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Atmospheric Chemistry of Selected Hydroxycarbonyls

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Using a relative rate method, rate constants have been measured at 296 ± 2 K for the gas-phase reactions of the OH radical with 1-hydroxy-2-butanone, 3-hydroxy-2-butanone, 1-hydroxy-3-butanone, 1-hydroxy-2-methyl-3-butanone, 3-hydroxy-3-methyl-2-butanone, and 4-hydroxy-3-hexanone, with rate constants (in units of 10^{-12} cm^3 molecule^{-1} s^{-1}) of 7.7 ± 1.7, 10.3 ± 2.2, 8.1 ± 1.8, 16.2 ± 3.4, 0.94 ± 0.37, and 15.1 ± 3.1, respectively, where the error limits include the estimated overall uncertainty in the rate constant for the reference compound. Rate constants were also measured for reactions with NO_3 radicals and O_3. Rate constants for the NO_3 radical reactions (in units of 10^{-16} cm^3 molecule^{-1} s^{-1}) were 1-hydroxy-2-butanone, <9; 3-hydroxy-2-butanone, 6.5 ± 2.2; 1-hydroxy-3-butanone, <22; 1-hydroxy-2-methyl-3-butanone, <22; 3-hydroxy-3-methyl-2-butanone, <2; and 4-hydroxy-3-hexanone, 12 ± 4, where the error limits include the estimated overall uncertainties in the rate constants for the reference compounds. No reactions with O_3 were observed, and upper limits to the rate constants of $<1.1 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} were derived for all six hydroxycarbonyls. The dominant tropospheric loss process for the hydroxycarbonyls studied here is calculated to be by reaction with the OH radical.

Introduction

Volatile organic compounds present in the atmosphere can undergo photolysis and chemical reaction with OH radicals, NO_3 radicals, and O_3,[1,2] with the OH radical reaction being an important, and often dominant, atmospheric loss process.[1,2] Hydroxycarbonyls are formed as atmospheric reaction products of organic compounds; for example, 1,4-hydroxycarbonyls are formed from the OH radical-initiated reactions of alkanes[3−5] and 1,2-hydroxycarbonyls can be formed from the OH radical-initiated reactions of alkenes.[5−9] Because of difficulties in the analysis of this class of compounds, few data are presently available concerning their atmospheric chemistry.[10−12] It is expected that the dominant atmospheric loss process for hydroxycarbonyls not containing $>C{=}C<$ bonds is by daytime reaction with the OH radical, with photolysis also being possible.[1,2] To date, rate constants for the reactions of the OH radical with hydroxycarbonyls have been measured only for glycolaldehyde[10] [$HOCH_2CHO$] and hydroxyacetone[11,12] [$HOCH_2C(O)CH_3$].

In this work, we have measured rate constants for the gas-phase reactions of the hydroxycarbonyls 1-hydroxy-2-butanone, 3-hydroxy-2-butanone, 1-hydroxy-3-butanone, 1-hydroxy-2-methyl-3-butanone, 3-hydroxy-3-methyl-2-butanone, and 4-hydroxy-3-hexanone with OH radicals, NO_3 radicals, and O_3 at 296 ± 2 K. In addition, we have investigated the products formed from the reactions of the OH radical with 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone.

Experimental Section

Experiments were carried out in a 7900 L Teflon chamber, equipped with two parallel banks of Sylvania F40/350BL black lamps 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.

Kinetic Studies. Rate constants for the OH radical and NO_3 radical reactions were determined using relative rate methods in which the relative disappearance rates of the hydroxycarbonyls and a reference compound, whose OH radical or NO_3 radical reaction rate constant is reliably known, were measured in the presence of OH radicals or NO_3 radicals.[13,14] Providing that the hydroxycarbonyls and the reference compound(s) reacted only with OH radicals or NO_3 radicals, then[13,14]

$$\ln\left(\frac{[\text{hydroxycarbonyl}]_{t_0}}{[\text{hydroxycarbonyl}]_t}\right) - D_t = \frac{k_1}{k_2}\left[\ln\left(\frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t}\right) - D_t\right] \quad \text{(I)}$$

where $[\text{hydroxycarbonyl}]_{t_0}$ and $[\text{reference compound}]_{t_0}$ are the concentrations of the hydroxycarbonyl and reference compound, respectively, at time t_0, $[\text{hydroxycarbonyl}]_t$ and $[\text{reference compound}]_t$ are the corresponding concentrations at time t, D_t is a factor to account for any dilution due to additions to the chamber during the reactions, and k_1 and k_2 are the rate constants for reactions 1 and 2, respectively.

$$\left.\begin{matrix}\text{OH}\\ \text{NO}_3\end{matrix}\right\} + \text{hydroxycarbonyl} \rightarrow \text{products} \quad (1)$$

$$\left.\begin{matrix}\text{OH}\\ \text{NO}_3\end{matrix}\right\} + \text{reference compound} \rightarrow \text{products} \quad (2)$$

OH radicals were generated by the photolysis of methyl nitrite (CH_3ONO) in air at wavelengths >300 nm,[15] and NO was added

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to the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals.[15] The initial reactant concentrations (in molecules cm^{-3} units) were CH_3ONO, $(2.1-2.4) \times 10^{14}$; NO, $(1.8-2.2) \times 10^{14}$; and hydroxycarbonyl and reference compound, $\sim 2.4 \times 10^{13}$ each. *n*-Octane was used as the reference compound for the OH radical rate constant determinations, and irradiations were carried out for 6−45 min. No additions were made to the chamber during the OH radical reactions, and hence $D_t = 0$ for these experiments. To assess the importance of photolysis of the hydroxycarbonyls during the OH radical rate constant determinations, the hydroxycarbonyls ($\sim 2.4 \times 10^{13}$ molecules cm^{-3} each) were photolyzed in air in the presence of 7.1×10^{15} molecules cm^{-3} of cyclohexane (to scavenge any OH radicals formed during the irradiation) for up to 60 min at the same light intensity as used in the kinetic experiments.

For the measurement of the rate constants for the reactions of the NO_3 radical with the hydroxycarbonyls, NO_3 radicals were generated in the dark by the thermal decomposition of N_2O_5,[16,17] and 1-butene, crotonaldehyde [$CH_3CH{=}CHCHO$], or methacrolein [$CH_2{=}C(CH_3)CHO$] were used as the reference compounds. The initial reactant concentrations (in molecules cm^{-3} units) were hydroxycarbonyl, $\sim 2.4 \times 10^{13}$; 1-butene, crotonaldehyde, or methacrolein, $\sim 2.4 \times 10^{13}$; NO_2, $(2.4-4.8) \times 10^{13}$; and one to four additions of N_2O_5 (each addition corresponding to an initial N_2O_5 concentration in the chamber of $(1.0-6.8) \times 10^{13}$ molecules cm^{-3}) were made to the chamber during an experiment. The factor D_t to take into account dilution was $D_t = 0.0012$ per N_2O_5 addition to the chamber.

The concentrations of the hydroxycarbonyls and the reference compounds were measured by gas chromatography with flame ionization detection (GC-FID) during the experiments. For the analysis of the hydroxycarbonyls, *n*-octane, crotonaldehyde and methacrolein, 100 cm^3 volume gas samples 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}. For the analysis of 1-butene, gas samples were collected from the chamber in 100 cm^3 all-glass, gastight syringes and transferred via a 1 cm^3 stainless steel loop and gas sampling valve onto a 30 m DB-5 megabore column held at −25 °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 for the hydroxycarbonyls were typically <2%. GC-FID response factors for the hydroxycarbonyls, the reference compounds, and selected products (see below) were determined by introducing measured amounts of the chemicals into the 7900 L chamber and conducting several replicate GC-FID analyses.[18] NO and initial NO_2 concentrations were measured using a Thermo Environmental Instruments, Inc., Model 42 chemiluminescent $NO-NO_x$ analyzer.

Rate constants, or upper limits thereof, for the reactions of the hydroxycarbonyls with O_3 were determined in the dark by measuring the decay rates of the hydroxycarbonyls in the presence of measured concentrations of O_3.[13,19] Cyclohexane was added to the reactant mixtures to scavenge any OH radicals formed in the reaction systems. Providing that any measured loss of the hydroxycarbonyls was due only to reaction with O_3, then

$$\ln([\text{hydroxycarbonyl}]_{t_0}/[\text{hydroxycarbonyl}]_t) = k_3[O_3](t - t_0) \quad \text{(II)}$$

where k_3 is the rate constant for the reaction

$$O_3 + \text{hydroxycarbonyl} \rightarrow \text{products} \quad (3)$$

The initial concentrations of the hydroxycarbonyls, cyclohexane, and O_3 were $\sim 2.4 \times 10^{13}$, 3.5×10^{15}, and 3.44×10^{13} molecules cm^{-3}, respectively, and the reactions were monitored for up to 3.8 h. The concentrations of the hydroxycarbonyls were measured by GC-FID as described above. Ozone concentrations were measured by ultraviolet absorption using a Dasibi 1003-AH ozone analyzer.

Product Studies. Products were identified and quantified from the reactions of the OH radical with 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone, from both the kinetic experiments (see above) and irradiated CH_3ONO−NO−3-hydroxy-2-butanone (or 4-hydroxy-3-hexanone)−air mixtures by GC-FID and by combined gas chromatography−mass spectrometry (GC−MS). The initial reactant concentrations and GC-FID analysis procedures were similar to those employed in the kinetic experiments described above. Gas samples were collected onto Tenax-TA solid adsorbent for the GC−MS analyses, with thermal desorption onto a 60 m DB-5 fused silica capillary column in a HP 5890 GC interfaced to a HP 5970 Mass Selective Detector and operated in the scanning mode.

Chemicals. The chemicals used, and their stated purities, were cyclohexane (high-purity solvent grade), American Burdick and Jackson; 2,3-butanedione (99%), crotonaldehyde (99+%), 3,4-hexanedione (95%), 1-hydroxy-2-butanone (95%), 3-hydroxy-2-butanone, 1-hydroxy-2-methyl-3-butanone (65%), methacrolein (95%), and *n*-octane (99+%), Aldrich Chemical Co.; 1-hydroxy-3-butanone (95+%), 4-hydroxy-3-hexanone (95+%), and 3-hydroxy-3-methyl-2-butanone (90+%), TCI America; and NO (≥99.0%) and 1-butene (≥99.0%), Matheson Gas Products. Methyl nitrite and N_2O_5 were prepared and stored as described previously,[15,16] and NO_2 was prepared just prior to use by reacting NO with an excess of O_2. O_3 in O_2 diluent was prepared as needed using a Welsbach T-408 ozone generator.

Results

Photolysis. Photolysis of the hydroxycarbonyls in air at the same light intensity as used in the OH radical rate constant determinations for up to 60 min showed <2% loss of any hydroxycarbonyl. Hence photolysis of the hydroxycarbonyls studied was of no importance during the CH_3ONO−NO−hydroxycarbonyl−*n*-octane−air irradiations employed for the determination of the OH radical reaction rate constants (which involved irradiation for ≤45 min). Furthermore, over the 5-h period of the photolysis experiment the concentrations of the hydroxycarbonyls changed by <2%, showing that dark decays of the hydroxycarbonyls were also negligible.

OH Radical Rate Constants. A series of CH_3ONO−NO−hydroxycarbonyl−*n*-octane−air irradiations were carried out, and the data obtained are plotted in accordance with eq I in Figures 1 and 2. Good straight line plots are observed, and the rate constant ratios k_1/k_2 obtained from least-squares analyses of the data are given in Table 1. These rate constant ratios are placed on an absolute basis by use of a rate constant k_2 for the reactions of the OH radical with *n*-octane at 296 K of 8.67×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (±20%).[5] The resulting rate constants k_1 are also given in Table 1.

OH Radical Reaction Products. GC-FID analyses of irradiated CH_3ONO−NO−hydroxycarbonyl−*n*-octane−air mixtures showed the formation of products from the 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone reactions (but not from the other hydroxycarbonyls). Matching of GC retention times and mass spectra with those of authentic standards showed that the products are 2,3-butanedione (biacetyl) from 3-hydroxy-2-butanone and 3,4-hexanedione from 4-hydroxy-3-hexanone.

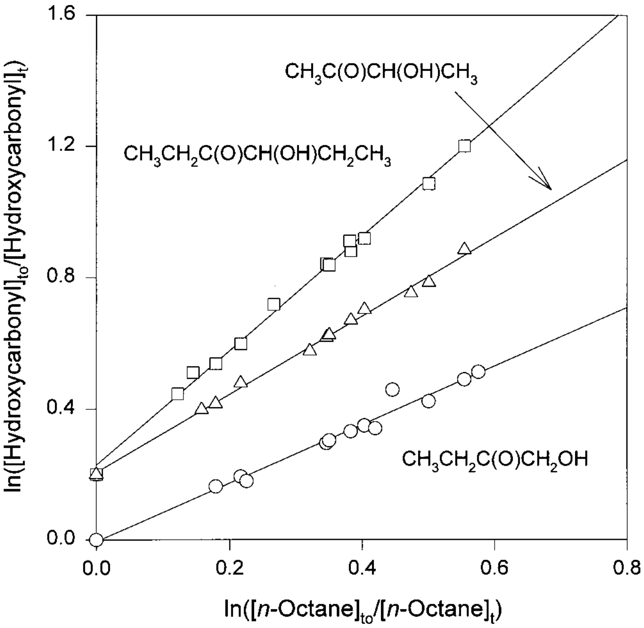

Figure 1. Plots of eq I for the gas-phase reactions of the OH radical with 1-hydroxy-2-butanone, 3-hydroxy-2-butanone, and 4-hydroxy-3-hexanone, with *n*-octane as the reference compound. The data for 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone have been displaced vertically by 0.2 unit for clarity.

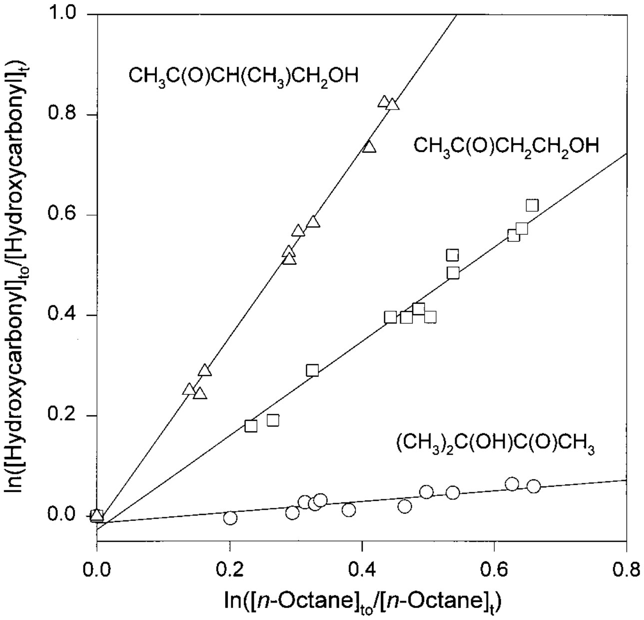

Figure 2. Plots of eq I for the gas-phase reactions of the OH radical with 3-hydroxy-3-methyl-2-butanone, 1-hydroxy-3-butanone, and 1-hydroxy-2-methyl-3-butanone, with *n*-octane as the reference compound.

Photolysis of 2,3-butanedione and 3,4-hexanedione in air in the presence of cyclohexane (to scavenge any OH radicals) led to photolysis rates of (1.25 ± 0.56) × 10^{-3} and (1.52 ± 0.18) × 10^{-3} min^{-1}, respectively, corresponding to losses of 5.5% and 7%, respectively, over the maximum total photolysis times of 45 min in the OH radical reactions. 2,3-Butanedione and 3,4-hexanedione also react with the OH radical, with rate constants at room temperature of 2.4 × 10^{-13} [1,20] and 2.5 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (estimated[21]), respectively. The measured concentrations of 2,3-butanedione and 3,4-hexanedione were corrected for photolysis and reaction with OH radicals (the maximum corrections being 3.4% and 13%, respectively), and plots of the amounts of 2,3-butanedione and 3,4-hexanedione formed, corrected for secondary reactions, against the amounts of 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone reacted are shown in Figure 3. Least-squares analyses leads to formation yields of 2,3-butanedione from 3-hydroxy-2-butanone of 0.79 ± 0.14 and of 3,4-hexanedione from 4-hydroxy-3-hexanone of 0.84 ± 0.07, where the indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for the hydroxycarbonyls and α-dicarbonyls of ±5% each.

TABLE 1: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 for the Gas-Phase Reactions of the OH Radical with Hydroxycarbonyls at 296 ± 2 K

hydroxycarbonyl	k_1/k_2 [a]	$10^{12}k_1$ [b] (cm^3 $molecule^{-1}$ s^{-1})
$CH_3CH_2C(O)CH_2OH$	0.893 ± 0.083	7.7 ± 1.7
$CH_3C(O)CH(OH)CH_3$	1.19 ± 0.05	10.3 ± 2.2
$CH_3C(O)CH_2CH_2OH$	0.940 ± 0.082	8.1 ± 1.8
$CH_3C(O)CH(CH_3)CH_2OH$	1.87 ± 0.09	16.2 ± 3.4
$(CH_3)_2C(OH)C(O)CH_3$	0.108 ± 0.036	0.94 ± 0.37
$CH_3CH_2C(O)CH(OH)CH_2CH_3$	1.74 ± 0.07	15.1 ± 3.1

[a] *n*-Octane used as the reference compound. The indicated errors are two least-squares standard deviations. [b] Placed on an absolute basis by use of a rate constant of k_2(*n*-octane) = 8.67 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (±20%) at 296 K.[5] The indicated errors include the estimated overall uncertainty in the rate constant k_2.

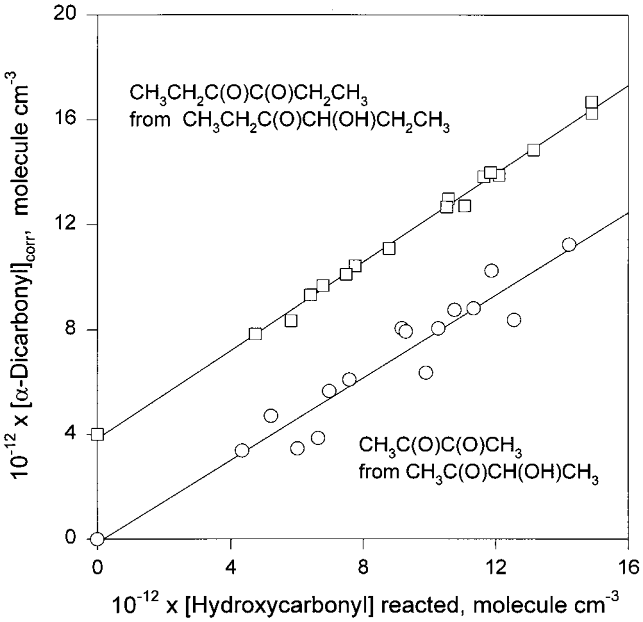

Figure 3. Plots of amounts of 2,3-butanedione and 3,4-hexanedione formed, corrected for secondary reactions (see text), against amounts of 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone reacted with the OH radical. The data for 3,4-hexanedione have been displaced vertically by 4.0 × 10^{12} molecules cm^{-3} for clarity.

NO_3 Radical Rate Constants. A series of reacting NO_3−N_2O_5−NO_2−hydroxycarbonyl−1-butene (or crotonaldehyde or methacrolein)−air mixtures were carried out. For 3-hydroxy-3-methyl-2-butanone, no reaction was observed (<3%) in experiments in which a large fraction of the initial 1-butene or methacrolein was consumed (78% and 59%, respectively), and upper limits to the rate constant ratios k_1/k_2 are given in Table 2. For the other five hydroxycarbonyls studied here, the measured concentrations decreased during the reactions, but with plots of eq I showing a significant nonzero intercept. Rate constant ratios obtained by least-squares analyses of the data from each experiment (in general, data from separate experiments could not be combined because of the varying nonzero

TABLE 2: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 for the Gas-Phase Reactions of the NO_3 Radical with Hydroxycarbonyls at 296 ± 2 K

hydroxycarbonyl	ref compd	k_1/k_2[a]	$10^{16}k_1$[b] (cm^3 $molecule^{-1}$ s^{-1})
$CH_3CH_2C(O)CH_2OH$	1-butene	≤ 0.05	≤ 6.6
	crotonaldehyde	0.054 ± 0.036	2.8 ± 1.9
	methacrolein	0.16 ± 0.07	5.3 ± 2.3
$CH_3C(O)CH(OH)CH_3$	1-butene	0.049 ± 0.015	6.5 ± 2.0
	crotonaldehyde	0.13 ± 0.04	6.6 ± 2.1
	methacrolein	0.26 ± 0.05	8.6 ± 1.7
	methacrolein	0.32 ± 0.04	10.6 ± 1.4
$CH_3C(O)CH_2CH_2OH$	1-butene	≤ 0.13	≤ 18
	methacrolein	0.48 ± 0.09	16 ± 3
$CH_3C(O)CH(CH_3)CH_2OH$	1-butene	≤ 0.12	≤ 16
	methacrolein	0.49 ± 0.07	16 ± 3
$(CH_3)_2C(OH)C(O)CH_3$	1-butene	<0.020	<2.7
	methacrolein	<0.039	<1.3
$CH_3CH_2C(O)CH(OH)CH_2CH_3$	1-butene	0.098 ± 0.037	13 ± 5
	1-butene	0.103 ± 0.016	14 ± 3
	crotonaldehyde	0.21 ± 0.05	11 ± 3
	crotonaldehyde	0.23 ± 0.03	12 ± 2
	methacrolein	0.43 ± 0.10	14 ± 4
	methacrolein	0.45 ± 0.05	15 ± 2

[a] Indicated errors are two least-squares standard deviations. [b] Placed on an absolute basis by use of rate constants of k_2(1-butene) = 1.32×10^{-14} cm^3 $molecule^{-1}$ s^{-1},[5] k_2(crotonaldehyde) = 5.12×10^{-15} cm^3 $molecule^{-1}$ s^{-1},[22] and k_2(methacrolein) = 3.3×10^{-15} cm^3 $molecule^{-1}$ s^{-1} [14] at 296 K.

intercepts) are given in Table 2; in some cases these are upper limits derived from the data points at the end of the reactions.

The rate constant ratios obtained using the different reference compounds are in reasonable agreement or, for certain experiments using 1-butene as the reference compound where only upper limits were derived, are consistent. It should be noted that 1-butene is the most reactive of the reference compounds employed, being a factor of ≥10 more reactive toward the NO_3 radical than are the hydroxycarbonyls studied here, and hence leading to most of the initial 1-butene being reacted away while only a small amount of the hydroxycarbonyls had reacted. The rate constant ratios k_1/k_2 are placed on an absolute basis by use of rate constants for the reactions of the NO_3 radical with 1-butene, crotonaldehyde, and methacrolein at 296 K of 1.32×10^{-14},[5] 5.12×10^{-15},[22] and 3.3×10^{-15} cm^3 $molecule^{-1}$ s^{-1},[14] respectively. The resulting rate constants k_1 are also given in Table 2.

2,3-Butanedione and 3,4-hexanedione were identified and quantified as products of the 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone reactions, respectively. The formation yields of these α-dicarbonyl products (defined as [amount of α-dicarbonyl formed]/[amount of hydroxycarbonyl reacted]) depended on the specific experiment, being in the range 54−77% for the formation of 2,3-butanedione from 3-hydroxy-2-butanone and 50−93% for the formation of 3,4-hexanedione from 4-hydroxy-3-hexanone (and with the formation yield often increasing during the reaction). Plots of (yield of α-dicarbonyl){ln([hydroxycarbonyl]$_{t_0}$/[hydroxycarbonyl]$_t$) − D_t} against {ln([reference compound]$_{t_0}$/[reference compound]$_t$) − D_t} should yield plots whose slopes are k_4/k_2, where reaction 4 is that leading to formation of the α-dicarbonyl.

$$NO_3 + RC(O)CH(OH)R \rightarrow HNO_3 + RC(O)\dot{C}(OH)R \quad (4)$$

$$RC(O)\dot{C}(OH)R + O_2 \rightarrow RC(O)C(O)R + HO_2 \quad (5)$$

Figure 4 shows such plots for the 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone reactions with methacrolein as the reference compound. Both plots again show nonzero intercepts (possibly due to wall losses of the hydroxycarbonyls during/immediately after introduction of the first aliquot of N_2O_5 into the chamber, although further N_2O_5 additions did not show similar effects), and least-squares analyses of the data after addition of N_2O_5 to the chamber lead to rate constant ratios k_4/k_2 and rate constants k_4 of 0.197 ± 0.030 and (6.5 ± 2.2) × 10^{-16} cm^3 $molecule^{-1}$ s^{-1}, respectively, for the 3-hydroxy-2-butanone reaction, and 0.358 ± 0.033 and (1.2 ± 0.4) × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} for the 4-hydroxy-3-hexanone reaction, where the indicated errors are two least-squares standard deviations (and those for the rate constants k_4 take into account the ±30% estimated overall uncertainty in the rate constant k_2 for methacrolein[14]).

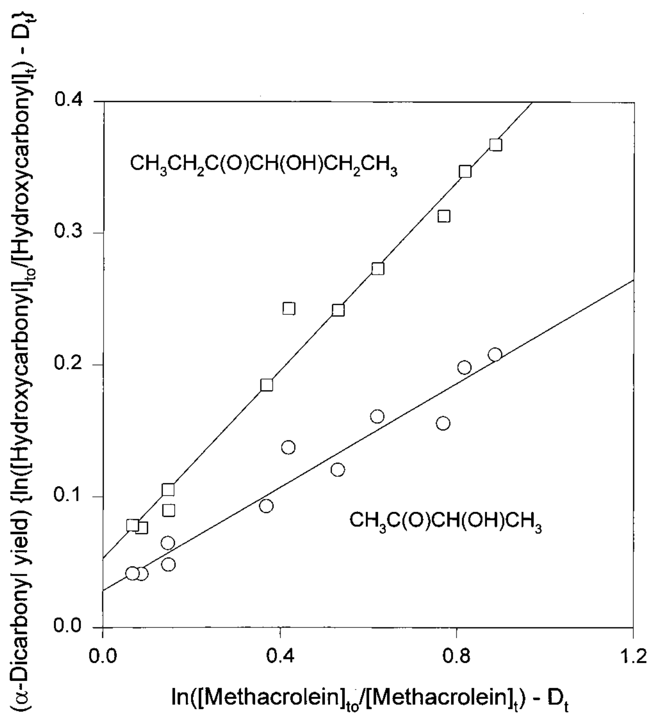

Figure 4. Plot of (yield of α-dicarbonyl){ln([hydroxycarbonyl]$_{t_0}$/[hydroxycarbonyl]$_t$) − D_t} against {ln([reference compound]$_{t_0}$/[reference compound]$_t$) − D_t} for the gas-phase reactions of the NO_3 radical with 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone, with methacrolein as the reference compound. Data from two experiments have been combined.

TABLE 3: Rate Constants k (cm^3 $molecule^{-1}$ s^{-1}) for the Gas-Phase Reactions of the Hydroxycarbonyls Studied with OH and NO_3 Radicals and O_3 at 296 ± 2 K, and Comparison of the OH Radical Reaction Rate Constants with Estimated Values

hydroxycarbonyl	$10^{19}k_{O_3}$	$10^{16}k_{NO_3}$[a]	$10^{12}k_{OH}$ measured	$10^{12}k_{OH}$ estimated[b]
$CH_3CH_2C(O)CH_2OH$	<1.1	<9	7.7 ± 1.7	3.8
$CH_3C(O)CH(OH)CH_3$	<1.1	6.5 ± 2.2[c]	10.3 ± 2.2	5.9
$CH_3C(O)CH_2CH_2OH$	<1.1	<22	8.1 ± 1.8	13.9
$CH_3C(O)CH(CH_3)CH_2OH$	<1.1	<22	16.2 ± 3.4	15.3
$(CH_3)_2C(OH)C(O)CH_3$	<1.1	<2	0.94 ± 0.37	1.3
$CH_3CH_2C(O)CH(OH)CH_2CH_3$	<1.1	12 ± 4[c]	15.1 ± 3.1	11.4

[a] Indicated errors include the estimated overall uncertainties in the rate constants for the reference compounds of ±30%. [b] As described by Kwok and Atkinson.[21] [c] These rate constants are those (k_4) measured for reaction pathway 4 [see text].

O_3 Rate Constants. The measured maximum losses of gas-phase hydroxycarbonyls in the presence of 3.44×10^{13} molecules cm^{-3} of O_3 over a period of 3.8 h were <2−3% in each case, and within the analytical uncertainties. Assuming maximum hydroxycarbonyl losses due to reaction with O_3 of 5% leads to upper limits to the rate constants at 296 ± 2 K of $k_3 < 1.1 \times 10^{-19}$ cm^3 $molecule^{-1}$ s^{-1} for each of these hydroxycarbonyls.

Discussion

The lack of observed reaction of the hydroxycarbonyls studied with O_3 is consistent with literature data for the reactions of O_3 with saturated aliphatic ketones and with saturated aliphatic compounds containing an −OH group.[13,23,24] Similarly, the rate constants derived here for the reactions of the NO_3 radical with the hydroxycarbonyls studied are consistent with expectations based on the reactions of the NO_3 radical with alcohols and glycol ethers,[14] in that reaction is expected to occur primarily (and almost totally) by H-atom abstraction from the C−H bonds of the −CH(OH)− and $-CH_2OH$ groups[14] [for example, by reaction 4]. Thus, $(CH_3)_2C(OH)C(O)CH_3$ is expected to be of low reactivity toward the NO_3 radical because of the lack of a C−H bond on the carbon to which the −OH group is attached, and our upper limit to the rate constant agrees with this expectation. Our room temperature rate constants for 1-hydroxy-2-butanone, 3-hydroxy-2-butanone, 1-hydroxy-3-butanone, 1-hydroxy-2-methyl-3-butanone, and 4-hydroxy-3-hexanone are similar to or slightly lower than those observed for 1- and 2-propanol, 1- and 2-butanol, 1-methoxy-2-propanol, and 2-butoxyethanol (which are in the range $(1.5-3.1) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}).[14] By analogy with the OH radical reactions,[21,25] the presence of the carbonyl group is expected to deactivate the C−H bonds attached to the carbon atom α to the >C=O group and activate those attached to the carbon atom β to the >C=O group. Our measured rate constants for the hydroxycarbonyls studied here qualitatively correlate with those for the corresponding OH radical reactions (Table 3), consistent with the expectation that both reactions proceed primarily (NO_3 radical reaction)[22] or to a large extent (OH radical reaction)[21] by H-atom abstraction from the C−H bonds of the −CH(OH)− and $-CH_2OH$ groups.[14,20−22] For the NO_3 radical reactions with 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone, the rate constants k_4 are close to the overall rate constants k_1, as expected,[14,22] and in Table 3 we cite the rate constants determined for the reaction pathway 4 as being the overall rate constants for these two hydroxycarbonyls. For 1-hydroxy-2-butanone, 1-hydroxy-3-butanone, and 1-hydroxy-2-methyl-3-butanone, the rate constants given in Table 3 are strictly upper limits (and are cited that way) because the measured disappearances of these hydroxycarbonyls could involve some wall losses in the presence of N_2O_5.

TABLE 4: Calculated Tropospheric Lifetimes for the Hydroxycarbonyls Studied Due to Their Gas-Phase Reactions with OH and NO_3 Radicals and O_3

hydroxycarbonyl	lifetime (days) due to reaction with OH radicals[a]	lifetime (days) due to reaction with NO_3 radicals[b]	lifetime (days) due to reaction with O_3[c]
$CH_3CH_2C(O)CH_2OH$	1.5	>51	>150
$CH_3C(O)CH(OH)CH_3$	1.1	71	>150
$CH_3C(O)CH_2CH_2OH$	1.4	>21	>150
$CH_3C(O)CH(CH_3)CH_2OH$	0.71	>21	>150
$(CH_3)_2C(OH)C(O)CH_3$	12	>230	>150
$CH_3CH_2C(O)CH(OH)CH_2CH_3$	0.77	39	>150

[a] With a 24-h average concentration of 1.0×10^6 molecules cm^{-3}.[26,27]
[b] With a 24-h average concentration of 2.5×10^8 molecules cm^{-3}.[22]
[c] With a 24-h average concentration of 7×10^{11} molecules cm^{-3}.[28]

Rate constants for the OH radical reactions with the hydroxycarbonyls calculated using the estimation method of Kwok and Atkinson[21] are in reasonable agreement (to within a factor of ∼2) with our measured rate constants (Table 3), suggesting that the estimation method gives a reasonably good indication of the reactive sites in these reactions. As is the case for the reactions of the OH radical with aliphatic alcohols and ketones,[1,2] the OH radical reactions proceed by H-atom abstraction from the various C−H bonds and (generally to a minor extent) from the O−H bond. As noted above, the OH radical reactions are expected to proceed mainly by H-atom abstraction from the C−H bonds of the −CH(OH)− and $-CH_2OH$ groups, with the H-atoms on these groups being activated by the presence of the −OH substituent group.[21] The α-dicarbonyl products observed from 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone clearly arise after H-atom abstraction from the activated tertiary H-atom of the −CH(OH)− group.

$$OH + RC(O)CH(OH)R \rightarrow H_2O + RC(O)\dot{C}(OH)R \quad (6)$$

$$RC(O)\dot{C}(OH)R + O_2 \rightarrow RC(O)C(O)R + HO_2 \quad (5)$$

Our observed α-dicarbonyl formation yields of 79 ± 14% for the formation of 2,3-butanedione from 3-hydroxy-2-butanone and 84 ± 7% for the formation of 3,4-hexanedione from 4-hydroxy-3-hexanone can be compared to the values of 87% and 55%, respectively, calculated by the estimation method.[21] While the calculated yield from 3-hydroxy-2-butanone agrees with the experimental data, that from 4-hydroxy-3-hexanone is significantly lower than the measured yield, suggesting a deficiency in the estimation method.

Our measured room temperature rate constants, combined with assumed ambient concentrations of OH radicals, NO_3 radicals, and O_3, are used to calculate the tropospheric lifetimes of the hydroxycarbonyls studied here with respect to gas-phase reactions with these reactive species. The lifetimes for the three reactions given in Table 4 were calculated using the following ambient tropospheric concentrations: OH radical, a 24-h average concentration of 1.0 × 10^6 molecules cm^{-3};[26,27] NO_3 radical, a 24-h average concentration of 2.5 × 10^8 molecules cm^{-3};[22] and O_3, a 24-h average concentration of 7 × 10^{11} molecules cm^{-3}.[28] The calculated lifetimes in Table 4 indicate that gas-phase reaction with the OH radical will dominate over reactions with the NO_3 radical and O_3. In addition, photolysis and/or wet and dry deposition may be significant tropospheric loss processes for these hydroxycarbonyls, and in particular wet and dry deposition of 3-hydroxy-3-methyl-2-butanone could be important given its long lifetime due to reaction with OH and NO_3 radicals and O_3 (Table 4). Orlando et al.[12] have investigated the photolysis of hydroxyacetone [$CH_3C(O)CH_2OH$] and shown that its absorption extends out to ~340 nm, although the quantum yield for photolysis is significantly less than unity[12] and results in a calculated tropospheric lifetime of >15 days.[12] Assuming that the photolysis data for hydroxyacetone[12] are representative of those for the hydroxyketones studied here, gas-phase reaction with the OH radical will then be the dominant tropospheric chemical loss process.

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