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1,4-Hydroxycarbonyl Products of the OH Radical Initiated Reactions of C₅—C₈ *n*-Alkanes in the Presence of NO

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Alkanes account for ~50% of nonmethane organic compounds present in urban atmospheres. Previous studies have shown that hydroxycarbonyls are important products of the OH radical initiated reactions of ≥C₅ *n*-alkanes, but isomer-specific identifications and quantifications of these products have not been carried out. In this work, we have used solid-phase microextraction fibers precoated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine for on-fiber derivatization of carbonyl-containing compounds with subsequent analyses by combined gas chromatography–mass spectrometry (GC-MS) and GC with flame ionization detection (GC-FID). GC-MS analyses showed the presence of the oximes of 5-hydroxy-2-pentanone and 4-hydroxy-pentanal 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-hydroxy-octanal from the *n*-octane reaction. The formation yields of these 1,4-hydroxycarbonyls were determined from GC-FID analyses. By use of the yields of 1,4-hydroxycarbonyls formed from *n*-hexane, *n*-heptane, and *n*-octane at 50% relative humidity (and those from *n*-pentane at both 5 and 50% relative humidity), then formation of 1,4-hydroxycarbonyls accounts for 54% of the reaction products from *n*-pentane, 57% from *n*-hexane, 51% from *n*-heptane, and 53% from *n*-octane. Combined with previously measured yields of carbonyls, alkyl nitrates, and hydroxyalkyl nitrates, we can now account for approximately 74–118% of the products formed from the *n*-pentane through *n*-octane reactions.

Introduction

Alkanes are important constituents of gasoline and vehicle exhaust (*1*) and comprise ~50% of the nonmethane organic compounds observed in ambient air in urban areas (*2*). In the atmosphere, alkanes react primarily with OH radicals (*3*,

4), leading to the formation of alkyl nitrates, carbonyls, hydroxyalkyl nitrates, and hydroxycarbonyls (*5–8*), as shown in Scheme 1 for H-atom abstraction from the 2 position in *n*-pentane, with the formation of hydroxycarbonyls appearing to account for the majority of the products for the ≥C₆ *n*-alkanes (*5–8*). However, this class of carbonyl-containing compound does not elute from gas chromatographic columns without prior derivatization (*5–9*), and isomer-specific identification and quantification of the hydroxycarbonyls formed from the OH radical initiated reactions of alkanes have not previously been achieved (*4, 6–8*), other than for the formation of 5-hydroxy-2-hexanone from the *n*-hexane reaction (*5*).

In this work, we have used solid-phase microextraction (SPME) fibers (*10*) coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) to allow in situ derivatization of hydroxycarbonyls for analysis as their oxime derivatives (*9, 11–16*) by gas chromatography with flame ionization detection (GC-FID) and combined GC–mass spectrometry (GC-MS). We have identified the hydroxycarbonyl products formed from the gas-phase reactions of OH radicals with *n*-pentane through *n*-octane in the presence of NO. Apart from 5-hydroxy-2-pentanone, the 1,4-hydroxycarbonyls observed as reaction products are not commercially available, and hence relative GC-FID response factors for the analysis (as the oxime derivatives) of the hydroxycarbonyls have been estimated (*15*) and used here for quantification.

Experimental Methods

Experiments were carried out in a ~7000-L Teflon chamber at 296 ± 2 K and 740 Torr total pressure of purified air at ~5 and ~50% relative humidity. 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 (CH₃ONO) in air at wavelengths >300 nm (*6–9, 14–16*), and NO was added to the reactant mixtures to suppress the formation of O₃ and NO₃ radicals.

The initial reactant concentrations (in molecule cm⁻³) were: CH₃ONO, ~2.4 × 10¹³; NO, ~2.4 × 10¹³; and alkane, (2.40–2.84) × 10¹³ for the *n*-pentane and *n*-hexane reactions; CH₃ONO, ~1.7 × 10¹³; NO, ~1.7 × 10¹³; and *n*-heptane, (1.72–1.92) × 10¹³ for the *n*-heptane reactions; and CH₃ONO, ~1.2 × 10¹³; NO, ~1.2 × 10¹³; and *n*-octane, (1.28–1.42) × 10¹³ for the *n*-octane reactions. In each experiment, a single irradiation was carried out at 20% of the maximum light intensity for 10–20 min, resulting in 9–31% consumption of the initially present alkane. 3-Pentanone, at a concentration of ~(7–8) × 10¹² molecule cm⁻³, was added to the chamber after the irradiation as an internal standard for quantification of the hydroxycarbonyl products.

For the analysis of *n*-hexane, *n*-heptane, *n*-octane, and the 3-pentanone internal standard, 100-cm³ gas samples were collected from the chamber onto Tenax-TA solid adsorbent with subsequent thermal desorption at ~250 °C onto a 30-m DB-1701 megabore column held at −40 °C and then temperature programmed to 250 °C at 8 °C min⁻¹. Analyses of *n*-pentane were carried out with gas samples being collected in a 100-cm³ all-glass, gastight syringe and introduced via a gas sampling loop onto a 30-m DB-5 megabore column initially held at −25 °C and then temperature programmed to 250 °C at 8 °C min⁻¹.
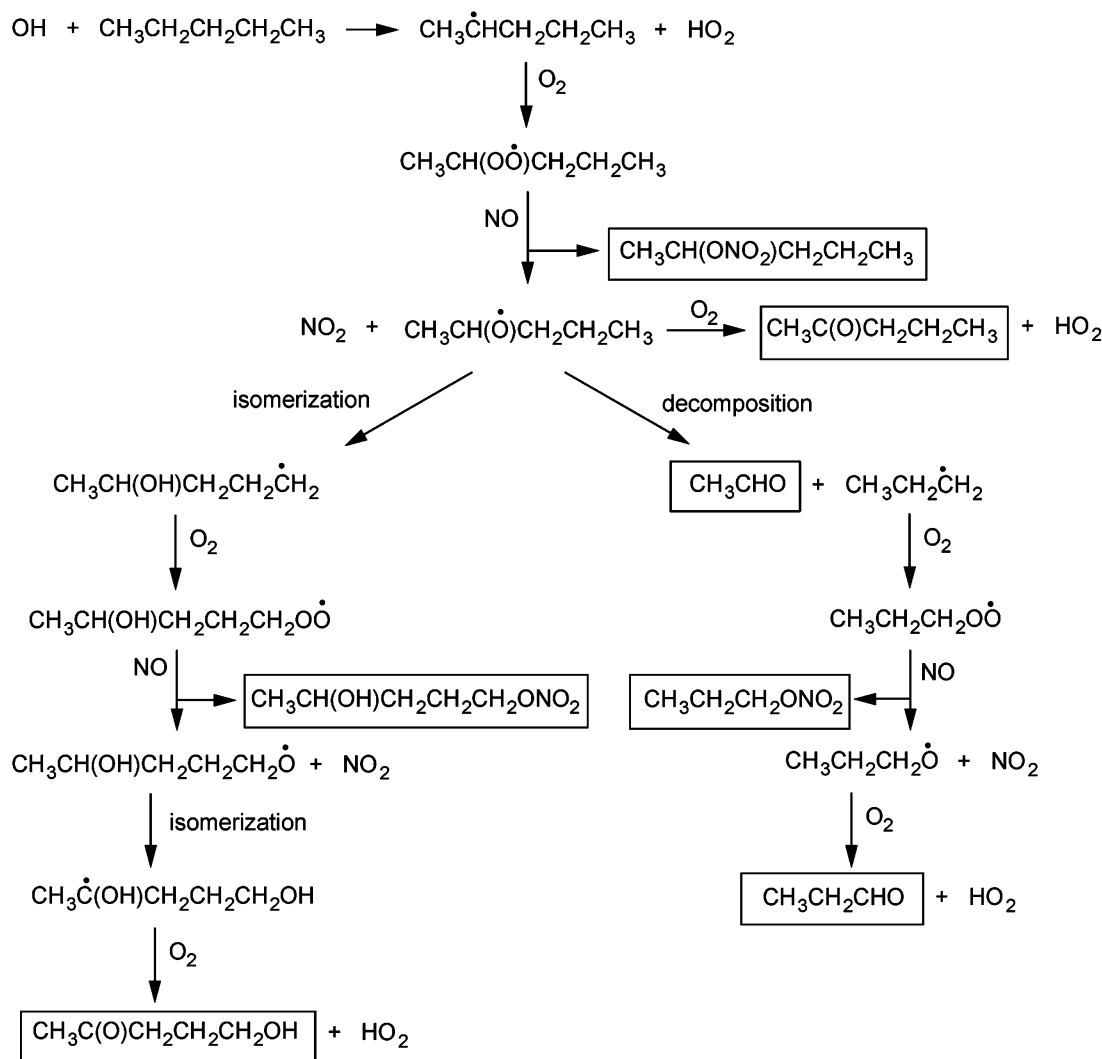
Carbonyl-containing products were identified by using on-fiber derivatization with SPME (*9, 11–16*). A 65-μm poly-(dimethylsiloxane)/divinylbenzene (PDMS/DVB) fiber was

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SCHEME 1

$$OH + CH_3CH_2CH_2CH_2CH_3 \longrightarrow CH_3\dot{C}HCH_2CH_2CH_3 + HO_2$$

$$\downarrow O_2$$

$$CH_3CH(O\dot{O})CH_2CH_2CH_3$$

$$\downarrow NO \longrightarrow \boxed{CH_3CH(ONO_2)CH_2CH_2CH_3}$$

$$NO_2 + CH_3CH(\dot{O})CH_2CH_2CH_3 \xrightarrow{O_2} \boxed{CH_3C(O)CH_2CH_2CH_3} + HO_2$$

isomerization (left arrow)   decomposition (right arrow)

$$CH_3CH(OH)CH_2CH_2\dot{C}H_2$$ | $$\boxed{CH_3CHO} + CH_3CH_2\dot{C}H_2$$

$$\downarrow O_2$$ | $$\downarrow O_2$$

$$CH_3CH(OH)CH_2CH_2CH_2O\dot{O}$$ | $$CH_3CH_2CH_2O\dot{O}$$

$$NO \downarrow \longrightarrow \boxed{CH_3CH(OH)CH_2CH_2CH_2ONO_2}$$ | $$\boxed{CH_3CH_2CH_2ONO_2} \longleftarrow \downarrow NO$$

$$CH_3CH(OH)CH_2CH_2CH_2\dot{O} + NO_2$$ | $$CH_3CH_2CH_2\dot{O} + NO_2$$

$$\downarrow \text{isomerization}$$ | $$\downarrow O_2$$

$$CH_3\dot{C}(OH)CH_2CH_2CH_2OH$$ | $$\boxed{CH_3CH_2CHO} + HO_2$$

$$\downarrow O_2$$

$$\boxed{CH_3C(O)CH_2CH_2CH_2OH} + HO_2$$

coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) (*15*). This involved headspace extraction from 4 mL of an aqueous solution (typically ∼20 mg mL^{-1} of PFBHA hydrochloride) in a 20-mL vial over a 30-min period, with 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 chamber contents for 5 min to form a PFBHA−carbonyl oxime according to the following equation (note that *Z* and *E* isomers may be formed).

PFBHA   Carbonyl

PFBHA-Carbonyl Oxime
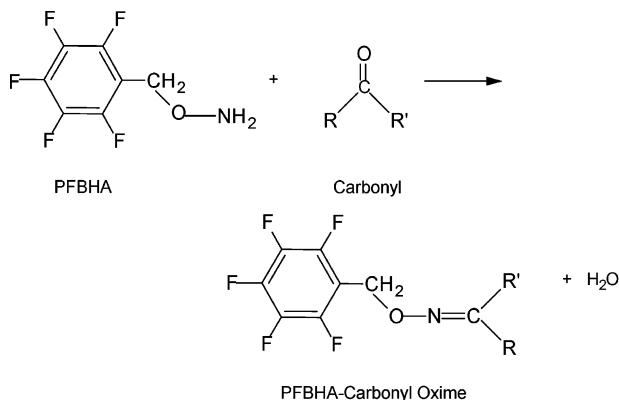
For GC-FID analyses, the exposed fiber was removed from the chamber and thermally desorbed in the 250 °C injection port of the gas chromatograph onto a 30-m DB-1 megabore column initially held at 40 °C, temperature programmed at 20 °C min^{-1} to 160 °C, then at 2 °C min^{-1} to 240 °C, and finally at 20 °C min^{-1} to 300 °C. Typically, two replicate analyses were carried out, with the time between the two replicate analyses being 71−166 min (and generally 71−87 min).

To ensure correct identification of the derivatized hydroxycarbonyl peaks quantified by GC-FID, the DB-1 column was first installed in an ion trap GC-MS and the individual hydroxycarbonyl isomers were distinguished on the basis of their mass spectra. GC-MS analyses of the coated fibers exposed to the chamber reaction products were carried out using a Varian 2000 GC/MS/MS ion trap with isobutane chemical ionization (CI). A range of sampling times was used to collect products from the chamber for GC-MS analysis, with generally shorter fiber coating times than were used for the FID analyses, where reproducible sampling by maximal fiber coating with the derivatization agent was sought.

A derivatized authentic standard of 5-hydroxy-2-pentanone was also analyzed by isobutane CI and electron impact (EI) MS using the Varian 2000 GC/MS/MS and also by EI using an HP-5971A GC-MSD quadrupole instrument. The 5-hydroxy-2-pentanone was analyzed either by taking a headspace sample with a PFBHA-coated fiber or by sampling from the Teflon chamber after introducing 5-hydroxy-2-pentanone into the chamber.
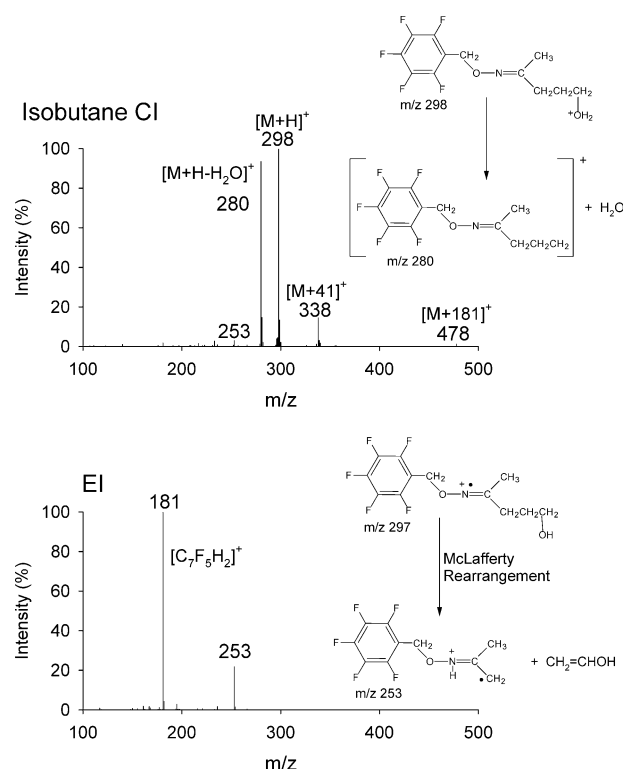
FIGURE 1. Isobutane CI mass spectrum from an ion trap (upper) and EI mass spectrum from a quadrupole instrument (lower) of the 5-hydroxy-2-pentanone oxime derivative.

The following chemicals, with their stated purities, were used: *n*-pentane (99+%), *n*-hexane (99+%), *n*-octane (99+%), 3-pentanone (99+%), and PFBHA hydrochloride (98+%), Aldrich Chemical Co.; *n*-heptane (99+%), Mallinckrodt; 5-hydroxy-2-pentanone (96%), TCI Americas; and NO (≥99.0%), Matheson Gas Products. Methyl nitrite was prepared as described by Taylor et al. (*17*) and stored at 77 K under vacuum.

Results

Identification of Hydroxycarbonyl Products. An authentic standard of 5-hydroxy-2-pentanone was derivatized using a PFBHA-coated fiber to obtain the GC-MS ion trap isobutane CI mass spectrum of the 5-hydroxy-2-pentanone oxime derivative shown in Figure 1, together with the EI spectrum from a quadrupole GC-MSD system. By use of the ion trap,

isobutane CI spectra typically give the protonated molecule $[M + H]^+$ as the base peak and a smaller adduct ion at $[M + 41]^+$ (*15*). For compounds containing an OH functional group, a loss of H_2O is common in ion-trap CI mass spectra using isobutane (*15*) and methane (*18*) as reagent gases, and this fragment may be the base peak in the spectrum (note the $[M + H - H_2O]^+$ ion at m/z 280 in Figure 1). Ion-trap analyses of PFBHA oxime derivatives also often exhibit small $[M + 181]^+$ adducts, especially at higher analyte concentrations (*18*). The presence of these ions may, therefore, be used to identify the compound as an hydroxycarbonyl and to determine its molecular weight.

As shown in Figure 1, a molecular ion is often absent (or minor) in the EI spectra of PFBHA oximes of carbonyls, and for this reason CI has often been utilized. The m/z 181 pentafluorotropylium fragment ion $[C_7F_5H_2]^+$ is generally the base peak in the EI spectra of PFBHA oximes and has been employed to classify carbonyl-containing compounds (*18*, *19*). As shown in Figure 1, there is a prominent diagnostic fragment ion in the EI spectra at m/z 253, and a small m/z 253 ion peak is also present in the CI spectrum. Hydrogen rearrangement through a six-membered ring intermediate has been reported for oximes, and this "McLafferty rearrangement" is anticipated to be the origin of the m/z 253 peak in the EI spectrum (*20*). The ion-trap EI spectra matched the EI spectrum shown in Figure 1 only at low concentrations, and at higher concentrations ions at m/z 298 and 280 became abundant, presumably as the result of self-chemical ionization (*21*). When using pentafluorobenzyl alcohol as a CI reagent, Charles and co-workers (*22*, *23*) have reported specific fragment ions from the reagent-promoted charge exchange or hydride abstraction in addition to the dominant proton addition. Therefore, the origin of the m/z 253 ion in the CI spectrum is suggested to be from a McLafferty rearrangement of the charge-transfer ionized oxime and may be utilized to identify the position of the carbonyl.

Le Lacheur and co-workers (*19*) reported that, for EI spectra, fragment ions at m/z 239 were diagnostic of aldehydes larger than propanal, those at m/z 253 were diagnostic of 2-ketones, and those at m/z 267 were diagnostic of 3-ketones. The fragment ions in our isobutane CI spectra are analogous to the diagnostic ions in the EI spectra and, therefore, can be used to distinguish among the 1,4-hydroxycarbonyl isomers (see Table 1).

In addition to their mass spectra, the elution order of the hydroxycarbonyl PFBHA derivatives from the DB-1 column was predictable, with retention increasing as the position of the derivatized carbonyl moved to the end of the molecule (see, for example, the hydroxyoctanone and hydroxyoctanal

TABLE 1. Retention Times and Diagnostic Ions Observed in the GC-MS Isobutane CI Ion Trap Mass Spectra of the Derivatized 1,4-hydroxycarbonyl Products

alkane	product	RTs[a]	M + H	M + H − H₂O	m/z 253[b]	m/z 239[c]	m/z 267[d]	m/z 281[e]
n-pentane	CH₃C(O)CH₂CH₂CH₂OH	23.9, 24.5	m/z = 298	m/z = 280	X			
	CH₃CH(OH)CH₂CH₂CHO	23.6	m/z = 298	m/z = 280		X		
n-hexane	CH₃C(O)CH₂CH₂CH(OH)CH₃	24.2, 24.9	m/z = 312	m/z = 294	X			
	CH₃CH₂C(O)CH₂CH₂CH₂OH	26.8, 27.3	m/z = 312	m/z = 294			X	
	CH₃CH₂CH(OH)CH₂CH₂CHO	27.7	m/z = 312	m/z = 294		X		
n-heptane	CH₃C(O)CH₂CH₂CH(OH)CH₂CH₃	28.3, 29.3	m/z = 326	m/z = 308	X			
	CH₃CH₂C(O)CH₂CH₂CH(OH)CH₃	27.4, 28.0	m/z = 326	m/z = 308			X	
	CH₃CH₂CH₂C(O)CH₂CH₂CH₂OH	30.6, 30.9	m/z = 326	m/z = 308				X
	CH₃CH₂CH₂CH(OH)CH₂CH₂CHO	32.2	m/z = 326	m/z = 308		X		
n-octane	CH₃C(O)CH₂CH₂CH(OH)CH₂CH₂CH₃	32.5, 33.6	m/z = 340	m/z = 322	X			
	CH₃CH₂C(O)CH₂CH₂CH(OH)CH₂CH₃	31.5, 32.5	m/z = 340	m/z = 322			X	
	CH₃CH₂CH₂C(O)CH₂CH₂CH(OH)CH₃	30.9, 31.2	m/z = 340	m/z = 322				X
	CH₃CH₂CH₂CH₂CH(OH)CH₂CH₂CHO	37.0	m/z = 340	m/z = 322		X		

[a] Retention times (min) on a DB-1 capillary column (*Z*- and *E*-oximes can be formed). [b] m/z 253 = $C_6F_5CH_2ON^+(H)C(C \cdot H_2)(CH_3)$; "X" indicates ion present in spectrum. [c] m/z 239 = $C_6F_5CH_2ON^+(H)C(C \cdot H_2)(H)$; "X" indicates ion present in spectrum. [d] m/z 267 = $C_6F_5CH_2ON^+(H)C(C \cdot H_2)(CH_2CH_3)$; "X" indicates ion present in spectrum. [e] m/z 281 = $C_6F_5CH_2ON^+(H)C(C \cdot H_2)(CH_2CH_2CH_3)$; "X" indicates ion present in spectrum.

TABLE 2. Hydroxycarbonyl Yields from the OH Radical Initiated Reactions of *n*-Pentane through *n*-Octane Together with the Rate Constants for Reactions of the OH Radical with the 1,4-Hydroxycarbonyls Used to Correct for Secondary Reaction and the Predicted Percentage Yields of the Precursor Peroxy Radical Formation from the *n*-Alkanes

alkane	hydroxycarbonyl	$10^{11} \times k_{OH}$ (cm^3 molecule^{-1} s^{-1})[a]	molar yield at 50% relative humidity unless noted[b]	precursor ROO· formation yield (%)[c]
n-pentane	5-hydroxy-2-pentanone	1.6[d]	0.49 ± 0.19[e]	57
	4-hydroxypentanal	3.85	0.052[f]	8
n-hexane	5-hydroxy-2-hexanone	1.78	0.243	42
	6-hydroxy-3-hexanone	1.50	0.258	52
	4-hydroxyhexanal	4.15	0.068	6
n-heptane	5-hydroxy-2-heptanone	2.17	0.184	33
	6-hydroxy-3-heptanone	1.90	0.159	41
	1-hydroxy-4-heptanone	1.85	0.105	21
	4-hydroxyheptanal	4.32	0.058	5
n-octane	5-hydroxy-2-octanone	2.34	} 0.378[g]	28
	6-hydroxy-3-octanone	2.28		34
	7-hydroxy-4-octanone	2.24	0.119	34
	4-hydroxyoctanal	4.46	0.028	4

[a] Estimated rate constants, calculated as described by Kwok and Atkinson (*25*) and Bethel et al. (*26*), unless noted otherwise. [b] As noted in the text, quantification from the SPME GC-FID peak areas required a response factor of the derivatized hydroxycarbonyl relative to the 3-pentanone oxime. The relative response factor for 5-hydroxy-2-pentanone was measured (see text). For the other hydroxycarbonyls, the response factors were estimated by multiplying the relative response factor measured for the carbonyl with the OH group in the hydroxycarbonyl replaced by a CH_3 group by a factor of 5.1 (*15*). Where the appropriate carbonyl was unavailable, the relative response factors were calculated by assuming that (a) an additional CH_2 group increases the response factor by a factor of 1.8 and (b) that, for a given carbon number, a branched carbonyl has a response 0.865 of that for the linear carbonyl (based on measured relative response factors of 8.3 for 5-methyl-2-hexanone and 9.6 for 2-heptanone) (*15*). When the estimated relative response factor was >25, a factor of 25 was used (*15*). Therefore, with the exception of the measured values for 5-hydroxy-2-pentanone, a relative response factor of 25 was used for all the hydroxycarbonyls except 6-hydroxy-3-hexanone and 1-hydroxy-4-heptanone for which the values were 20 and 17, respectively. [c] Percent of H-atom abstraction predicted to occur at the CH_2 or CH_3 group leading to precursor alkyl peroxy radical formation with subsequent reactions (see, for example, Scheme 1) leading to formation of the listed 1,4-hydroxycarbonyl, as well as alkyl nitrates, carbonyls, and 1,4-hydroxyalkylnitrates (*7*). [d] Measured reaction rate constant (*9*). [e] Combined data at 5 and 50% relative humidity; the errors are two standard deviations combined with estimated uncertainties in the measured SPME/GC-FID response factor for 5-hydroxy-2-pentanone of ±20% and in the GC-FID response factor for *n*-pentane of ±5%. [f] Combined data at 5 and 50% relative humidity. [g] The GC peaks of the oximes overlapped (see Table 1).

retention times in Table 1) and, with the exception of the *n*-pentane system, the derivatized hydroxyaldehydes eluted last. In the *n*-pentane, *n*-hexane, and *n*-heptane systems, the isomer with a terminal OH substitution showed an increased retention time. Isomer-specific quantifications were achieved by employing the same column in the GC-FID analyses.

A series of irradiated CH$_3$ONO–NO–*n*-alkane–air irradiations were carried out to identify and quantify 1,4-hydroxycarbonyls. The GC-MS analyses of coated SPME fibers exposed to irradiated CH$_3$ONO–NO–*n*-alkane–air mixtures showed the presence of the oximes of 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 (Table 1).

Hydroxycarbonyl Formation Yields. CH$_3$ONO–NO–*n*-alkane–air irradiations were carried out for each *n*-alkane, with a single irradiation per experiment and with two replicate analyses after the irradiation. Quantification of the 1,4-hydroxycarbonyls from the GC peak areas of their oximes requires measurement or estimation of the SPME/GC-FID response factors of the oximes of the 1,4-hydroxycarbonyls (i.e., of the GC-FID peak areas of the oximes for a known concentration of the 1,4-hydroxycarbonyl in the chamber, using the same sampling and analysis procedure as used in the product experiments). Although the GC-FID responses of the derivatized carbonyls are expected to be similar for a given number of carbon atoms, the major factor determining our measured SPME/GC-FID responses is the on-fiber derivatization efficiency. We have previously (*15*) measured the SPME/GC-FID response factors of the oximes of 34 carbonyl-containing compounds relative to that of the oxime of 3-pentanone. Reisen et al. (*15*) observed that the relative

SPME/GC-FID response factors increased in the series RCHO > CH$_3$C(O)R > CH$_3$CH$_2$C(O)R > CH$_3$CH$_2$CH$_2$C(O)R (where R = alkyl) for a constant carbon number. Furthermore, for a given structure (RCHO, CH$_3$C(O)R, or CH$_3$CH$_2$C(O)R), the relative response factor increased with carbon number, decreased with increased branching in R, and substitution of an OH group for a CH$_3$ group increased the response factor (*15*). Reisen et al. (*15*) concluded that the response factor for a hydroxycarbonyl could be estimated as being a factor of ∼5 higher than that of the carbonyl with the OH group replaced by a CH$_3$ group (for example, CH$_3$C(O)CH$_2$CH$_2$CH$_2$-OH vs CH$_3$C(O)CH$_2$CH$_2$CH$_2$CH$_3$). Reisen et al. (*15*) also concluded that, for the same sampling and analysis procedure used here, the maximum value of the relative response factor was ∼25.

We used this estimation method (*15*) to calculate the SPME/GC-FID response factors of the oximes of the 1,4-hydroxycarbonyls relative to that of the oxime of 3-pentanone, using the data reported by Reisen et al. (*15*). While three SMPE fibers were used in this work, the measured response factors for 5-hydroxy-2-pentanone relative to that for 3-pentanone using these fibers (an average of 16 with a range of 12.9–20.5 from 10 independent measurements for the 3 fibers at 5% and/or 50% relative humidity) were not significantly different from the value of 15.0 reported by Reisen et al. (*15*). The product formation yields shown in Table 2 were calculated from the area counts of the oximes in the GC-FID analyses, relative to those of the oxime of 3-pentanone, combined with the measured SPME/GC-FID response factor for 5-hydroxy-2-pentanone (appropriate for the fiber used and the relative humidity) and the estimated response factors for the other 1,4-hydroxycarbonyls (see Reisen et al. (*15*) and the footnotes to Table 2 for details of the estimations). The measured 1,4-hydroxycarbonyl concentrations were corrected for secondary reactions with OH radicals (*24*), using the measured rate constants for the C$_5$–C$_8$ *n*-alkanes (*3*), the measured rate constant of 1.6×10^{-11} cm^3 molecule^{-1} s^{-1} for
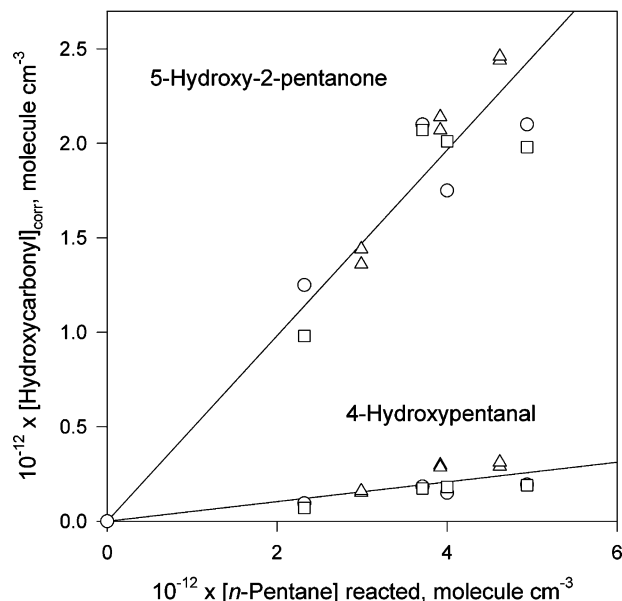
FIGURE 2. Plots of the amounts of 4-hydroxypentanal and 5-hydroxy-2-pentanone formed (corrected for reaction with the OH radical, see text) against the amounts of *n*-pentane reacted with the OH radical. ○, first analysis at ~5% relative humidity; □, second analysis at ~5% relative humidity; △, ~50% relative humidity, first and second replicate analyses. Lines are least-squares fits constrained to pass through the origin.
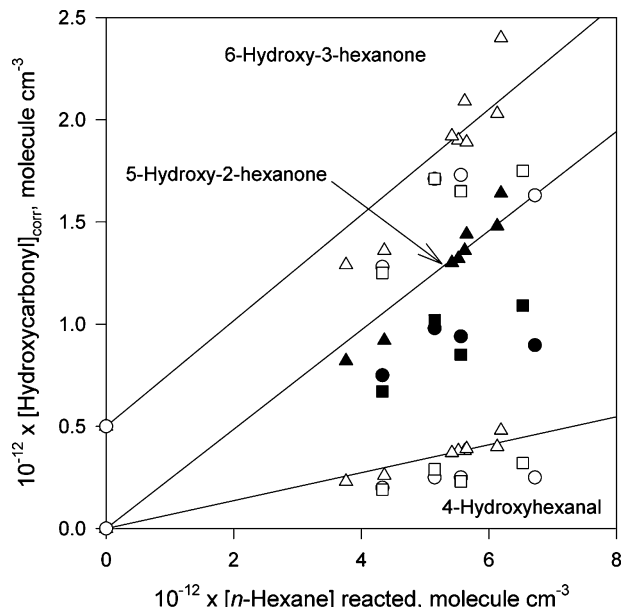

FIGURE 3. Plots of the amounts of 4-hydroxyhexanal, 5-hydroxy-2-hexanone, and 6-hydroxy-3-hexanone formed (corrected for reaction with the OH radical, see text) against the amounts of *n*-hexane reacted with the OH radical. The first analyses at 5% RH are shown as circles (○, for 4-hydroxyhexanal and 6-hydroxy-3-hexanone; ●, for 5-hydroxy-2-hexanone), the repeat analyses at the same extent of reaction are shown as squares (□, for 4-hydroxyhexanal and 6-hydroxy-3-hexanone; ■, for 5-hydroxy-2-hexanone). The replicate data at 50% relative humidity are shown as triangles (△, for 4-hydroxyhexanal and 6-hydroxy-3-hexanone; ▲, for 5-hydroxy-2-hexanone). Lines are least-squares fits of the 50% relative humidity data constrained to pass through the origin. The data for 6-hydroxy-3-hexanone have been displaced vertically by 5×10^{11} molecule cm^{-3} for clarity.

5-hydroxy-2-pentanone (*9*), and the estimated (*25*, *26*) rate constants ranging from $(1.5-4.5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for the 1,4-hydroxycarbonyls (other than 5-hydroxy-2-pentanone) formed from the OH reactions of C_5-C_8 *n*-alkanes (see Table 2). Note that because the correction factor (which was ≤1.63 for the hydroxyketones and ≤2.61 for the hydroxyaldehydes) depends on the rate constant ratio $k(OH + hydroxycarbonyl)/k(OH + alkane)$ (*24*), we have used rate constants for the alkanes from Atkinson (*3*) to be consistent with the estimation method of Kwok and Atkinson (*25*) and Bethel et al. (*26*).

Experiments to determine the 1,4-hydroxycarbonyl formation yields from the reactions of *n*-pentane through *n*-octane were carried out at approximately 5 and 50% relative humidity. For the *n*-pentane reaction, replicate analyses of the 1,4-hydroxycarbonyls after reaction showed no evidence for losses in the time period (71−113 min) between the replicate analyses at either 5 or 50% relative humidity, and the formation yields measured at 5 and 50% relative humidity were in good agreement, as shown by the data in Figure 2. For the *n*-hexane reaction, no evidence for losses of the 1,4-hydroxycarbonyls during the time period (75−153 min) between the replicate analyses was observed, but the formation yields of the 1,4-hydroxycarbonyls were higher at 50% relative humidity compared to those at 5% relative humidity (Figure 3). For the *n*-heptane and *n*-octane reactions, the hydroxyketones (but not 4-hydroxyheptanal or 4-hydroxyoctanal) were observed to decrease significantly over the 71−166 min time period between replicate analyses after the reaction at ~5% relative humidity but not at ~50% relative humidity, and the formation yields of the 1,4-hydroxycarbonyls were significantly higher at 50% relative humidity compared to those at 5% relative humidity, as shown in Figure 4 for the *n*-octane data. These observations are interpreted in terms of the 1,4-hydroxycarbonyls undergoing cyclization and loss of water to form the corresponding dihydrofurans (for example, formation of 4,5-dihydro-2-methylfuran from 5-hydroxy-2-pentanone has been observed under dry conditions (*27*, *28*)). This dehydration is expected to be more important at 5% relative humidity

than at 50% relative humidity and also apparently is more important for the larger 1,4-hydroxycarbonyls, as confirmed by experiments in which the 1,4-hydroxycarbonyls formed from the *n*-pentane through *n*-octane reactions have been monitored over extended periods of time (*29*, *30*).

By use of the yields of 1,4-hydroxycarbonyls formed from *n*-hexane, *n*-heptane, and *n*-octane at 50% relative humidity and those from *n*-pentane at both 5 and 50% relative humidity, the formation of 1,4-hydroxycarbonyls accounts for 54% of the reaction products from *n*-pentane, 57% from *n*-hexane, 51% from *n*-heptane, and 53% from *n*-octane (Table 3). Combined with the previously measured yields of carbonyls, alkyl nitrates and hydroxyalkyl nitrates shown in Table 3 (*6*, *7*, *31*), we can now account for approximately 74−118% of the products formed from *n*-pentane through *n*-octane. Clearly, authentic standards of the 1,4-hydroxycarbonyls formed from the *n*-hexane, *n*-heptane, and *n*-octane reactions are needed to allow accurate determination of their formation yields and associated uncertainties through measurement rather than estimation of their SPME-FID response factors. As shown in Scheme 1, the first-generation products from the *n*-alkanes are alkyl nitrates, carbonyls formed from alkoxy radical decompositions and reactions with O_2 (which are of minor or no importance for the ≥ C_6 *n*-alkanes, as evident from Table 3), and 1,4-hydroxyalkyl nitrates and 1,4-hydroxycarbonyls arising after alkoxy radical isomerization. As noted above, the 1,4-hydroxycarbonyls may undergo cyclization and loss of water to form highly reactive substituted dihydrofurans (*27*, *28*, *30*).

Our present 1,4-hydroxycarbonyl formation yields obtained using the SPME/GC-FID technique are in agreement with the formation yields previously estimated using direct air sampling atmospheric pressure ionization mass spec-
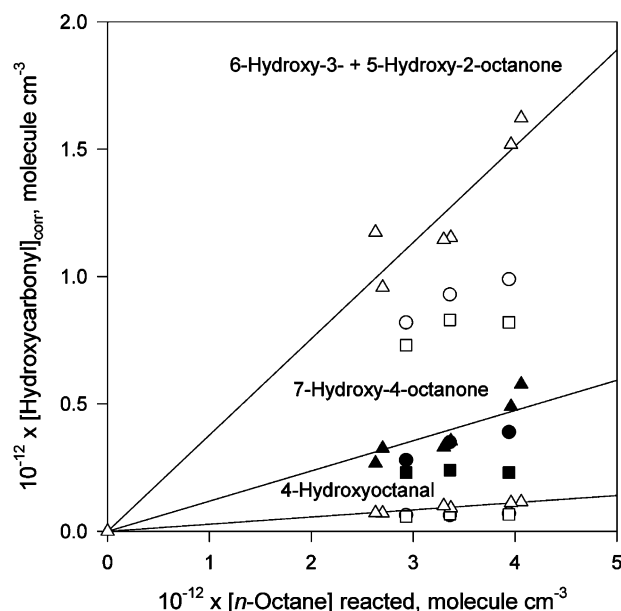
FIGURE 4. Plots of the amounts of 4-hydroxyoctanal, 5-hydroxy-2-octanone + 6-hydroxy-3-octanone, and 7-hydroxy-4-octanone formed (corrected for reaction with the OH radical, see text) against the amounts of *n*-octane reacted with the OH radical. The first analyses at 5% relative humidity are shown as circles (○, for 4-hydroxyoctanal and 6-hydroxy-3- + 5-hydroxy-2-octanone; ●, for 7-hydroxy-4-octanone), the repeat analyses at the same extent of reaction are shown as squares (□, for 4-hydroxyoctanal and 6-hydroxy-3- + 5-hydroxy-2-octanone; ■, for 7-hydroxy-4-octanone). The replicate data at 50% relative humidity are shown as triangles (△, for 4-hydroxyoctanal and 6-hydroxy-3- + 5-hydroxy-2-octanone; ▲, for 7-hydroxy-4-octanone). Lines are least-squares fits of the 50% relative humidity data constrained to pass through the origin.

trometry (API-MS) in the negative-ion mode using NO_2^- ions to form NO_2^- adducts of hydroxycarbonyls (7) at ~5% relative humidity. In our previous API-MS study (7), only total hydroxycarbonyl yields were obtained, and these are listed in parentheses in Table 3. There are significant uncertainties associated with each measurement method, especially for the *n*-hexane through *n*-octane reactions where the coated SPME/GC-FID response factors have to be estimated, and the use of 5-hydroxy-2-pentanone as an internal standard in our previous API-MS analyses assumed identical API response for all hydroxycarbonyls (7). Additionally, because the API-MS yields were obtained at ~5% relative humidity, the yields for the *n*-hexane, *n*-heptane, and *n*-octane reactions are expected to be low due to cyclization of the 1,4-hydroxy-carbonyls with subsequent dehydration to form dihydro-furans. However, there is generally good agreement between the total hydroxycarbonyl yields derived from the API-MS analyses (7) and the sum of the individual hydroxycarbonyl yields measured here (Table 3) with, as may be expected, the biggest discrepancy being for the *n*-octane reaction.

Our present data confirm the importance of hydroxy-carbonyls as products of the reactions of OH radicals with *n*-alkanes (5–9), and the isomer-specific identifications made here show that 1,4-hydroxycarbonyls are formed, consistent with previous predictions (3, 32). The only previous isomer-specific analyses were made by Eberhard et al. (5) using high-performance liquid chromatography MS, and they identified 5-hydroxy-2-hexanone as a major product of the photolysis of 2-hexyl nitrite and from the OH radical initiated reaction of *n*-hexane, with reported yields of 68 ± 48 and 96 ± 30%, respectively. However, no evidence for the formation of 6-hydroxy-3-hexanone from the photolysis of 3-hexyl nitrite nor from the OH radical initiated reaction of *n*-hexane was obtained (5). The data of Eberhard et al. (5) showing dominant isomerization of the 2-hexoxy radical (from photolysis of 2-hexyl nitrite) are consistent with our present observation of significant 5-hydroxy-2-hexanone formation from *n*-hexane (see Table 3). However, we also observe formation of 6-hydroxy-3-hexanone from the *n*-hexane reaction in comparable yield to 5-hydroxy-2-hexanone, and the 5-hydroxy-2-hexanone yield of Eberhard et al. (5) from *n*-hexane is inconsistent with predictions that H-atom abstraction from the 2-position CH_2 group in *n*-hexane accounts for only 40–45% of the overall reaction (25). It should be noted that Eberhard et al. (5) carried out their experiments in dry synthetic air, and cyclization of the hydroxyhexanones with subsequent dehydration to form reactive dihydrofurans could have been important.

The second isomerization shown in Scheme 1 is predicted to be more rapid than the first isomerization (3, 33), dominating over reaction of the $CH_3CH(OH)CH_2CH_2CH_2O^•$ radical with O_2 to form 4-hydroxypentanal. The dominant occurrence of the second isomerization after formation of the various alkyl radicals from *n*-pentane through *n*-octane is confirmed by the products we observed and their yields, i.e., the formation of 5-hydroxy-2-pentanone (quantified using an authentic standard for SPME/GC-FID calibration) in 49 ± 19% yield from the *n*-pentane reaction and the low yield of the 4-hydroxyaldehydes from all four alkanes.

The pattern of hydroxycarbonyl formation observed here is that expected from the formation yields of the precursor alkyl radicals (25). Although the yield of the hydroxycarbonyls will be less than the predicted percentage of the precursor ROO• radicals formed after H-atom abstraction at a given CH_2 or CH_3 group (see Table 2) because of alkyl nitrate formation and, for the *n*-pentane and *n*-hexane systems, of decomposition and reaction with O_2 of the 2-pentoxy, 3-pentoxy, and 3-hexoxy radicals (see Scheme 1 and Table 3), the relative abundances of the 1,4-hydroxycarbonyl isomers matches closely the predicted ratio of precursor ROO• formation. Thus, the yields of 5-hydroxy-2-hexanone and 6-hydroxy-3-hexanone are similar (24 and 26%, respectively), consistent with the expectation that H-atom abstraction from the 2- and 3-positions of *n*-hexane are of comparable importance (25). Similarly, the formation yields of the three isomeric hydroxyheptanones (5-hydroxy-2-heptanone, 6-hy-

TABLE 3. First-Generation Product Yields from the OH Radical Initiated Reactions of *n*-Pentane through *n*-Octane

product	molar yield (%) from			
	n-pentane	*n*-hexane	*n*-heptane	*n*-octane
alkyl nitrates	10.5 ± 1.4[a]	14.1 ± 2.0[b]	17.8 ± 2.4[b]	22.6 ± 3.2[b]
carbonyls from RO• decomposition	20[a]	4[c]	<1[c]	<1[c]
carbonyls from RO• reaction with O_2	30.4 ± 3.2[a]	6.0 ± 0.5[d]	<1[e]	<1[e]
hydroxyalkyl nitrates[b]	2.6	4.6	4.7	5.4
1,4-hydroxycarbonyls	54 ± 20 (36[b])	57 (53[b])	51 (46[b])	53 (27[b])
total	118 ± 23	86	74	81

[a] From Atkinson et al. (31). [b] From Arey et al. (7). [c] Assuming that the relative importance of decomposition vs reaction with O_2 is similar to that for the 3-pentoxy radical (31). [d] From data cited in Kwok et al. (6). [e] Aschmann and Atkinson, unpublished data.

droxy-3-heptanone, and 1-hydroxy-4-heptanone) formed from *n*-heptane after initial H-atom abstraction from the 2-, 3-, and 4-position CH$_2$ groups are 18, 16, and 11%, respectively, reasonably consistent with the 1.0:1.2:0.6 ratio expected from the partial rate constants calculated using the Kwok and Atkinson estimation method (*25*) and shown in Table 2. As predicted (*25*), the yields of the 4-hydroxyaldehydes are the lowest, being comparable to the estimated fraction of H-atom abstraction from the CH$_3$ groups (*25*).

The data presented in Table 2 show that 1,4-hydroxycarbonyls are indeed formed from the OH radical-initiated reactions of *n*-alkanes and that these 1,4-hydroxycarbonyls are the major products of the OH radical initiated reactions of ≥C$_5$ *n*-alkanes in the presence of NO. The atmospherically important reactions of the 1,4-hydroxycarbonyls, including cyclization with dehydration to form more reactive dihydrofurans, need further investigation.

Acknowledgments

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