here.

We have previously observed[29] that the hydroxyketones for which rate constants were measured in this study [i.e., $CH_3CH_2C(O)CH_2OH$, $CH_3C(O)CH_2CH_2OH$, and $(CH_3)_2C(OH)CH_2C(O)CH_3$] show no losses (<2%) over time periods of 5 h, including 60 min of photolysis at the same light intensity as that used here. Furthermore, we have observed in recent studies[13,18] that dark losses of the hydroxyaldehydes $CH_3CH_2CH(OH)CHO$, $HOCH_2CHO$, $CH_3CH(OH)CH_2CHO$, $CH_3CH(OH)CHO$, $(CH_3)_2C(OH)CHO$, and $HOCH_2CH_2CHO$ (formed from CH_3ONO−NO−air irradiations of their precursor alcohol or diol) in our Teflon chambers were <5% over time periods of 1.2−3.2 h (again reasonably comparable to the time periods between the first irradiation and the last sample collection, which averaged 3.4 h and had a range of 1.3−4.4 h (except for one experiment in which this time was 6.3 h)). Bacher et al.[16] have shown that glycolaldehyde absorbs out to ~340 nm with a quantum yield for photolysis which may be close to unity and calculated a tropospheric lifetime of glycolaldehyde due to photolysis of >2.5 days for summertime mid-latitude conditions.[16] Using this upper limit to the photolysis rate of glycolaldehyde as representative of those for the hydroxyaldehydes studied here, photolysis of the hydroxyaldehydes at the light intensities and irradiation times used during the experiments (≤40 min at ~50% of the 12 h average mid-latitude solar intensity) is expected to be of no importance (<2% loss).

Therefore, dark losses and photolysis of the alcohols and the hydroxycarbonyl products during the experiments were <5% and essentially within the analytical measurement uncertainties. However, 2-methyl-3-buten-2-ol and *cis*-3-hexen-1-ol react with O_3 and with NO_3 radicals in addition to their reactions with OH radicals,[22] with O_3 and NO_3 radicals potentially being formed as the irradiations proceed and NO is converted to NO_2 (by reactions of HO_2 and organic peroxy radicals with NO) and NO_2 is formed by the photolysis of methyl nitrite. However, the measured NO concentrations at the end of the experiments were in the range $(0.94-1.9) \times 10^{13}$ molecule cm^{-3} for the experiments with 2-methyl-3-buten-2-ol and in the range $(0.97-1.7) \times 10^{13}$ molecule cm^{-3} for those with *cis*-3-hexen-1-ol. These final NO concentrations were sufficiently large that formation of O_3 and, hence, of NO_3 radicals was of no importance, and hence, losses of 2-methyl-3-buten-2-ol and *cis*-3-hexen-1-ol due to reactions with O_3 and NO_3 radicals could be neglected.

The rate constants, k_2, derived in this work for the hydroxyaldehydes $CH_3CH_2CH(OH)CHO$, $CH_3CH(OH)CH_2CHO$, $CH_3CH(OH)CHO$, $(CH_3)_2C(OH)CHO$, and $HOCH_2CH_2CHO$ are the first reported for these compounds. Our present rate constant, k_2, for the hydroxyketone $CH_3CH_2C(O)CH_2OH$ is in good agreement with our previous, more-direct measurement.[29] While our present rate constant, k_2, for the hydroxyketone $CH_3C(O)CH_2CH_2OH$ is a factor of 1.8 higher than our previous and more-direct relative rate measurement,[29] our present data for $CH_3C(O)CH_2CH_2OH$ are subject to significant scatter (Figure 3). Our present upper limit to the rate constant k_2 for 4-hydroxy-4-methyl-2-pentanone [$(CH_3)_2C(OH)CH_2C(O)CH_3$] (Table 1) is consistent with the two literature values,[21,30] which are in good agreement. Furthermore, our present upper limit of k_2(OH + 4-hydroxy-4-methyl-2-pentanone)/k_1(OH + 2-methyl-2,4-pentanediol) ≤ 0.15 is consistent with the ratio of 0.14 ± 0.04 obtained from our previous measurements of the rate constants for the reactions of OH radicals with 4-hydroxy-4-methyl-2-pentanone[30] and 2-methyl-2,4-pentanediol.[18] However, the rate constants measured recently by Magneron et al.[21] at 298 ± 3 K for 4-hydroxy-4-methyl-2-pentanone and 2-methyl-2,4-pentanediol, of $(3.6 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $(1.5 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively, lead to a rate constant ratio of k_2(OH + 4-hydroxy-4-methyl-2-pentanone)/k_1(OH + 2-methyl-2,4-pentanediol) = 0.24 ± 0.08, significantly higher than our present upper limit (Table 1). This discrepancy suggests that the rate constant for 2-methyl-2,4-pentanediol measured by Magneron et al.[21] is too low, possibly because of wall adsorption/desorption problems in the 140 L volume Teflon chamber used[21] and/or unrecognized analytical problems (the rate constant reported by Magneron et al.[21] was obtained using in situ Fourier transform infrared absorption spectroscopy, and GC-FID analyses were stated[21] to have resulted in higher, but more scattered, rate constants).

The two values of the rate constant for the reaction of OH radicals with glycolaldehyde obtained here are at the lower end of the three literature values[15−17] (Table 1). The rate constant obtained here for propanal is in good agreement with the literature data[17,31−36] (Table 1).

The room-temperature rate constants obtained here for the hydroxyaldehydes $CH_3CH_2CH(OH)CHO$, $CH_3CH(OH)CH_2CHO$, $CH_3CH(OH)CHO$, $(CH_3)_2C(OH)CHO$, and $HOCH_2CH_2CHO$ are consistent with expectations. Thus, the rate constants (in units of 10^{-12} cm^3 molecule^{-1} s^{-1}) increase from $HOCH_2CHO$ (13)[17] to $HOCH_2CH_2CHO$ (20) and from $CH_3CH(OH)CHO$ (17) to $CH_3CH_2CH(OH)CHO$ (24) and $CH_3CH(OH)CH_2CHO$ (30), consistent with the presence of the additional CH_2 group. The rate constants for $HOCH_2CHO$ (1.3×10^{-11} cm^3 molecule^{-1} s^{-1}),[17] $CH_3CH(OH)CHO$ (1.7×10^{-11} cm^3 molecule^{-1} s^{-1}), and $(CH_3)_2C(OH)CHO$ (1.4×10^{-11} cm^3 molecule^{-1} s^{-1}) are similar, suggesting that the majority of the reactions with $CH_3CH(OH)CHO$ and $(CH_3)_2C(OH)CHO$ proceed by H-atom abstraction from the CHO group, as is the case for $HOCH_2CHO$.[15,17]

Finally, the room-temperature rate constants obtained here for the reactions of OH radicals with $CH_3CH_2CH(OH)CHO$, $CH_3CH(OH)CH_2CHO$, $CH_3CH(OH)CHO$, $(CH_3)_2C(OH)CHO$, and $HOCH_2CH_2CHO$ lead to calculated lifetimes of 5−10 h at an OH radical concentration of 2×10^6 molecule cm^{-3}, the 12 h daytime annual global tropospheric average.[39,40]

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