

Effect of water vapor concentration on the conversion of a series of 1,4-hydroxycarbonyls to dihydrofurans

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Abstract

It has previously been shown that in dry air 5-hydroxy-2-pentanone cyclizes and dehydrates to form 4,5-dihydro-2-methylfuran. A series of C₅–C₈ 1,4-hydroxycarbonyls were generated in situ from the OH radical-initiated reactions of their *n*-alkane precursors, and their dark decays in air investigated as a function of water vapor concentration. To remove any reactive dihydrofurans formed, in some experiments O₃ was added after 120–240 min and the 1,4-hydroxycarbonyls monitored for a further time period. In general, at low water vapor concentrations the 1,4-hydroxycarbonyl decayed in the dark in the absence of added O₃, with the concentration reaching a plateau indicating that an equilibrium between the 1,4-hydroxycarbonyl and the dihydrofuran had been attained. Addition of O₃ led to further decay of the hydroxycarbonyl. At higher water vapor concentrations, no significant decay of the 1,4-hydroxycarbonyl was observed in the absence of added O₃, but addition of O₃ resulted in a measurable decay of the 1,4-hydroxycarbonyl. Finally, at yet higher water vapor concentrations, no decay of the 1,4-hydroxycarbonyl was observed in the absence or presence of O₃. At >50% relative humidity at 296 K, the C₅–C₈ 1,4-hydroxycarbonyls examined here were stable against cyclization and dehydration.

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1. Introduction

Alkanes are important constituents of gasoline and vehicle exhaust [1] and account for ~50% of the non-methane volatile organic compounds observed in ambient air in urban areas [2]. In the atmosphere, alkanes react primarily with OH radicals [3], leading in the presence of NO to the formation of alkyl nitrates, carbonyls, 1,4-hydroxyalkyl nitrates, and 1,4-hydroxycarbonyls [4–8], with the formation of 1,4-hydroxycarbonyls accounting for ≥50% of the products from the ≥C₆ *n*-alkanes [7,8]. Reisen et al. [8] identified and quantified each of the predicted 1,4-hydroxycarbonyls formed from the OH radical-initiated reactions of *n*-pentane through *n*-octane. 5-Hydroxy-2-pentanone is the only commercially available 1,4-hydroxycarbonyl, and it reacts with OH radicals with a room temperature rate constant

of $(1.6 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [9]. More recently, Baker et al. [10] generated a series of C₅–C₈ 1,4-hydroxyketones in situ from their *n*-alkane precursors and obtained rate constants for their reactions with the OH radical.

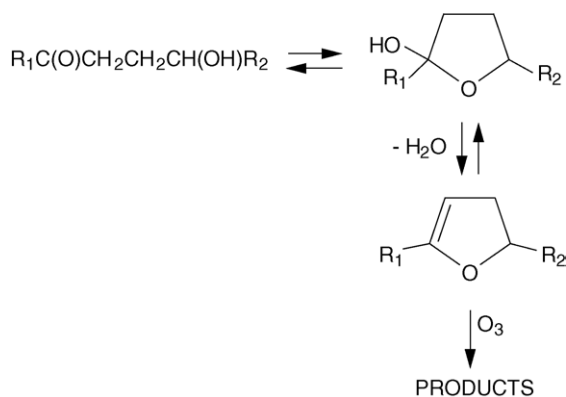
In reaction chambers in dry air or N₂, 5-hydroxy-2-pentanone cyclizes to form the hemi-acetal which then loses water to form 4,5-dihydro-2-methylfuran [11,12], as shown in Scheme 1. Consequently, both Reisen et al. [8] and Baker et al. [10] carried out their studies at ~50% relative humidity to avoid losses of the 1,4-hydroxycarbonyls due to cyclization and dehydration. 4,5-Dihydro-2-methylfuran, the cyclized dehydration product of 5-hydroxy-2-pentanone, is highly reactive towards OH and NO₃ radicals and O₃ [12], with measured rate constants (in units of cm³ molecule⁻¹ s⁻¹) of 2.2×10^{-10} , 1.7×10^{-10} and 3.5×10^{-15} , respectively [12].

Because of the high reactivity of the dihydrofurans, it is important to understand the conditions under which 1,4-hydroxycarbonyls will cyclize and dehydrate. Therefore, in this work we have generated a series of C₅–C₈ 1,4-hydroxycarbonyls in situ from their *n*-alkane precursors [10] and investigated their

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Scheme 1.

dark decays in air as a function of water vapor concentration. 1,4-Hydroxycarbonyls do not elute from gas chromatographic columns without prior derivatization [4,7,8] and solid phase microextraction (SPME) fibers pre-coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) were utilized to allow in situ on-fiber derivatization of the 1,4-hydroxycarbonyls for analysis as their oxime derivatives by gas chromatography with flame ionization detection (GC–FID) [8–10].

2. Experimental methods

Experiments were carried out in a ~ 70001 Teflon chamber at 296 ± 4 K and 735 Torr total pressure of purified air containing various water vapor concentrations up to 3.5×10^{17} molecule cm^{-3} (corresponding to 51% relative humidity at 296 K). The chamber is equipped with a Teflon-coated fan to ensure rapid mixing of the reactants during their introduction into the chamber, and has two parallel banks of blacklamps for irradiation. Hydroxyl (OH) radicals were generated by the photolysis of methyl nitrite (CH_3ONO) in air at wavelengths >300 nm [8,10], and NO was added to the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals.

The 1,4-hydroxycarbonyls, 5-hydroxy-2-pentanone and 4-hydroxypentanal from the *n*-pentane reaction; 5-hydroxy-2-hexanone, 6-hydroxy-3-hexanone and 4-hydroxyhexanal from the *n*-hexane reaction; 5-hydroxy-2-heptanone, 6-hydroxy-3-heptanone, 1-hydroxy-4-heptanone and 4-hydroxyheptanal from the *n*-heptane reaction; and 5-hydroxy-2-octanone, 6-hydroxy-3-octanone, 7-hydroxy-4-octanone and 4-hydroxyoctanal from the *n*-octane reaction [8] were generated in situ from the OH radical-initiated reactions of *n*-pentane through *n*-octane [8,10]. 5-Hydroxy-2-pentanone, which is commercially available, was also introduced into the chamber in separate experiments and its behavior investigated.

For in situ formation of the 1,4-hydroxycarbonyls from the irradiation of CH_3ONO –NO–*n*-alkane–air mixtures, the initial reactant concentrations (in molecule cm^{-3}) were: CH_3ONO and NO, $\sim 2.4 \times 10^{13}$ molecule cm^{-3} each; *n*-pentane, $\sim 2.4 \times 10^{13}$, *n*-hexane, $\sim 2.2 \times 10^{13}$, *n*-heptane, $\sim 1.7 \times 10^{13}$, or *n*-octane, $\sim 2.4 \times 10^{13}$, with one experiment with *n*-octane having initial CH_3ONO , NO and *n*-octane concentrations of $\sim 1.2 \times 10^{13}$ molecule cm^{-3} each. The CH_3ONO concentra-

tions were purposefully kept relatively low in order to avoid the formation of high concentrations of HCHO (from photolysis of methyl nitrite), which would be derivatized and it was thought might lead to depletion of the derivatizing agent. In each experiment, a single irradiation to generate in situ the 1,4-hydroxycarbonyls was carried out for 10–20 min at 20% of the maximum light intensity. 3-Pentanone, at a concentration of $\sim 2.4 \times 10^{12}$ molecule cm^{-3} , was added to the chamber after the irradiation as an internal standard to check on the analyses of the 1,4-hydroxycarbonyl products. In addition to in situ generation of 1,4-hydroxycarbonyls, a series of experiments were carried out in which 1.2×10^{12} molecule cm^{-3} of 5-hydroxy-2-pentanone and $\sim 2.4 \times 10^{12}$ molecule cm^{-3} of 3-pentanone (the latter as an internal standard) were introduced into the chamber. The purified air used as the diluent gas contained $\sim 3 \times 10^{16}$ molecule cm^{-3} of water vapor, and H_2O was added to those experiments conducted at higher water vapor concentrations. One experiment with 5-hydroxy-2-pentanone was conducted using cylinder N_2 as the diluent gas (by twice emptying the collapsible chamber and filling with cylinder N_2).

After the irradiation of CH_3ONO –NO–*n*-alkane–air mixtures and addition of 3-pentanone internal standard, or introduction of 5-hydroxy-2-pentanone plus 3-pentanone, the 1,4-hydroxycarbonyls were monitored in the dark for a period of up to 111–340 min. In several experiments, after this initial period of monitoring, O_3 (corresponding to a concentration of $\sim (0.6\text{--}3.0) \times 10^{13}$ molecule cm^{-3} in the chamber and sufficient to ensure that the remaining NO present was reacted away and that O_3 was present in the chamber) was added to the chamber to react with any dihydrofurans present and hence facilitate conversion of 1,4-hydroxycarbonyls to dihydrofurans (Scheme 1). The 1,4-hydroxycarbonyl concentrations were monitored for an additional 12–163 min (and in all but two cases for up to 70–163 min) after addition of O_3 to the chamber.

The 1,4-hydroxycarbonyls were identified and monitored using on-fiber derivatization with SPME [8–10,13]. A 65 μm polydimethylsiloxane/divinylbenzene PDMS/DVB fiber was coated with PFBHA [8–10,13], involving headspace extraction from 2 ml of an aqueous solution (~ 170 mg of PFBHA hydrochloride per 100 ml of water) in a 20 ml vial over a 30 min period with rapid agitation using a magnetic stirrer. The PFBHA coating of the fiber was carried out under nitrogen gas to minimize any acetone contamination from laboratory air. The coated fiber was then exposed to the reactants in the chamber for 5 min to form a PFBHA-carbonyl oxime [13]. For GC–FID analyses, the exposed fiber was then removed from the chamber and thermally desorbed for 2 min (injection port temperature at 250°C) onto a 30 m DB-1, 0.32 mm i.d., capillary column (3 μm phase thickness) held at 40°C and then temperature programmed at $20^\circ\text{C min}^{-1}$ to 160°C , then at 2°C min^{-1} to 240°C , and then at $20^\circ\text{C min}^{-1}$ to 300°C . GC–MS analyses of exposed fibers were carried out in a similar manner, using a Varian 2000 GC/MS/MS with isobutane chemical ionization.

The water vapor concentration was measured at the end of each experiment by drawing chamber air over a thermometer and measuring the dry and wet bulb temperatures to obtain the temperature and relative humidity of the chamber diluent

air, which was then converted to water vapor concentrations [14]. The uncertainty in the water concentration measurements is estimated to be $\pm 2 \times 10^{16}$ molecule cm^{-3} (i.e., $\pm 3\%$ relative humidity at 296 K). O_3 concentrations were measured by ultraviolet absorption using a Dasibi AH-1003 ozone analyzer.

The following chemicals, with their stated purities, were used: *n*-pentane (99+%), *n*-hexane (99+%), *n*-octane (99+%) and 3-pentanone (99+%), Aldrich Chemical Company; 5-hydroxy-2-pentanone (96%), TCI America; *n*-heptane (99+%), Mallinckrodt; and NO ($\geq 99.0\%$), Matheson Gas Products. Methyl nitrite was prepared as described by Taylor et al. [15] and stored at 77 K under vacuum. Ozone was generated as needed using a Welsbach T-408 ozone generator.

3. Results

Using gas chromatography–mass spectrometry for isomer-specific identifications, the 1,4-hydroxycarbonyl products formed from the OH radical-initiated reactions of *n*-pentane through *n*-octane have previously been reported from this laboratory [8]. Our present 1,4-hydroxycarbonyl assignments are based on this earlier work [8] and here we monitored their relative concentrations, as oxime derivatives, by GC–FID [10]. The oximes of the 1,4-hydroxycarbonyls exist as *Z*- and *E*-isomers,

with the ratio of the two isomer peaks being constant and characteristic for a particular 1,4-hydroxycarbonyl. For each of the 1,4-hydroxycarbonyls, one or both of the GC peaks of the oximes was used to monitor their concentration during the experiments, using only GC peaks that were not interfered with by other GC peaks.

The 1,4-hydroxycarbonyl concentrations were monitored in the dark after introduction into the chamber (5-hydroxy-2-pentanone) or after in situ generation, and in several experiments O_3 was added to the chamber after ~ 120 – 240 min and the hydroxycarbonyls monitored for an additional 12–163 min (70–163 min in all but two cases). 1,4-Hydroxycarbonyls are not expected to react with O_3 , with room temperature rate constants for reaction with O_3 of $< 10^{-20}$ cm^3 molecule $^{-1}$ s $^{-1}$ being anticipated by analogy with other saturated carbonyls [16] and alcohols [17]. Hence at the O_3 concentrations measured in the chamber after addition of O_3 ($\leq 1.2 \times 10^{13}$ molecule cm^{-3}), no losses of the 1,4-hydroxycarbonyls would occur due to reaction with O_3 . However, any dihydrofurans present would react rapidly. For example, the lifetime of 4,5-dihydro-2-methylfuran (the only dihydrofuran for which data are available [12]) would be ~ 0.4 min at an O_3 concentration of 1.2×10^{13} molecule cm^{-3} . Based on previous measurements of 5-hydroxy-2-pentanone using the present on-fiber SPME derivatization/GC–FID anal-

Table 1

Effect of water vapor concentration on the observed decays of 5-hydroxy-2-pentanone (introduced into the chamber) in the dark prior to and after addition of O_3 to the chamber

$10^{-16} \times [\text{H}_2\text{O}]$ (molecule cm^{-3}) ^a	Observed decays prior to O_3 addition and duration (min) ^b	Observed decays after O_3 addition and duration (min) ^{b,c}
N_2 diluent ^d	35% loss over initial 189 min, then constant over remaining 121 min	No addition
2	<20% decay (125 min)	32% decay over 163 min
~ 3	<20% decay (340 min)	No addition
~ 7	<20% decay (180 min)	No addition
12	<20% decay (120 min)	<20% decay (149 min)
21	<20% decay (232 min)	No addition
35	<20% decay (215 min)	No addition

^a Based on replicate measurements, the uncertainty in the water vapor concentration is estimated as $\pm 2 \times 10^{16}$ molecule cm^{-3} .

^b A measured loss of $\geq 20\%$ gas-phase 5-hydroxy-2-pentanone was used as the criterion for a “decay” of 5-hydroxy-2-pentanone, based on the analytical uncertainties using the SPME on-fiber derivatization/GC–FID analysis method (this work and [9]).

^c After addition of $(6\text{--}12) \times 10^{12}$ molecule cm^{-3} of O_3 to the chamber; duration is time monitored after O_3 addition.

^d Diluent gas was $>80\%$ cylinder N_2 and the water vapor concentration was likely significantly lower than the 3×10^{16} molecule cm^{-3} measured using the wet bulb/dry bulb thermometer.

Table 2

Effect of water vapor concentration on the observed decays of 4-hydroxypentanal and 5-hydroxy-2-pentanone (formed in situ) in the dark prior to and after addition of O_3 to the chamber

$10^{-16} \times [\text{H}_2\text{O}]$ (molecule cm^{-3}) ^a	Observed decays prior to O_3 addition and duration (min) ^b	Observed decays after O_3 addition and duration (min) ^{b,c}
3	<20% decays (185 min)	No addition
5	<20% decays (111 min)	36% decay of 5-hydroxy-2-pentanone over 156 min; <20% decay of 4-hydroxypentanal
17	<20% decays (247 min)	No addition
20	<20% decays (120 min)	No addition
28	<20% decays (247 min)	No addition

^a Measurement uncertainty in the water vapor concentration is estimated as $\pm 2 \times 10^{16}$ molecule cm^{-3} .

^b A measured loss of $\geq 20\%$ gas-phase hydroxycarbonyl was used as the criterion for a “decay”.

^c After addition of $(6\text{--}12) \times 10^{12}$ molecule cm^{-3} of O_3 to the chamber; duration is time monitored after O_3 addition.

Table 3
Effect of water vapor concentration on the observed decays of 4-hydroxyhexanal (4HHAL), 5-hydroxy-2-hexanone (5H2HO) and 6-hydroxy-3-hexanone (6H3HO), formed in situ, in the dark prior to and after addition of O₃ to the chamber

10 ⁻¹⁶ × [H ₂ O] (molecule cm ⁻³) ^a	Observed decays prior to O ₃ addition and duration (min) ^b	Observed decays after O ₃ addition and duration (min) ^{b,c}
3	<20% decays (285 min)	No addition
3	Decays of 5H2HO (29%) and 6H3HO (27%) over 232 min; <20% decay of 4HHAL	Decays of 4HHAL (25%), 5H2HO (additional 23%) and 6H3HO (additional 11%) over 105 min
9	<20% decays (175 min)	Decays of 5H2HO (48%) and 6H3HO (22%) over 162 min; <20% decay of 4HHAL
10	<20% decays (195 min)	No addition
16 (see Fig. 2)	<20% decays (173 min)	<20% decays (98 min)

^a Measurement uncertainty in the water vapor concentration is estimated as $\pm 2 \times 10^{16}$ molecule cm⁻³.

^b A measured loss of $\geq 20\%$ gas-phase hydroxycarbonyl was used as the criterion for a “decay”.

^c After addition of $(6-12) \times 10^{12}$ molecule cm⁻³ of O₃ to the chamber; duration is time monitored after O₃ addition.

ysis method, the measurement uncertainty at the two standard deviation level is $\sim \pm 20\%$ [9], and this is consistent with the reproducibility of the data obtained by Reisen et al. [8] and Baker et al. [10] for the 1,4-hydroxycarbonyls studied here. Hence we use a criteria that a 1,4-hydroxycarbonyl decay occurred if the measured 1,4-hydroxycarbonyl concentration decreased from its initial measurement by $\geq 20\%$.

Our observations are summarized in Tables 1–5 and selected examples are shown in Figs. 1 and 2. The three patterns of behavior observed are illustrated by Figs. 1 and 2, and are summarized in Fig. 3. At low water vapor concentrations, the 1,4-hydroxyketones decayed in the dark in the absence of added O₃, with the concentration generally leveling off and indicating that an equilibrium between the 1,4-hydroxycarbonyl and the dihydrofuran had been attained. This behavior is illustrated in Fig. 1 for 5-hydroxy-2-octanone, 6-hydroxy-3-

octanone and 7-hydroxy-4-octanone at a water vapor concentration of 3×10^{16} molecule cm⁻³.

The observations of Cavalli et al. [11] and Martin et al. [12], using in situ Fourier transform infrared (FT-IR) spectroscopy, of formation of 4,5-dihydro-2-methylfuran from 5-hydroxy-2-pentanone in the dark in N₂ and dry air shows that the dihydrofurans (and not just the cyclic hemi-acetals) are formed as the 1,4-hydroxycarbonyls decay. Formation of the dihydrofurans is also supported by our observations with added O₃. Addition of O₃ (such that the remaining NO was reacted away and O₃ was present in the chamber) led to additional decays of the 1,4-hydroxycarbonyls (and to a decrease in the measured O₃ concentration), with an equilibrium again being attained between the 1,4-hydroxycarbonyl and the dihydrofuran at a lower 1,4-hydroxycarbonyl concentration (Fig. 1). The data in Fig. 1 after addition of O₃ show that the lifetimes of 5-hydroxy-2-octanone

Table 4
Effect of water vapor concentration on the observed decays of 4-hydroxyheptanal (4HHAL), 5-hydroxy-2-heptanone (5H2HO), 6-hydroxy-3-heptanone (6H3HO) and 1-hydroxy-4-heptanone (1H4HO), formed in situ, in the dark prior to and after addition of O₃ to the chamber

10 ⁻¹⁶ × [H ₂ O] (molecule cm ⁻³) ^a	Observed decays prior to O ₃ addition and duration (min) ^b	Observed decays after O ₃ addition and duration (min) ^{b,c}
3	Decays of 5H2HO (33%), 6H3HO (29%) and 1H4HO (38%) over 141 min; <20% decay of 4HHAL	Decays of 4HHAL (25%), 5H2HO (additional 44%), 6H3HO (additional 21%) and 1H4HO (additional 38%) over 114 min
4	Decays of 5H2HO (27%) and 1H4HO (29%) over 180 min; <20% decays of 4HHAL or 6H3HO	Decays of 5H2HO (additional 47%), 6H3HO (42%) and 1H4HO (additional 37%) over 105 min; <20% decay of 4HHAL
9 (see Fig. 2)	<20% decays (178 min)	Decays of 5H2HO (46%), 6H3HO (33%) and 1H4HO (37%) over 99 min; 20% decay of 4HHAL
16	<20% decays (118 min)	Decays of 5H2HO (51%), 6H3HO (46%) and 1H4HO (52%) over 153 min; <20% decay of 4HHAL
21	<20% decays (120 min)	Decay of 5H2HO (28%) over 123 min; <20% decays of 4HHAL, 6H3HO and 1H4HO
32	<20% decays (125 min)	Decay of 5H2HO (31%) over 98 min; <20% decays of 4HHAL, 6H3HO and 1H4HO
32	<20% decays (115 min)	<20% decays (148 min)
34	<20% decays (175 min)	No addition

^a Measurement uncertainty in the water vapor concentration is estimated as $\pm 2 \times 10^{16}$ molecule cm⁻³.

^b A measured loss of $\geq 20\%$ gas-phase hydroxycarbonyl was used as the criterion for a “decay”.

^c After addition of $(6-12) \times 10^{12}$ molecule cm⁻³ of O₃ to the chamber; duration is time monitored after O₃ addition.

Table 5

Effect of water vapor concentration on the observed decays of 4-hydroxyoctanal (4HOAL), 5-hydroxy-2-octanone (5H2OO), 6-hydroxy-3-octanone (6H3OO) and 7-hydroxy-4-octanone (7H4OO), formed in situ, in the dark prior to and after addition of O₃ to the chamber

10 ⁻¹⁶ × [H ₂ O] (molecule cm ⁻³) ^a	Observed decays prior to O ₃ addition and duration (min) ^b	Observed decays after O ₃ addition and duration (min) ^{b,c}
3	Decays of 5H2OO (70%), 6H3OO (20%) and 7H4OO (79%) over 154 min; <20% decay of 4HOAL	No addition
3	Decay of 7H4OO (33%) over 218 min; <20% decays of 4HOAL, 5H2OO and 6H3OO	No addition
3 (see Fig. 1)	Decays of 5H2OO (48%) and 7H4OO (73%) over 180 min; <20% decays of 4HOAL and 6H3OO	Decays of 5H2OO (additional 32%), 6H3OO (26%) and 7H4OO (additional 14%) over 70 min; <20% decay of 4HOAL
8	Decays of 5H2OO (37%) and 7H4OO (68%) over 147 min; <20% decays of 4HOAL and 6H3OO	Decays of 4HOAL (41%), 5H2OO (additional 37%), 6H3OO (20%) and 7H4OO (additional 18%) over 120 min
11	Decay of 7H4OO (21%) over 247 min; <20% decays of 4HOAL, 5H2OO and 6H3OO	No addition
16	Decays of 4HOAL (20%) and 7H4OO (28%) over 260 min; <20% decays of 5H2OO and 6H3OO	No addition
16	Decay of 7H4OO (23%) over 142 min; <20% decays of 4HOAL, 5H2OO and 6H3OO	Decay of 7H4OO (additional 10%) over 12 min; <20% decays of 4HOAL, 5H2OO and 6H3OO
21	Decay of 7H4OO (22%) over 148 min; <20% decays of 4HOAL, 5H2OO and 6H3OO	Decays of 4HOAL (29%), 5H2OO (57%) and 7H4OO (additional 53%) over 145 min; <20% decay of 6H3OO
23	<20% decays over 241 min	No addition
24	Decay of 7H4OO (24%) over 123 min; <20% decays of 4HOAL, 5H2OO and 6H3OO	Decays of 4HOAL (44%), 5H2OO (62%), 6H3OO (24%) and 7H4OO (additional 59%) over 156 min
28	Decay of 7H4OO (23%) over 122 min; <20% decays of 4HOAL, 5H2OO and 6H3OO	Decays of 5H2OO (42%) and 7H4OO (additional 33%) over 140 min; <20% decays of 4HOAL and 6H3OO
33	<20% decays (202 min)	No addition
34	<20% decays (160 min)	<20% decays (13 min)

^a Measurement uncertainty in the water vapor concentration is estimated as $\pm 2 \times 10^{16}$ molecule cm⁻³.

^b A measured loss of $\geq 20\%$ gas-phase hydroxycarbonyl was used as the criterion for a "decay".

^c After addition of $(6-12) \times 10^{12}$ molecule cm⁻³ of O₃ to the chamber; duration is time monitored after O₃ addition.

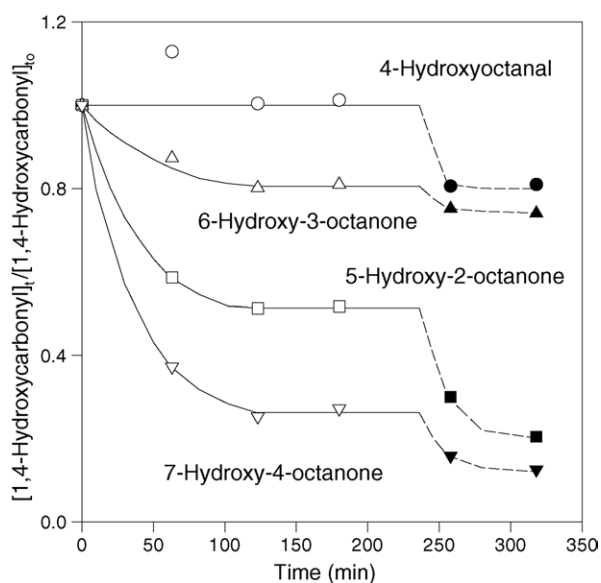


Fig. 1. Plots of $[1,4\text{-hydroxycarbonyl}]_t/[1,4\text{-hydroxycarbonyl}]_{t_0}$ against time for 4-hydroxyoctanal, 5-hydroxy-2-octanone, 6-hydroxy-3-octanone and 7-hydroxy-4-octanone formed in situ by reaction of OH radicals with *n*-octane and monitored in the dark (open symbols) and after addition of $\sim 6 \times 10^{12}$ molecule cm⁻³ of O₃ (filled symbols). The water vapor concentration was 3×10^{16} molecule cm⁻³. The solid lines (prior to O₃ addition) and dashed lines (after O₃ addition) are for illustrative purposes.

and 7-hydroxy-4-octanone with respect to conversion to the dihydrofurans are ~ 10 min, assuming that the dihydrofurans were removed rapidly by reaction with O₃ and that the rate-determining step was conversion of the 1,4-hydroxycarbonyl to its corresponding dihydrofuran.

The second pattern of behavior is illustrated by the 1,4-hydroxycarbonyls formed from the OH radical reaction with *n*-heptane and shown in Fig. 2. As shown in Fig. 3, at intermediate water vapor concentrations no significant decays of 1,4-hydroxycarbonyls were observed in the absence of added O₃, but addition of O₃ resulted in measurable decays. This behavior can be explained by the equilibrium between the 1,4-hydroxycarbonyl and dihydrofuran being largely towards the 1,4-hydroxycarbonyl, with addition of O₃ reacting with the small equilibrium concentration of dihydrofuran at a rate sufficient to result in decay of the 1,4-hydroxycarbonyl to maintain the equilibrium.

Finally, the third behavior observed was no decay in the absence or presence of O₃, indicating that under these conditions the 1,4-hydroxycarbonyl \leftrightarrow dihydrofuran equilibrium so favored the 1,4-hydroxycarbonyl that insufficient dihydrofuran was present to result in any significant loss of (dihydrofuran + 1,4-hydroxycarbonyl). This behavior is shown in Fig. 2 by the 1,4-hydroxycarbonyls formed from the *n*-hexane reaction at a water concentration of 1.6×10^{17} molecule cm⁻³, as well as by 4-hydroxyheptanal (Fig. 2) and 4-hydroxyoctanal (Fig. 1).

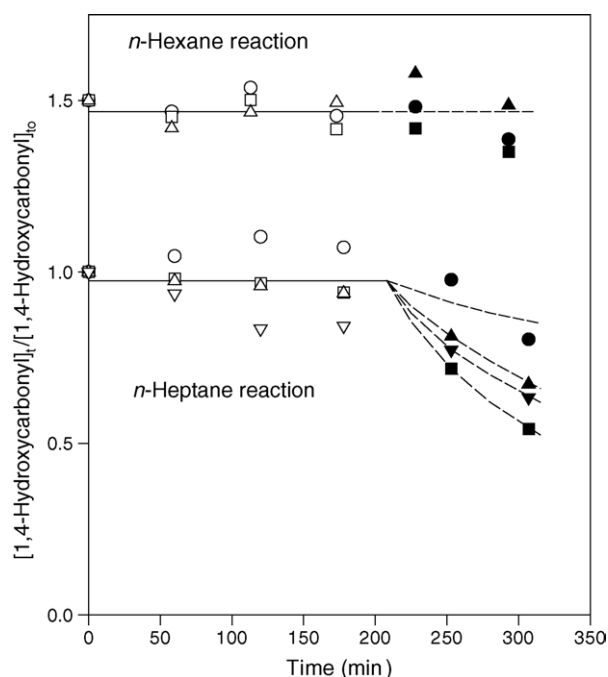


Fig. 2. Plots of $[1,4\text{-hydroxycarbonyl}]_t/[1,4\text{-hydroxycarbonyl}]_0$ against time for: (●)—4-hydroxyhexanal and 4-hydroxyheptanal; (■)—5-hydroxy-2-hexanone and 5-hydroxy-2-heptanone; (▲)—6-hydroxy-3-hexanone and 6-hydroxy-3-heptanone; (▼)—1-hydroxy-4-heptanone formed in situ by reaction of OH radicals with *n*-hexane and *n*-heptane and monitored in the dark (open symbols) and after addition of $\sim 1.2 \times 10^{13}$ molecule cm^{-3} of O_3 (filled symbols). The water vapor concentrations were 1.6×10^{17} molecule cm^{-3} for the *n*-hexane reaction and 9×10^{16} molecule cm^{-3} for the *n*-heptane reaction. The data for 4-hydroxyhexanal and the hydroxyhexanones have been displaced vertically by 0.5 units for clarity. The solid lines (prior to O_3 addition) and dashed lines (after O_3 addition) are for illustrative purposes.

The effects of water vapor concentration on the stability of the 1,4-hydroxycarbonyls are summarized in Fig. 3. The formation yields of the 4-hydroxyaldehydes from the OH radical-initiated reactions of *n*-pentane through *n*-octane reactions are low [8] and the GC peaks of their oximes were small making our data for the 4-hydroxyaldehydes somewhat less certain than those for the 1,4-hydroxyketones. However, as seen in Fig. 3, no decays for 4-hydroxypentanal, 4-hydroxyhexanal, 4-hydroxyheptanal and 4-hydroxyoctanal were observed in the absence of O_3 at any water vapor concentration used (the single apparent exception, the measured 20% decrease in the 4-hydroxyoctanal concentration over a 260 min period at 1.6×10^{17} molecule cm^{-3} of water vapor in the absence of O_3 (Table 5) was not confirmed by a replicate experiment at the same water vapor concentration, nor by experiments at lower water vapor concentrations). The stability of the hydroxyaldehydes may be due to the dihydrofuran formed being a 5-alkyl-4,5-dihydrofuran ($\text{R}_1 = \text{H}$ in Scheme 1) whereas the 1,4-hydroxyketones all form 4,5-dihydro-2-alkylfurans ($\text{R}_1 = \text{alkyl}$ in Scheme 1).

Defining an equilibrium constant K for the 1,4-hydroxycarbonyl \leftrightarrow dihydrofuran + H_2O interconversion (Scheme 1) as $K = ([\text{dihydrofuran}][\text{H}_2\text{O}]/[1,4\text{-hydroxycarbonyl}])$, then the data obtained in the absence of added O_3 can be used to derive values of K for certain of the 1,4-hydroxycarbonyls, assuming that the measured decrease in the 1,4-hydroxycarbonyl con-

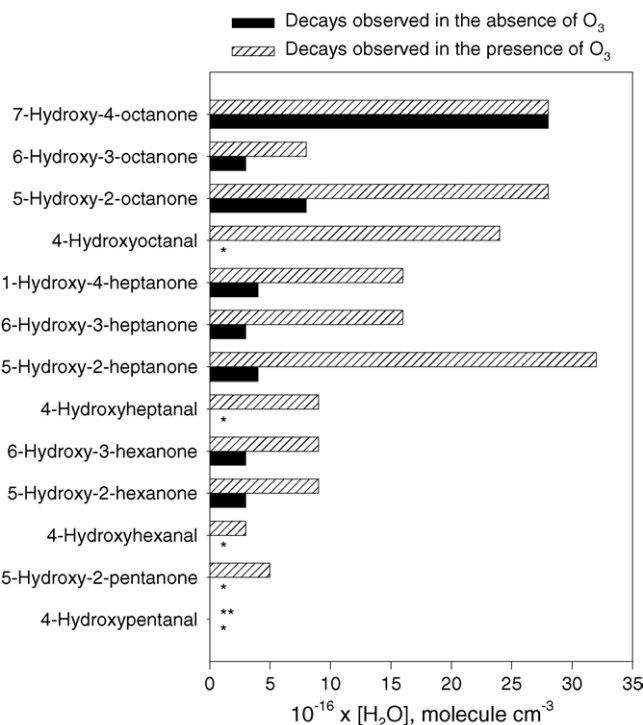


Fig. 3. Water vapor concentrations at which individual 1,4-hydroxycarbonyls exhibited decays in the dark in the absence of added O_3 (black bars) and decays in the presence of added O_3 (striped bars). (*) No decay observed in the absence of O_3 , even at the minimum water vapor concentration used of 3×10^{16} molecule cm^{-3} [for 5-hydroxy-2-pentanone decay was observed in dry N_2 (see Table 1)]; (**) no decay observed in the presence of O_3 , even at the minimum water vapor used of 3×10^{16} molecule cm^{-3} .

centration is accompanied by a stoichiometric formation of the corresponding dihydrofuran. In many cases, equilibrium was not attained prior to the end of the experiment or the addition of O_3 , and hence only lower limits to K could then be derived. The equilibrium constants K at 296 ± 4 K obtained from the data summarized in Tables 3–5 are: for 5-hydroxy-2-hexanone, $\geq 1 \times 10^{16}$ molecule cm^{-3} (from 1 experiment at $[\text{H}_2\text{O}] = 3 \times 10^{16}$ molecule cm^{-3}); for 6-hydroxy-3-hexanone, $\geq 1 \times 10^{16}$ molecule cm^{-3} (from 1 experiment at $[\text{H}_2\text{O}] = 3 \times 10^{16}$ molecule cm^{-3}); for 1-hydroxy-4-heptanone, $\geq 1.5 \times 10^{16}$ molecule cm^{-3} (from 2 experiments at $[\text{H}_2\text{O}] = (3\text{--}4) \times 10^{16}$ molecule cm^{-3}); for 5-hydroxy-2-heptanone, $\geq 1.5 \times 10^{16}$ molecule cm^{-3} (from 2 experiments at $[\text{H}_2\text{O}] = (3\text{--}4) \times 10^{16}$ molecule cm^{-3}); for 6-hydroxy-3-heptanone, $\geq 1 \times 10^{16}$ molecule cm^{-3} (from 1 experiment at $[\text{H}_2\text{O}] = 3 \times 10^{16}$ molecule cm^{-3}); for 5-hydroxy-2-octanone, $\sim 5 \times 10^{16}$ molecule cm^{-3} (from three experiments at $[\text{H}_2\text{O}] = (3\text{--}8) \times 10^{16}$ molecule cm^{-3}); for 6-hydroxy-3-octanone, $\sim 7 \times 10^{15}$ molecule cm^{-3} (from two experiments at $[\text{H}_2\text{O}] = 3 \times 10^{16}$ molecule cm^{-3}); and for 7-hydroxy-4-octanone, $\sim 8 \times 10^{16}$ molecule cm^{-3} , with an uncertainty of a factor of ~ 2 (from 10 experiments at $[\text{H}_2\text{O}] = (3\text{--}28) \times 10^{16}$ molecule cm^{-3}). For the other 1,4-hydroxycarbonyls monitored here, $K < 7 \times 10^{15}$ molecule cm^{-3} at 296 ± 4 K.

The other effect of structure on the stability of the 1,4-hydroxyketones as a function of water vapor that is evident

from Fig. 3 is a trend for the decays of the 1,4-hydroxyketones (i.e., interconversion to the dihydrofuran species) to occur until progressively higher water vapor concentrations as the carbon number of the 1,4-hydroxyketone increases, although there are also obvious differences between 1,4-hydroxyketones of the same carbon number. The decay trends shown in Fig. 3, and the stability of the 4-hydroxyaldehydes at $\geq 5\%$ relative humidity at room temperature, are consistent with the observations of Reisen et al. [8] and Baker et al. [10]. Specifically, Reisen et al. [8] observed a decrease in the concentrations of 1,4-hydroxyheptanones and 1,4-hydroxyoctanones between replicate analyses at $\sim 3 \times 10^{16}$ molecule cm^{-3} of water vapor ($\sim 5\%$ relative humidity), but not at $\sim 3.4 \times 10^{17}$ molecule cm^{-3} of water vapor ($\sim 50\%$ relative humidity) at 296 K. Baker et al. [10], in irradiated $\text{CH}_3\text{ONO}-\text{NO}-n\text{-alkane}$ -air mixtures carried out to large extents of reaction, observed enhanced losses of 1,4-hydroxyhexanones over those anticipated for reaction with OH radicals at $\sim 3 \times 10^{16}$ molecule cm^{-3} of water vapor, but not at $\sim 3.4 \times 10^{17}$ molecule cm^{-3} of water vapor, and attributed the enhanced decays to conversion of the 1,4-hydroxyhexanones to dihydrofurans followed by rapid reaction of the dihydrofurans with OH radicals. Fig. 3 suggests that under the conditions of the Baker et al. [10] study at $\sim 50\%$ relative humidity, some of the hydroxyheptanones and hydroxyoctanones would decay via conversion to dihydrofurans which would be rapidly removed by reaction, and this is consistent with the observations of Baker et al. [10] of enhanced losses of the three 1,4-hydroxyoctanones and of 7-hydroxy-4-heptanone and 5-hydroxy-2-heptanone.

Clearly, the 1,4-hydroxycarbonyls, and especially the larger 1,4-hydroxyketones, can undergo cyclization and loss of water to form highly reactive alkyl-substituted dihydrofurans at water vapor concentrations representative of the ambient atmosphere. The alkyl-substituted dihydrofurans are approximately an order of magnitude more reactive towards OH radicals than are their precursor 1,4-hydroxyketones, and also react rapidly with NO_3 radicals and O_3 [12], with estimated atmospheric lifetimes of < 1 h during both day time and night time [12]. This additional dark conversion reaction of 1,4-hydroxyketones combined with the subsequent reactions of the resulting, more reactive dihydrofurans needs to be considered in modeling the atmospheric behavior and ozone-forming potential of alkanes. Indeed, the formation and subsequent reactions of the dihydrofurans appear to be involved in production of secondary organic aerosol [18]. Thus, Gong et al. [18] postulate that nitrate-substituted 1,4-hydroxycarbonyls formed after initial reaction of NO_3 radicals

with linear alkenes undergo cyclization and dehydration to form nitrate-substituted dihydrofurans which react further to form multi-functional, aerosol-phase, compounds.

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