Hydroxycarbonyl Products of the Reactions of Selected Diols with the OH Radical

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Received: December 11, 2002; In Final Form: April 17, 2003

The hydroxycarbonyl products formed from the gas-phase reactions of 1,2-, 1,3-, and 2,3-butanediol and 2-methyl-2,4-pentanediol have been investigated using solid-phase micro extraction fibers coated with the derivatizing reagent *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride. Following on-fiber derivatization of carbonyl-containing products, they were analyzed by subsequent thermal desorption and gas chromatography with flame ionization detection (GC-FID) and combined gas chromatography−mass spectrometry. In addition to the hydroxyketone products previously observed by gas chromatography without prior derivatization, the hydroxyaldehyde products observed as their oximes were $CH_3CH_2CH(OH)CHO$ and $HOCH_2CHO$ from 1,2-butanediol; $CH_3CH(OH)CH_2CHO$, $HOCH_2CHO$, and $CH_3CH(OH)CHO$ from 1,3-butanediol; $CH_3CH(OH)CHO$ from 2,3-butanediol; and $CH_3CH(OH)CHO$ from 2-methyl-2,4-pentanediol. These hydroxyaldehydes were quantified using estimated GC-FID response factors developed for on-fiber derivatization sampling, and the observed hydroxycarbonyl products account for 71−103% of the reaction pathways for these four diols. The reaction products, and their formation yields, predicted from mechanisms based on the literature database for reactions of OH radicals with volatile organic compounds, agree with our experimental data.

Introduction

Volatile organic compounds present in the atmosphere can undergo photolysis and chemical reaction with OH radicals, NO_3 radicals, and O_3,[1] with the OH radical reaction being an important, and often dominant, atmospheric loss process.[1] Diols are used as solvents[2] and can also be formed in the atmosphere from the OH radical-initiated reactions of alkenes under low-NO_x conditions.[1,3−5] To date, room-temperature rate constants have been reported for the gas-phase reactions of OH radicals with 1,2-ethanediol,[6−9] 1,2-propanediol,[6,7,9] 2-methyl-2,4-pentanediol,[10] and 1,2-, 1,3-, and 2,3-butanediol.[10] During our previous kinetic and product study of the reactions of OH radicals with 2-methyl-2,4-pentanediol and 1,2-, 1,3-, and 2,3-butanediol,[10] we identified and quantified hydroxyketone products formed from these reactions and, because hydroxyaldehyde products also expected from certain of these reactions were not observed, concluded that without derivatization hydroxyaldehydes would not elute from the gas chromatographic columns used.

In this study, we have further investigated the products formed from the reactions of OH radicals with 2-methyl-2,4-pentanediol and 1,2-, 1,3-, and 2,3-butanediol, using solid-phase micro extraction (SPME) fibers[11] coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride[12] for on-fiber derivatization of carbonyl compounds, with subsequent gas chromatographic analyses of their oxime derivatives.

Experimental Section

All experiments were carried out in a 7500 L Teflon chamber, equipped with two parallel banks of blacklamps for irradiation, at 296 ± 2 K and 740 Torr total pressure of purified air at ∼5% relative humidity. This chamber is fitted with a Teflon-coated fan to ensure the rapid mixing of reactants during their introduction into the chamber. OH radicals were generated by the photolysis of methyl nitrite (CH_3ONO) in air at wavelengths >300 nm,[13] and NO was added to the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals. The initial reactant concentrations (molecule cm^{-3}) were CH_3ONO, $\sim 4.8 \times 10^{13}$; NO, $\sim 4.8 \times 10^{13}$; and diol, $\sim 1.2 \times 10^{13}$. Irradiations were carried out for 1.5−5 min, resulting in up to 61% consumption of the initially present diol.

The concentrations of the diols were measured during the experiments by gas chromatography with flame ionization detection (GC-FID).[10] Gas samples of 100 cm^3 volume were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ∼225 °C onto a 30 m DB-1701 megabore column held at 0 °C and then temperature programmed to 200 °C at 8 °C min^{-1}. Based on replicate analyses in the dark, the GC-FID measurement uncertainties for the diols were in the range 1−5%, except for 1,3-butanediol for which the uncertainties were in the range 4−9%. The hydroxyaldehyde and hydroxyketone products were sampled using a 65 μm poly(dimethylsiloxane)/divinylbenzene SPME fiber.[14] The fiber was coated prior to use with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) for on-fiber derivatization of carbonyl compounds. The derivatization reagent was loaded onto the SPME fiber for 1 h using headspace extraction from a 20 mg mL^{-1} PFBHA solution immediately before sampling in the chamber.[14] The coated fiber was inserted into the chamber and exposed to the chamber contents for 5 min with the chamber mixing fan on. The fiber was then removed and introduced into the inlet port of the GC-FID with subsequent thermal desorption at 250 °C onto a 30 m DB-1701 megabore column held at 40 °C and then temperature programmed to 260 °C at 8 °C min^{-1}. Identification was carried out by gas chromatography−mass spectrometry (GC-MS), using

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10.1021/jp027693l CCC: $25.00
Published on Web 07/16/2003

TABLE 1: Hydroxycarbonyl Products Predicted and Observed, and Their Predicted and Measured Yields, from the Gas-Phase Reactions of the OH Radical with Diols at 296 ± 2 K

		molar formation yield (%)		
diol	product	Tenax[a]	SPME[b]	est.[c]
$CH_3CH_2CH(OH)CH_2OH$	$CH_3CH_2C(O)CH_2OH$[d]	66 ± 11		64
	$CH_3CH_2CH(OH)CHO$		27	25
	$HOCH_2CHO$[e]		10 ± 4	9
	$HOCH_2CH_2CH(OH)CHO$			<1
$CH_3CH(OH)CH_2CH_2OH$	$CH_3C(O)CH_2CH_2OH$[d]	50 ± 9		40
	$CH_3CH(OH)CH_2CHO$		15	19
	$CH_3CH(OH)CHO$[f]		0.7	3
	$HOCH_2CHO$[e]		10 ± 4	34
	$HOCH_2CH(OH)CH_2CHO$			2
$CH_3CH(OH)CH(OH)CH_3$	$CH_3C(O)CH(OH)CH_3$[d]	89 ± 9		97
	$CH_3CH(OH)CHO$[f]		2.0	2
$(CH_3)_2C(OH)CH_2CH(OH)CH_3$	$(CH_3)_2C(OH)CH_2C(O)CH_3$[d]	47 ± 9		47
	$CH_3CH(OH)CHO$[f]		24	43
	$(CH_3)_2C(OH)CH_2CHO$		observed	2
	$HOCH_2C(OH)(CH_3)CH_2C(O)CH_3$			7

[a] From Bethel et al.[10] with products sampled on Tenax adsorbent. Indicated errors are two least-squares standard deviations combined with estimated overall uncertainty in the GC-FID response factors for the diols and hydroxyketones of ±5% each.[10] [b] This work; see text for details of how these yields are obtained. The estimated overall uncertainties are a factor of ~2, except for $HOCH_2CHO$ where the indicated errors are two standard deviations and include the uncertainties in the measured formation yields for the reference hydroxyketone $CH_3CH_2C(O)CH_2OH$ or $CH_3C(O)CH_2CH_2OH$.[10] [c] Estimated based on the predicted percentages of the initial OH radical reaction proceeding by H-atom abstraction from the various CH, CH_2, CH_3, and OH groups[10,18] and the estimated reaction rates of the intermediate alkoxy radicals,[3,25−27] assuming that all α-hydroxy radicals react solely with O_2[24] and neglecting organic nitrate formation from reaction 9b and analogous reactions. [d] Identification based on matching of GC retention times and mass spectra with those of authentic standards. [e] Identification based on comparison of GC retention times and mass spectra of the oximes from reactions of 1,2- and 1,3-butanediol with OH radicals with those from reaction of OH radicals with 2-methyl-3-buten-2-ol.[15,16] [f] Identical oximes were formed from the reactions of OH radicals with 1,3- and 2,3-butanediol and 2-methyl-2,4-pentanediol, and this identical molecular weight 74 product is attributed to $CH_3CH(OH)CHO$ from consideration of the likely reaction mechanisms (see text).

a Varian 2000 MS/MS with isobutane chemical ionization and a DB-1701 column, using a similar procedure to that for the GC-FID analyses. GC retention times and mass spectra were previously obtained for a number of standard hydroxyketones.[14] In addition, an irradiation of a CH_3ONO−NO−2-methyl-3-buten-2-ol−air mixture was carried out, with similar initial reactant concentrations as used in the diol experiments, to obtain GC retention times and mass spectra of the oximes of glycolaldehyde [$HOCH_2CHO$], a known product of the OH radical-initiated reaction of 2-methyl-3-buten-2-ol.[15,16]

Chemicals. The chemicals used, and their stated purities, were 1,2-butanediol (99%), 1,3-butanediol (99+%), 2,3-butanediol (98%), 1-hydroxy-2-butanone (95%), 3-hydroxy-2-butanone, 4-hydroxy-4-methyl-2-pentanone (99%), 2-methyl-2,4-pentanediol (99%), *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (98+%), and 2-methyl-3-buten-2-ol (98%), Aldrich Chemical Co.; 4-hydroxy-2-butanone (95+%), TCI America; and NO (≥99.0%), Matheson Gas Products. Methyl nitrite was prepared and stored as described previously.[13]

Results

GC-MS analyses of irradiated CH_3ONO−NO−diol−air mixtures, using the SPME fiber coated with derivatizing reagent to sample the chamber contents, showed the formation of a number of oximes from each diol (Table 1). The hydroxyketones previously identified and quantified[10] were identified as their oxime derivatives from comparison of the GC retention times and mass spectra with those of the oximes of authentic standards. The oximes gave strong $[M + H]^+$ ions with minor $[M + 40]^+$ adduct ions, where the value of M is 195 mass units above the molecular weight of the carbonyl product (note that asymmetric carbonyls may produce *Z*- and *E*- forms of the oximes). Glycolaldehyde was shown to be formed from the reactions of 1,2- and 1,3-butanediol (Table 1) by comparison with GC-FID and GC-MS analyses, using the same coated SPME fiber method, of an irradiated CH_3ONO−NO−2-methyl-3-buten-2-ol−air mixture which is known to form glycolaldehyde as a reaction product.[15,16]

Additional oxime products were observed in the GC-FID and GC-MS analyses and, based on their molecular weights, the fact that they must be hydroxyaldehydes (i.e., they were not observed without derivatization), and consistency with the reaction pathways discussed below, were assigned the structures listed in Table 1. The oximes of the molecular weight 74 product(s) observed from the 1,3-butanediol, 2,3-butanediol and 2-methyl-2,4-pentanediol reactions had identical GC retention times and mass spectra, indicating that the same carbonyl-containing product is formed from each of these diols. From consideration of the likely reaction schemes (see below), this molecular weight 74 product is attributed to the hydroxyaldehyde $CH_3CH(OH)CHO$. The products (other than the hydroxyketones) of molecular weight 88 observed in the 1,2- and 1,3-butanediol reactions are attributed to the hydroxyaldehydes $CH_3CH_2CH(OH)CHO$ and $CH_3CH(OH)CH_2CHO$, respectively.

We have recently measured GC-FID response factors for the oximes of 33 $\leq C_8$ aldehydes, ketones, and hydroxycarbonyls.[14] In these experiments, two or three carbonyl compounds were introduced into the chamber at a concentration of $\sim(2.4-7.2) \times 10^{12}$ molecule cm^{-3} each and sampled with the coated SPME fiber, with subsequent GC-FID analysis of the oximes.[14] We therefore have relative response factors (see Table 2) for SPME/GC-FID analyses of the oximes of 1-hydroxy-2-butanone, 4-hydroxy-2-butanone, 3-hydroxy-2-butanone, 4-hydroxy-4-methyl-2-pentanone, and glycolaldehyde. The response factor for glycolaldehyde was obtained from the OH radical-initiated reaction of 2-methyl-3-buten-2-ol, using a glycolaldehyde formation yield of 58%,[15] and taking into account the small loss of glycolaldehyde (<4%) because of its secondary reaction with OH radicals. Based on the measured relative response factors, it is predicted that the response factor for an hydroxyaldehyde or hydroxyketone is a factor of 5.1 higher (with an uncertainty of a factor of ~2) than that of the corresponding

TABLE 2: Analytical Relative Response Factors for the Oximes of the Products Observed and OH Radical Reaction Rate Constants for the Diols and Products

reactant or product	SPME/GC-FID response factor relative to 3-pentanone	$10^{12} \times k_{OH}$ (cm^3 molecule^{-1} s^{-1})
$CH_3CH_2CH(OH)CH_2OH$		27.0 ± 1.4^a
$CH_3CH(OH)CH_2CH_2OH$		33.2 ± 1.1^a
$CH_3CH(OH)CH(OH)CH_3$		23.6 ± 4.2^a
$(CH_3)_2C(OH)CH_2CH(OH)CH_3$		27.7 ± 2.4^a
$CH_3CH_2C(O)CH_2OH$	5.6^b	7.7 ± 0.8^c
$CH_3C(O)CH_2CH_2OH$	12.5^b	8.1 ± 0.8^c
$CH_3C(O)CH(OH)CH_3$	7.3^b	10.3 ± 0.5^c
$(CH_3)_2C(OH)CH_2C(O)CH_3$	3.1^b	4.0 ± 0.9^c
$HOCH_2CHO$	18.8^d	13^e
$CH_3CH_2CH(OH)CHO$	25^f	30^g
$CH_3CH(OH)CH_2CHO$	25^f	30^g
$CH_3CH(OH)CHO$	25^f	30^g

[a] From Bethel et al.[10] The indicated uncertainties do not take into account the uncertainty in the rate constant for the reaction of OH radicals with the reference compound *n*-octane. [b] From Reisen et al.[14] The estimated overall uncertainties in these relative response factors are $\sim\pm 20\%$. [c] From Aschmann et al.[17] The indicated uncertainties do not take into account the uncertainty in the rate constant for the reaction of OH radicals with the reference compound *n*-octane. [d] Obtained from coated SPME/GC-FID analysis of 3 irradiated $CH_3ONO-NO-$2-methyl-3-buten-2-ol−air mixtures, with 4-hydroxy-3-hexanone and (in one experiment) 1-hydroxy-2-butanone added after the irradiation as an internal standard(s) and using our previously measured glycolaldehyde formation yield of $58 \pm 4\%$ (a weighted average of the measured formation yields of glycolaldehyde and its coproduct acetone)[15] and taking into account the small loss of glycolaldehyde (<4%) because of its secondary reaction with OH radicals. The estimated overall uncertainty in this relative response factor is $\pm 20\%$. [e] From IUPAC.[30] [f] Estimated from the measured relative response factors for $(CH_3)_2CHCHO$, $CH_3CH_2CH(CH_3)CHO$, and $(CH_3)_2CHCH_2CHO$; see text and Reisen et al.[14] Estimated overall uncertainties in these relative response factors are a factor of ~ 2. [g] Estimated. Although the rate constants calculated as described in Bethel et al.[10] are (in units of 10^{-11} cm^3 molecule^{-1} s^{-1}) $CH_3CH(OH)CHO$, 4.95; $CH_3CH_2CH(OH)CHO$, 5.8; and $CH_3CH(OH)CH_2CHO$, 4.7, the literature database suggests that these estimated OH radical reaction rate constants for hydroxyaldehydes are too high.[10] Accordingly, an approximate rate constant of 3.0×10^{-11} cm^3 molecule^{-1} s^{-1} was used for all three hydroxyaldehydes.

aldehyde or ketone with the −OH group replaced by a methyl group.[14] For example, the response factor for the sum of the oximes of $CH_3CH(OH)CHO$ is estimated to be a factor of 5.1 higher than for the oximes of $(CH_3)_2CHCHO$. The relative response factors for the 33 $\leq C_8$ carbonyl compounds studied were all ≤ 23,[14] with the highest response factors being for hexanal (22.3), glycolaldehyde (18.8), pentanal (16.0), and 5-hydroxy-2-pentanone (15.0).[14] Based on the response factors for straight-chain aldehydes, 2-ketones, and 3-ketones,[14] that for 5-hydroxy-2-pentanone is expected to be a factor of ~ 1.8 higher than the value of 12.5 measured for 4-hydroxy-2-butanone,[14] suggesting there is a maximum value of the response factor of $\sim 15-25$ for the SPME sampling and analysis procedure used here. Therefore, because the estimated response factors (relative to that for the oximes of 3-pentanone) for $CH_3CH(OH)CHO$, $CH_3CH_2CH(OH)CHO$, and $CH_3CH(OH)CH_2CHO$ are >25, we use a constant value of 25 for all three of these hydroxyaldehydes (Table 2).

The GC-FID measurements provide the peak areas for the various oximes of the carbonyl-containing compounds, and Figure 1 shows a plot of the peak areas of the oximes of the hydroxyketones and hydroxyaldehydes observed from the 1,3-butanediol reaction against the percentage reaction for three replicate experiments with the same initial 1,3-butanediol concentrations. The hydroxyaldehyde and hydroxyketone products also react with OH radicals, and the decreases in yield with increasing percentage of reaction are evident in Figure 1.

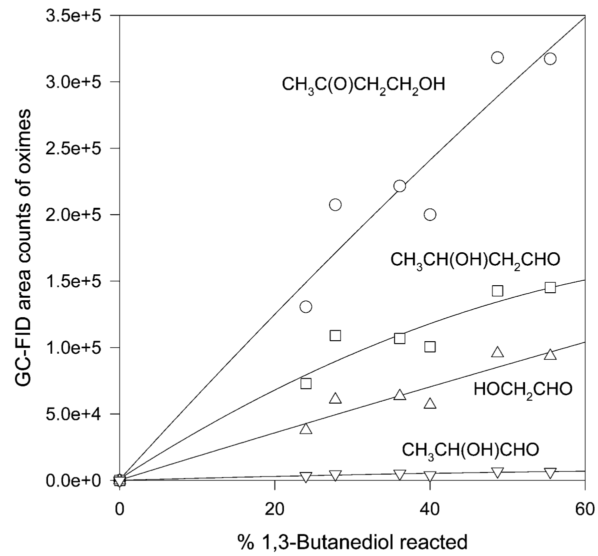

Figure 1. Plot of the GC-FID peak areas for the oximes of the hydroxycarbonyls observed, against the percentage of 1,3-butanediol reacted with the OH radical. The measured initial concentrations of 1,3-butanediol in the three experiments were the same, within the measurements uncertainties of $\pm 5-9\%$ (see text).

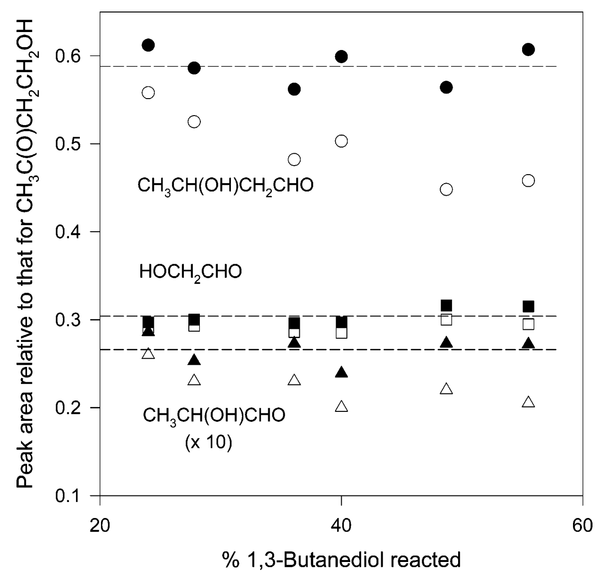

Figure 2. Plots of the GC peak areas (see Figure 1) of the oximes of the hydroxyaldehydes $CH_3CH(OH)CH_2CHO$, $HOCH_2CHO$, and $CH_3CH(OH)CHO$ ratioed to the peak area of the oximes of the hydroxyketone $CH_3C(O)CH_2CH_2OH$. ○, □, △ − Experimental data; ●, ■, ▲ − experimental data corrected for reactions of $CH_3CH(OH)CH_2CHO$, $HOCH_2CHO$, $CH_3CH(OH)CHO$, and $CH_3C(O)CH_2CH_2OH$ with OH radicals; (- - -) − ratios obtained by averaging the corrected data.

We have previously measured the hydroxyketone formation yields (for example, of 4-hydroxy-2-butanone in the case of the 1,3-butanediol reaction)[10] and here we have used these hydroxyketones as internal standards. For example, the ratio of the hydroxyaldehyde oxime peak areas to that of the oximes of the hydroxyketone product as a function of the percent of 1,3-butanediol reacted is shown in Figure 2. The decrease in the ratio of the GC-FID peak areas of the hydroxyaldehydes relative to 4-hydroxy-2-butanone with increasing extent of reaction shows that $CH_3CH(OH)CH_2CHO$ and $CH_3CH(OH)CHO$ are more reactive toward OH radicals than is $CH_3C(O)CH_2CH_2OH$. Using the fraction of the initial diol reacted (determined from the Tenax/GC-FID analyses) and the known[10,17] or estimated[10,18] rate constants for reaction of the diols and hydroxycarbonyl products with OH radicals listed in Table 2, the hydroxyaldehyde/hydroxyketone GC-FID peak area ratios were corrected to take into account secondary reactions with OH radicals.[10] As expected, the corrected GC-FID peak area ratios do not vary with extent of reaction (filled symbols in Figure 2) and the averages of the individual ratios were used (dashed lines in Figure 2). The GC-FID response factors for the oximes of the various hydroxycarbonyls, relative to that for the oximes of 3-pentanone, obtained using the coated SPME fiber for sample collection and on-fiber derivatization,[14] are also given in Table 2. These relative response factors were then combined with the corrected hydroxyaldehyde/hydroxyketone GC-FID peak area ratios and with the hydroxyketone formation yields previously determined by Bethel et al.[10] to obtain the hydroxyaldehyde formation yields. The resulting hydroxyaldehyde yields for each diol studied are given in Table 1.

For the hydroxycarbonyl products, keto−enol tautomerization can potentially occur[19]

$$RR'{-}CH{-}C(O){-}R'' \leftrightarrow RR'{-}C{=}C(OH){-}R'' \qquad (1)$$

For simple aldehydes and ketones, the keto form is the most stable and the equilibrium lies well to the left (i.e., in the keto form).[19] However, for compounds such as 2,4-pentanedione[19] [$CH_3C(O)CH_2C(O)CH_3$] and dimethyl-1,3-acetonedicarboxylate[20] [$CH_3OC(O)CH_2C(O)CH_2C(O)OCH_3$] in which a conjugated double-bond system makes the enol-form more energetically favorable

$$CH_3C(O)CH_2C(O)CH_3 \leftrightarrow CH_3C(OH){=}CHC(O)CH_3 \qquad (2)$$

the enol form can become important (and even dominant).[19] Because of the lack of structural features leading to conjugated double bond character in the enol form (and hence stabilization of the enol form), the hydroxycarbonyl products identified and quantified in this work [$CH_3CH_2C(O)CH_2OH$, $CH_3CH_2CH(OH)CHO$, $HOCH_2CHO$, $CH_3C(O)CH_2CH_2OH$, $CH_3CH(OH)CH_2CHO$, $CH_3CH(OH)CHO$, $CH_3C(O)CH(OH)CH_3$, and $(CH_3)_2C(OH)CH_2C(O)CH_3$] are anticipated to exist as the keto form (i.e., as written). Indeed, the keto forms of these hydroxycarbonyls are calculated to be ∼14−21 kcal mol^{-1} more stable than the enol forms,[21,22] using the group additivity method of Benson[22] to estimate the heats of formation of the enol forms. Moreover, our previous analyses[5,10] of the hydroxyketones $CH_3CH_2C(O)CH_2OH$, $CH_3C(O)CH_2CH_2OH$, $CH_3C(O)CH(OH)CH_3$, and $(CH_3)_2C(OH)CH_2C(O)CH_3$ showed good agreement of the measured GC-FID response factors (when gas samples were collected onto Tenax solid adsorbent with subsequent thermal desorption onto the GC column) with the calculated Effective Carbon Numbers,[23] suggesting quantitative compound collection and analysis.

Discussion

As previously discussed by Bethel et al.,[10] H-atom abstraction from the C−H bonds of the CH and/or CH_2 groups to which the OH group is attached is predicted to be important in the reactions of OH radicals with the four diols studied here, with the rapid reaction of the resulting α-hydroxyalkyl radicals with O_2 forming hydroxyketone or hydroxyaldehyde products.[24] Taking the 1,2-butanediol reaction as an example, the reactions

$$OH + CH_3CH_2CH(OH)CH_2OH \rightarrow H_2O + CH_3CH_2C^{\bullet}(OH)CH_2OH \qquad (3)$$

$$OH + CH_3CH_2CH(OH)CH_2OH \rightarrow H_2O + CH_3CH_2CH(OH)C^{\bullet}HOH \qquad (4)$$

followed by reactions of the α-hydroxyalkyl radicals with O_2[24]

$$CH_3CH_2C^{\bullet}(OH)CH_2OH + O_2 \rightarrow CH_3CH_2C(O)CH_2OH + HO_2 \qquad (5)$$

$$CH_3CH_2CH(OH)C^{\bullet}HOH + O_2 \rightarrow CH_3CH_2CH(OH)CHO + HO_2 \qquad (6)$$

result in the formation of 1-hydroxy-2-butanone and 2-hydroxybutanal from 1,2-butanediol.

Analogous reactions lead to the formation of 3-hydroxy-2-butanone from 2,3-butanediol, 4-hydroxy-2-butanone and 3-hydroxybutanal from 1,3-butanediol, and 4-hydroxy-4-methyl-2-pentanone from 2-methyl-2,4-pentanediol. As indicated in Table 1, several other hydroxycarbonyls were observed in addition to these major products, and the formation routes to these compounds are discussed below.

1,2-Butanediol. H-atom abstraction from the C−H bonds at the 2-position CH(OH) group and the 1-position CH_2OH group lead to the formation of $CH_3CH_2C(O)CH_2OH$ and $CH_3CH_2CH(OH)CHO$, respectively, by reactions 3−6. H-atom abstraction from the 3-position CH_2 group leads to formation of the 1,2-hydroxyalkoxy radical $CH_3CH(O^{\bullet})CH(OH)CH_2OH$ (reactions 7, 8, and 9a) and a small amount of a nitrate (reactions 7, 8, and 9b)

$$OH + CH_3CH_2CH(OH)CH_2OH \rightarrow H_2O + CH_3C^{\bullet}HCH(OH)CH_2OH \qquad (7)$$

$$CH_3C^{\bullet}HCH(OH)CH_2OH + O_2 \rightarrow CH_3CH(OO^{\bullet})CH(OH)CH_2OH \qquad (8)$$

$$CH_3CH(OO^{\bullet})CH(OH)CH_2OH + NO \rightarrow CH_3CH(O^{\bullet})CH(OH)CH_2OH + NO_2 \qquad (9a)$$

$$CH_3CH(OO^{\bullet})CH(OH)CH_2OH + NO \rightarrow CH_3CH(ONO_2)CH(OH)CH_2OH \qquad (9b)$$

The 1,2-hydroxyalkoxy radical is predicted[3,25−27] (using listed or estimated heats of formation for the various species from refs 21, 28, and 29) to dominantly decompose rather than react with O_2

$$CH_3CH(O^{\bullet})CH(OH)CH_2OH \rightarrow CH_3CHO + HOCH_2C^{\bullet}HOH \qquad (10)$$

with the α-hydroxy radical reacting with O_2 to form glycolaldehyde. It should be noted that CH_3CHO could not be quantified using SPME because of background interferences

$$HOCH_2C^{\bullet}HOH + O_2 \rightarrow HOCH_2CHO + HO_2 \qquad (11)$$

By analogous reactions to reactions 7−9, H-atom abstraction from the 4-position CH_3 group, which is predicted to account for <1% of the overall OH radical reaction,[10,18] leads to the alkoxy radical $^{\bullet}OCH_2CH_2CH(OH)CH_2OH$ which is predicted[3,25−27] to dominantly isomerize through a six-membered transition state to ultimately form $HOCH_2CH_2CH(OH)CHO$.

The hydroxycarbonyls observed (Table 1) are in accord with the expected reactions, and our measured yields are in good agreement with predictions made using the estimation method of Kwok and Atkinson[18] and Bethel et al.[10] to calculate the percentages of the overall OH radical reaction occurring at the various C−H bonds, combined with estimates of the fates of the various hydroxyalkoxy radicals (as discussed above and shown in Table 1).

1,3-Butanediol. H-atom abstraction from the C−H bonds of the 3-position CH(OH) and 1-position CH_2OH groups leads to formation of $CH_3C(O)CH_2CH_2OH$ and $CH_3CH(OH)CH_2CHO$, respectively (see above). H-atom abstraction from the 2-position CH_2 group leads, by reactions analogous to reactions 7−9, to the hydroxyalkoxy radical $CH_3CH(OH)CH(O^{\bullet})CH_2OH$, which is predicted[3,25−27] to dominantly decompose, mainly (∼93%) by the pathway

$$CH_3CH(OH)CH(O^{\bullet})CH_2OH \rightarrow CH_3C^{\bullet}HOH + HOCH_2CHO \quad (12a)$$

with the alternative decomposition pathway 12b being minor, and with the α-hydroxy radicals $CH_3C^{\bullet}HOH$ and $C^{\bullet}H_2OH$ reacting with O_2[24] to form CH_3CHO and HCHO, respectively (not quantified here due to background interferences).

$$CH_3CH(OH)CH(O^{\bullet})CH_2OH \rightarrow CH_3CH(OH)CHO + {}^{\bullet}CH_2OH \quad (12b)$$

H-atom abstraction from the 4-position CH_3 group, which is expected to account for ∼2% of the overall OH radical reaction,[10,18] leads to the hydroxyalkoxy radical $^{\bullet}OCH_2CH(OH)CH_2CH_2OH$ which is predicted[3,25−27] to mainly isomerize to ultimately form $HOCH_2CH(OH)CH_2CHO$.

Again as shown in Table 1, the hydroxycarbonyls observed are in accord with the expected reactions, and our measured yields are in reasonable agreement with predictions.

2,3-Butanediol. H-atom abstraction from the two equivalent CH(OH) groups leads to the formation of $CH_3C(O)CH(OH)CH_3$. H-atom abstraction from the two equivalent CH_3 groups leads, after reactions analogous to reactions 7−9, to formation of the hydroxyalkoxy radical $^{\bullet}OCH_2CH(OH)CH(OH)CH_3$, which is predicted[3,25−27] to decompose and isomerize at approximately similar rates. Isomerization is expected to lead to formation of $HOCH_2CH(OH)CH(OH)CHO$, whereas decomposition forms HCHO plus $CH_3CH(OH)CHO$. As shown in Table 1, the dominant product observed was $CH_3C(O)CH(OH)CH_3$ together with a minor amount of $CH_3CH(OH)CHO$.

2-Methyl-2,4-pentanediol. H-atom abstraction from the 4-position CH(OH) group leads to formation of 4-hydroxy-4-methyl-2-pentanone, $(CH_3)_2C(OH)CH_2C(O)CH_3$ (Table 1). The other major initial reaction involves H-atom abstraction from the 3-position CH_2 group, leading (after reactions analogous to reactions 7−9) to the hydroxyalkoxy radical $(CH_3)_2C(OH)CH(O^{\bullet})CH(OH)CH_3$, which is predicted to dominantly decompose by the pathway[3,25−27]

$$(CH_3)_2C(OH)CH(O^{\bullet})CH(OH)CH_3 \rightarrow CH_3CH(OH)CHO + CH_3C^{\bullet}(OH)CH_3 \quad (13)$$

followed by reaction of $CH_3C^{\bullet}(OH)CH_3$ with O_2 to form $CH_3C(O)CH_3$ plus HO_2.

The minor initial reaction pathways involving H-atom abstraction from the CH_3 groups (predicted[10,18] to account for <10% of the overall reaction) are expected to lead to formation of $(CH_3)_2C(OH)CH_2CHO$ plus HCHO after H-atom abstraction from the 5-position CH_3 group and $HOCH_2C(OH)(CH_3)CH_2C(O)CH_3$ after H-atom abstraction from the two equivalent 1-position CH_3 groups followed by isomerization of the initially formed alkoxy radical. The major hydroxycarbonyls observed here were those expected, with the $(CH_3)_2C(OH)CH_2CHO$ product predicted to be formed in ∼2% yield (see Table 1) being observed in the GC-MS analysis but too minor for GC-FID quantification. No oxime attributable to the dihydroxyketone was observed.

Conclusion

The predicted hydroxycarbonyls and their associated yields, obtained from estimates of the percentages of the OH radical reaction proceeding by H-atom abstraction from the various C−H groups combined with estimates of the reaction rates of the intermediate alkoxy radicals, are given in Table 1 (H-atom abstraction from the O−H bonds is expected to account for <1% of the overall reactions in all cases and is neglected here). Using SPME sampling with on-fiber derivatization, we have been able to observe the hydroxycarbonyls predicted to be formed in >1−2% yield (the predicted dihydroxycarbonyl $HOCH_2C(OH)(CH_3)CH_2C(O)CH_3$ was not observed). Taking into account the likely uncertainties in the hydroxyaldehyde quantifications, the predicted formation yields are in generally reasonable agreement with the measured yields, and we can account for 71−103% of the reaction pathways occurring. Clearly, the use of coated SPME fibers with on-fiber derivatization and GC-MS and GC-FID analyses can provide qualitative and quantitative information concerning the formation of hydroxyaldehydes which was not available using earlier sampling techniques.

Acknowledgment. The authors gratefully thank the California Air Resources Board (Contract No. 99-330) for supporting this research. Although this research has been funded by the California Air Resources Board, the results and content of this publication do not necessarily reflect the views and opinions of this agency.

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