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Rate Coefficients and Product Yields from Reaction of OH with 1-Penten-3-ol, (*Z*)-2-Penten-1-ol, and Allyl Alcohol (2-Propen-1-ol)

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The atmospheric chemistry of two recently discovered biogenic volatile organic compounds (VOCs), 1-penten-3-ol and (*Z*)-2-penten-1-ol, has been studied at 298 K using an environmental chamber/FTIR apparatus. Rate coefficients for their reaction with OH (determined by the relative rate technique) were found to be $(6.7 \pm 0.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $(10.6 \pm 1.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 1-penten-3-ol and (*Z*)-2-penten-1-ol, respectively. Products observed (with molar yields in brackets) from the OH-initiated oxidation of these species in 1 atm air at 298 K were glycolaldehyde (47 ± 6%) and formaldehyde (35 ± 4%) from 1-penten-3-ol; and propanal (91 ± 13%), glycolaldehyde (87 ± 11%) and formaldehyde (11 ± 2%) from (Z)-2-penten-1-ol. As a model for the more complex unsaturated alcohols, similar studies were also carried out on a simpler species, allyl alcohol (2-propen-1-ol, $CH_2{=}CHCH_2OH$). Reaction of this species with OH was found to proceed with a rate coefficient of $(4.5 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Products observed were formaldehyde (98 ± 12%), glycolaldehyde (90 ± 12%), and acrolein (5 ± 2%). Data obtained are used to assess the atmospheric fate and impact of the pentenols and to further develop structure−activity rules for the determination of OH rate coefficients with unsaturated species.

Introduction

Emissions of volatile organic compounds (VOCs) from vegetation exceed those from anthropogenic sources[1,2] and are known to exert a profound influence on tropospheric chemistry.[3−5] In addition to emissions from healthy plants, release of VOCs is known to occur as a result of leaf damage (for example, from grazing, cutting, harvesting, freezing, and drying).[6−9] The most heavily documented wound-induced emissions are a series of C6 compounds and their derivatives, (*Z*)-3-hexenal, (*Z*)-3-hexenol, (*E*)-2-hexenal, (*Z*)-3-hexenyl acetate, *n*-hexanal, *n*-hexanol, and hexyl acetate.[7,8,10,11] However, in a recent study using an in situ proton-transfer mass spectrometer system, Karl et al.[9] report the observation of C5 oxygenated species, including 1-penten-3-ol and (*Z*)-2-penten-1-ol, in ambient air in the Austrian Alps. The origins of these pentenol species, which reached concentrations of a few ppbv, are believed to be from freeze-damaged leaves as a result of peroxidation of fatty acids.[9,12]

At present, insufficient information is available to assess the atmospheric fate of these pentenol species. As with other unsaturated alcohols (and unsaturated species in general[13]), these compounds will be rather short-lived in the atmosphere (lifetime of a few hours), with reaction with OH, O_3, and NO_3 all playing a role in their atmospheric destruction. While rate coefficients for reaction of O_3 with 1-penten-3-ol and (*Z*)-2-penten-1-ol have been reported,[14] the OH- and NO_3-initiated oxidation of these species has yet to be studied.

In this paper, rate coefficients for the reaction of OH radicals with 1-penten-3-ol and (*Z*)-2-penten-1-ol are determined, as are the products of the OH-initiated oxidation of these species in air. The data are used to assess the atmospheric lifetime and fate of the pentenols. Complementary studies on a simpler model compound, allyl alcohol (2-propen-1-ol), are also reported.

Experimental Section

All experiments discussed here were carried out at 298 K in a stainless steel environmental chamber that has been described previously.[15,16] The cell is 2 m in length and has a volume of 47 L. It is interfaced to a Bomem DA3.01 Fourier transform spectrometer (operating in the infrared) via a set of Hanst-type multipass optics, which provided an optical path length of 32.6 m. Quantitative analysis of the chamber contents was accomplished by recording infrared spectra over the range 800−3900 cm^{-1} at a spectral resolution of 1 cm^{-1}. Typically, spectra were obtained from the coaddition of 200 interferograms, which required about 4 min of acquisition time.

Rate coefficients for the reaction of OH with the three unsaturated alcohols (1-penten-3-ol, (*Z*)-2-penten-1-ol, and allyl alcohol) were obtained using standard relative rate techniques, using propene as the reference compound and ethyl nitrite photolysis as the OH source. Photolyses were carried out using a Xe-arc lamp, filtered to provide radiation over the range 240−400 nm. Mixtures containing ethyl nitrite ($(0.7{-}1.1) \times 10^{15}$ molecule cm^{-3}), the alcohol under study ($(0.6{-}1.4) \times 10^{15}$ molecule cm^{-3}), propene ($(4{-}7) \times 10^{14}$ molecule cm^{-3}), and NO ($(4{-}9) \times 10^{14}$ molecule cm^{-3}) in synthetic air (700 Torr) were irradiated three to five times (for periods of 3−5 min), with an infrared spectrum being recorded following each irradiation. The minor components of the mixture were added to the reaction chamber via expansion from smaller calibrated volumes, while N_2 (boil-off from a liquid N_2 dewar) and O_2 (UHP Grade, U. S. Welding) were added directly to the chamber. Relative rate coefficients were obtained from the relative rate of disappearance of the unsaturated alcohol versus that of propene:

$$\ln\{[\text{alcohol}]_o/[\text{alcohol}]_t\} = k_{\text{alcohol}}/k_{\text{propene}} \ln\{[\text{propene}]_o/[\text{propene}]_t\}$$

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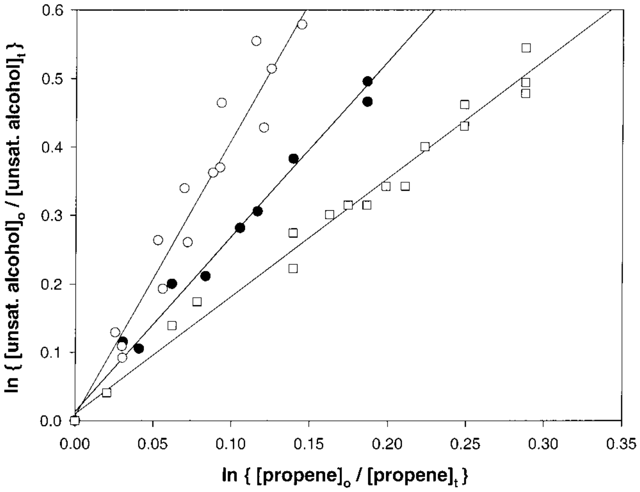

Figure 1. Plots of the decay of allyl alcohol (open squares), 1-penten-3-ol (filled circles), or (*Z*)-2-penten-1-ol (open circles) versus that of propene in the photolysis of CH_3ONO/unsaturated alcohol/propene/NO/air mixtures at 700 Torr total pressure, 298 K.

For completeness, rate coefficient ratios for the reaction of OH with 1-penten-3-ol and (*Z*)-2-penten-1-ol were determined using analogous procedures. Control experiments showed that propene and the unsaturated alcohols were not lost to any significant extent via heterogeneous processes over the time scale of a relative rate experiment.

Product studies involved the photolysis of mixtures containing ethyl nitrite ($(0.7-1.2) \times 10^{15}$ molecule cm^{-3}), the alcohol under study ($(0.5-1.5) \times 10^{15}$ molecule cm^{-3}), and NO ($(5-10) \times 10^{14}$ molecule cm^{-3}) in 700 Torr of synthetic air. Each fill of the chamber was irradiated three to five times (each photolysis 5 min), and an infrared spectrum was recorded following each irradiation. Concentrations of starting materials and products (formaldehyde, CH_2O; glycolaldehyde, $HOCH_2CHO$; propanal, CH_3CH_2CHO; acrolein, $CH_2{=}CHCHO$) were quantified by spectral stripping routines, using standard spectra recorded in our laboratory. Absorption cross sections for glycolaldehyde obtained in our lab agree favorably with those from Niki et al.[17] and Tuazon et al.[18] Small corrections (typically 5%) to observed product concentrations were made for secondary chemistry (reaction with OH[19,20] and, in the case of glycolaldehyde, a slow heterogeneous loss to the chamber walls, which occurs with a rate coefficient of 1.5×10^{-5} s^{-1}).[20]

Chemicals were obtained from the following sources: allyl alcohol (Aldrich, 99+%), 1-penten-3-ol (Aldrich, 99+%), (*Z*)-2-penten-1-ol (Aldrich, 95%), propene (Matheson, UHP), NO (Linde, UHP). Ethyl nitrite (CH_3CH_2ONO) was synthesized from the dropwise addition of concentrated H_2SO_4 to an ethanol/sodium nitrite slurry[21] and stored in dry ice. The alcohols and ethyl nitrite were purified/degassed by several freeze−pump−thaw cycles before use.

Results

OH Rate Coefficients. Rate coefficients for the reaction of OH with allyl alcohol (k_1), 1-penten-3-ol (k_2), and (*Z*)-2-penten-1-ol (k_3) were obtained relative to propene (k_4):

$$OH + HOCH_2CH{=}CH_2 \rightarrow \text{products} \qquad (R1)$$

$$OH + CH_2{=}CHCH(OH)CH_2CH_3 \rightarrow \text{products} \qquad (R2)$$

$$OH + HOCH_2CH{=}CHCH_2CH_3 \rightarrow \text{products} \qquad (R3)$$

$$OH + CH_3CH{=}CH_2 \rightarrow \text{products} \qquad (R4)$$

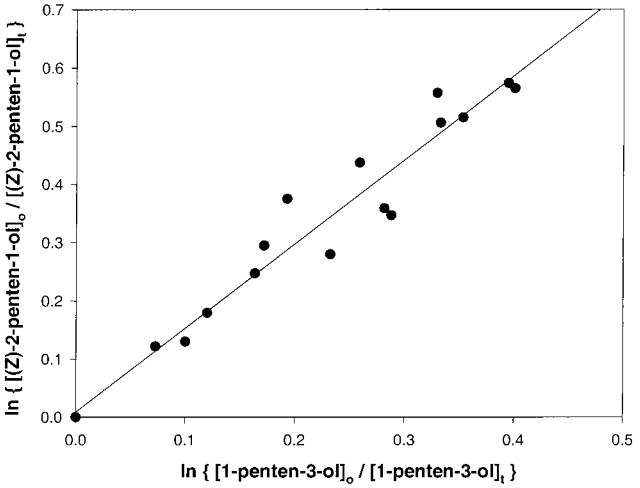

Figure 2. Plots of the decay of (*Z*)-2-penten-1-ol versus that of 1-penten-3-ol in the photolysis of CH_3ONO/1-penten-3-ol/(*Z*)-2-penten-1-ol/NO/air mixtures at 700 Torr total pressure, 298 K.

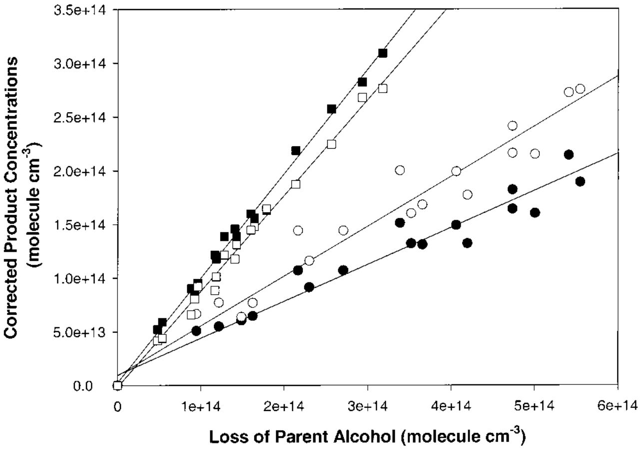

Figure 3. Observed product concentrations (corrected for secondary chemistry) as a function of unsaturated alcohol consumption, in the photolysis of CH_3ONO/unsaturated alcohol/NO/air mixtures at 700 Torr total pressure, 298 K: open squares, glycolaldehyde from allyl alcohol; filled squares, formaldehyde from allyl alcohol; open circles, glycolaldehyde from 1-penten-3-ol; filled circles, formaldehyde from 1-penten-3-ol.

Relative rate data are shown in Figure 1. Standard linear least-squares analysis of these data yields the following rate coefficient ratios: $k_1/k_4 = 1.72 \pm 0.12$, $k_2/k_4 = 2.56 \pm 0.16$, $k_3/k_4 = 4.04 \pm 0.45$. Using the accepted value[13] for k_4 at 700 Torr and 298 K, 2.63×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, yields the following values for k_1 through k_3 under these conditions: $k_1 = (4.5 \pm 0.6) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, $k_2 = (6.7 \pm 0.9) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, and $k_3 = (10.6 \pm 1.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Quoted uncertainties in the values for k_1-k_3 include 2σ precision errors and uncertainties in the reference rate coefficient (estimated at 10%). As a consistency check, the rate coefficient ratio k_3/k_2 was also determined at 298 K from the photolysis of CH_3CH_2ONO/1-penten-3-ol/(*Z*)-2-penten-1-ol/NO mixtures in 700 Torr synthetic air. As shown in Figure 2, a value of $k_3/k_2 = 1.44 \pm 0.12$ was obtained, consistent (within experimental uncertainty) with the ratio determined from the measurements made relative to k_4, $k_3/k_2 = 1.58 \pm 0.22$.

Product Yield Data. Products of the OH-initiated oxidation of allyl alcohol, 1-penten-3-ol, and (*Z*)-2-penten-1-ol were also determined in the environmental chamber system. As shown in Figure 3, products observed following reaction of OH with allyl alcohol were formaldehyde and glycolaldehyde, with molar

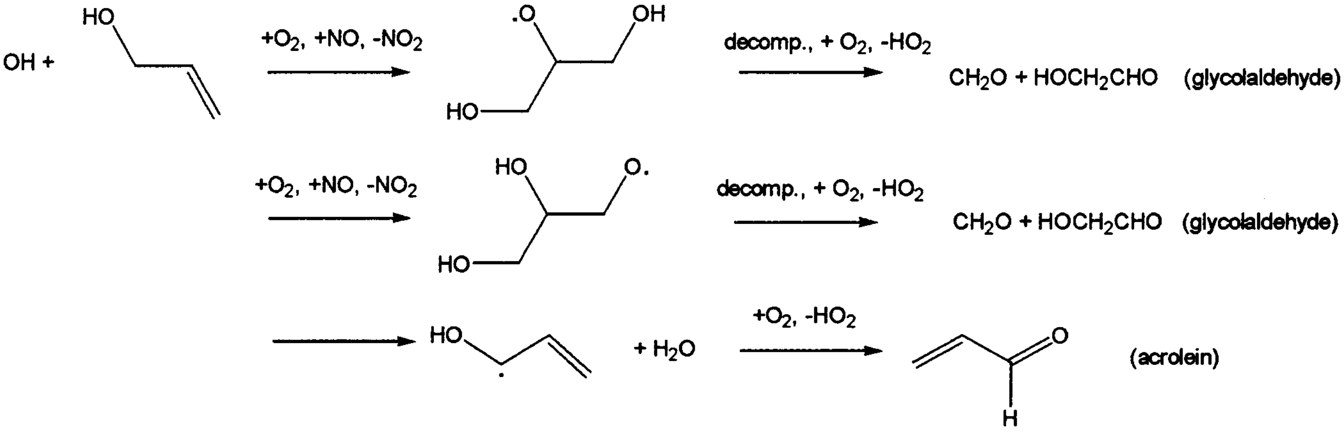

Figure 4. Chemistry occurring in the OH-initiated oxidation of allyl alcohol.

TABLE 1: Rate Coefficients for Alkenes and Their 1-Hydroxy-Substituted Counterparts at 1 atm Total Pressure, 298 K[a]

parent alkene	OH rate coefficient	corresponding unsaturated alcohol	OH rate coefficient	enhancement factor
propene $CH_3CH{=}CH_2$	2.6	allyl alcohol $HOCH_2CH{=}CH_2$	4.5[b] 5.5[c]	1.9
1-butene $CH_3CH_2CH{=}CH_2$	3.1	1-buten-3-ol $CH_3CH(OH)CH{=}CH_2$	5.9[c]	1.9
3-methyl-1-butene $(CH_3)_2CHCH{=}CH_2$	3.2	2-methyl-3-buten-2-ol $(CH_3)_2C(OH)CH{=}CH_2$	6.3[d]	2.0
1-pentene $CH_3CH_2CH_2CH{=}CH_2$	3.1	1-penten-3-ol $CH_3CH_2CH(OH)CH{=}CH_2$	6.7[b]	2.2
(*Z*)-2-pentene $CH_3CH_2CH{=}CHCH_3$	6.6	(*Z*)-2-penten-1-ol $CH_3CH_2CH{=}CHCH_2OH$	10.6[b]	1.6

[a] Rate coefficients are given in units of 10^{-11} cm^3 molecule^{-1} s^{-1}. Data for the parent alkenes are from ref 13. [b] This work. [c] From ref 24. [d] Average of data from refs 16, 24, 26.

TABLE 2: Rate Coefficients and Estimated Atmospheric Lifetimes for 1-Penten-3-ol and (*Z*)-2-Penten-1-ol with Respect to Reaction with OH, O_3, and NO_3[a]

pentenol	k_{OH}[b]	lifetime vs OH, h	k_{O_3}[c]	lifetime vs O_3, h	k_{NO_3}[d]	lifetime vs NO_3, h
1-penten-3-ol	6.7×10^{-11}	2.1	1.8×10^{-17}	11	1.4×10^{-14}	20
(*Z*)-2-penten-1-ol	10.6×10^{-11}	1.3	1.7×10^{-16}	1.2	1.4×10^{-14}	20

[a] All rate coefficients in cm^3 molecule^{-1} s^{-1}. Lifetimes estimated using [OH] = 2×10^6 molecule cm^{-3} (daytime only), [O_3] = 1.4×10^{12} molecule cm^{-3}, and [NO_3] = 1×10^9 molecule cm^{-3} (nighttime only).[1] [b] This work. [c] From ref 14. [d] Estimates are based on measurements of refs 29 and 30.

yields of 98 ± 12% and 90 ± 12%, respectively. Acrolein was also identified in the product spectra but, due to the small yield, could only be quantified at large allyl alcohol conversion. The yield of acrolein is estimated to be 5 ± 2%. The identified products account for 98 ± 12% of the reacted carbon. As shown in Figure 4, glycolaldehyde and formaldehyde are the expected coproducts obtained following OH-addition to either end of the double bond in allyl alcohol, while the presence of acrolein is evidence for a minor abstraction channel. The near-100% identification of products in the allyl alcohol oxidation experiments gives us confidence in our ability to quantify glycolaldehyde and other products obtained in the pentenol oxidation experiments discussed below.

The OH-initiated oxidation of 1-penten-3-ol resulted in the formation of glycolaldehyde and formaldehyde, as shown in Figure 3, with molar yields of 47 ± 6% and 35 ± 4%, respectively. The chemistry occurring following addition of OH to the 1-penten-3-ol double bond is shown in Figure 5. As seen from the figure, the formation of glycolaldehyde is expected to be accompanied by propanal formation, while CH_2O should occur along with 2-hydroxybutanal. Propanal was clearly present in the product spectra. Though difficult to quantify accurately due to spectral overlap with the various other carbonyl species, its concentration was found to be within ±30% of that of glycolaldehyde. Assuming the two coproducts to be present, 82 ± 8% of the reacted carbon is accounted for. The lack of 100% carbon balance suggests that other channels play a role in the chemistry. One possibility is isomerization of the 2,3-dihydroxy-1-pentoxy radical, which would likely lead to 2,3,4-trihydroxypentanal or 2,3-dihydroxypropanal (see Figure 5). The isomerization (rate coefficient $\approx 3 \times 10^6$ s^{-1})[22] is likely to be a minor but nonnegligible fate of the 2,3-dihydroxy-1-pentoxy radical (rate coefficient for dissociation $\approx 10^7$ s^{-1} by analogy to 2-hydroxy-1-propoxy radical[23]). Also, a small contribution from H-abstraction at the C3 carbon[24] to produce ethyl vinyl ketone (EVK) is a possibility. By analogy to methyl vinyl ketone (MVK), relatively strong absorption features for EVK are expected near 950 and 1710 cm^{-1}. Weak, unidentified features in these regions are evident in the product spectra; however, based on the assumption that MVK and EVK have similar absorption cross sections, the EVK yield is unlikely to be greater than 7%.

Products obtained in the OH-initiated oxidation of (*Z*)-2-penten-1-ol were glycolaldehyde, propanal, and formaldehyde, with molar yields of 87 ± 11%, 91 ± 13%, and 11 ± 2%, respectively (see Figure 6). The observed products account for 100 ± 14% of the reacted carbon. Furthermore, the equal yields of glycolaldehyde and propanal are consistent with the expected

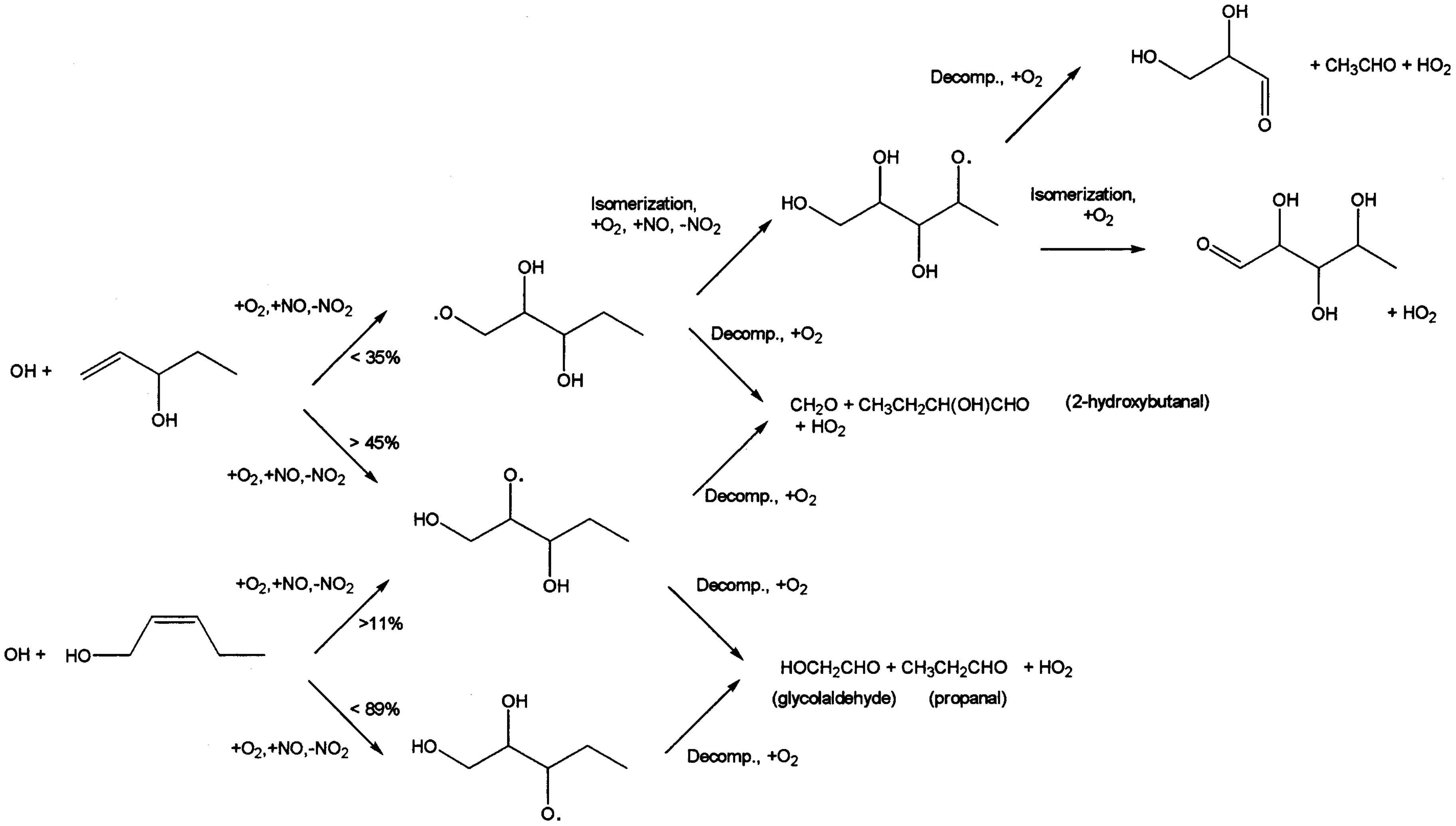

Figure 5. Chemistry occurring following the addition of OH to 1-penten-3-ol and (*Z*)-2-penten-1-ol.

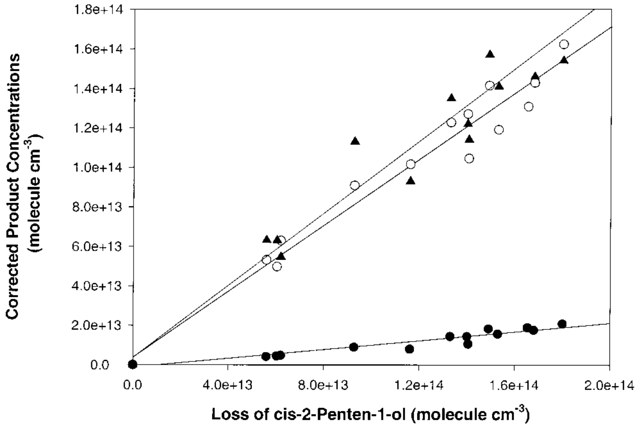

Figure 6. Observed product concentrations (corrected for secondary chemistry) as a function of (*Z*)-2-penten-1-ol consumption, in the photolysis of CH_3ONO/(*Z*)-2-penten-1-ol/NO/air mixtures at 700 Torr total pressure, 298 K: open circles, glycolaldehyde; filled circles, formaldehyde; filled triangles, propanal.

mechanism. As shown in Figure 5, OH addition to the C3 carbon in (*Z*)-2-penten-1-ol could lead to either propanal and glycolaldehyde, or formaldehyde and 2-hydroxybutanal, while addition at the C2 site would likely lead exclusively to the formation of propanal and glycolaldehyde. As was the case for 1-penten-3-ol, a minor contribution from abstraction (at the C1 site, leading to 2-pentenal) cannot be excluded. Note that no isomerizations via transition states containing six-membered rings are possible from the oxy radicals generated in the (*Z*)-2-penten-1-ol system.

Discussion and Conclusions

The atmospheric chemistry of allyl alcohol has recently been studied by Papagni et al.[24] Their value for the rate coefficient of OH with allyl alcohol, $k_1 = (5.5 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, is consistent (within experimental uncertainties) with our value, $(4.5 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Although a full product study was not conducted by Papagni et al.,[24] they did observe acrolein in 5% yield, thus confirming the existence of a minor abstraction channel. Previous studies of k_1 at elevated temperature conducted by Gordon and Mulac[25] ($k_1 = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 440 K) are broadly consistent with the room-temperature data (assuming a weak negative temperature dependence for k_1). However, we note that Gordon and Mulac[25] reported a positive temperature dependence for the OH rate coefficient with a number of alkenes (albeit over a limited temperature range). We are unaware of any previous studies of the reaction of OH with either 1-penten-3-ol or (*Z*)-2-penten-1-ol.

OH rate coefficient data are now available for a number of unsaturated alcohols in which the hydroxy group is located adjacent to the C=C double bond.[16,24−27] These data, along with OH rate coefficient data for the corresponding unsubstituted alkene,[13] are collected in Table 1. As was also noted by Papagni et al.,[24] a clear trend is observed, with the unsaturated alcohol reacting 1.9 ± 0.3 times faster than the corresponding alkene. The magnitude of the rate coefficient enhancement is somewhat larger than the enhancement factor recommended by Kwok and Atkinson,[28] 1.6, which was based on the Gordon and Mulac[25] data for k_1 at elevated temperature. Because the products observed in the OH-initiated oxidation of the pentenols can be formed from multiple pathways (Figure 5), product yields obtained in our experiments do not allow any firm conclusions regarding the position of attack of the OH on the unsaturated alcohols. However, the large yields of formaldehyde obtained in the oxidation of both 1-penten-3-ol and 2-methyl-3-buten-2-ol (MBO)[16] may indicate that OH addition to the side of the C=C double bond adjacent to the hydroxy group is being activated.

Measured and estimated rate coefficient data for reaction of OH (this work), O_3,[14] and NO_3 with 1-penten-3-ol and (*Z*)-2-penten-1-ol are collected in Table 2. As no NO_3 data are available, these rate coefficients were based on data[29,30] for NO_3 reaction with 2-methyl-3-buten-2-ol, but-1-en-3-ol, and allyl alcohol. It is clear from the lifetime estimates in Table 2 that reaction with OH will play a major role in the atmospheric destruction of the pentenols (lifetimes 1−2 h), though reaction with O_3 will be competitive, particularly in the case of (*Z*)-2-penten-1-ol. Reaction with NO_3 may also play a significant role in the nighttime chemistry of the pentenols. The major products obtained in the OH-initiated oxidation of the pentenols are all aldehydes (formaldehyde, glycolaldehyde, propanal, and 2-hydroxybutanal), and they will react with OH and photolyze in the atmosphere with overall time constants of less than 1 day. The high reactivity of the parent pentenols and of their major reaction products implies that large emissions of these species will play a significant role in boundary layer ozone production. Finally, we note that further oxidation of propanal and possibly 2-hydroxybutanal will, in part, generate peroxypropionyl nitrate (PPN). The production of PPN from the pentenols and hexenyl-type wound compounds[8,31,32] may contribute to recent observations of elevated PPN/PAN ratios in rural air.[32]

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References and Notes

(1) Brasseur, G. P.; Orlando, J. J.; Tyndall, G. S., Eds., *Atmospheric Chemistry and Global Change*; Oxford University Press: New York, 1999.

(2) Guenther, A. B.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P. *J. Geophys. Res.* **1995**, *100*, 8873.

(3) Trainer, M.; Williams, E. J.; Parrish, D. D.; Buhr, M. P.; Allwine, E. J.; Westberg, H. H.; Fehsenfeld, F. C.; Liu, S. C. *Nature* **1987**, *329*, 705.

(4) Chameides, W. L.: Lindsay, R. L.; Richardson, J.; Kiang, C. S. *Science* **1988**, *241*, 1473.

(5) Fehsenfeld, F. C.; Calvert, J. G.; Fall, R.; Goldan, P. D.; Guenther, A. B.; Hewitt, C. N.; Lamb, B.; Liu, S.; Trainer, M.; Westberg, H. H.; Zimmerman, P. *Global Biogeochem. Cycles* **1992**, *6*, 389.

(6) Gardner, H. W. *Biochim. Biophys. Acta* **1991**, *1084*, 221.

(7) de Gouw, J. A.; Howard, C. J.; Custer, T.; Fall, R. *Geophys. Res. Lett.* **1999**, *26*, 811.

(8) Fall, R.; Karl, T.; Hansel, A.; Jordan, A.; Lindinger, W. *J. Geophys. Res.* **1999**, *104*, 15963.

(9) Karl, T.; Fall, R.; Crutzen, P. J.; Jordan, A.; Lindinger, W. *J. Geophys. Res.* **2001**, in press.

(10) Kirstine, W.; Galbally, I.; Ye, Y.; Hooper, M. *J. Geophys. Res.* **1998**, *103*, 10605.

(11) Helmig, D.; Klinger, L. F.; Guenther, A.; Vierling, L.; Geron, C.; Zimmerman, P. *Chemosphere* **1999**, *38*, 2163.

(12) Fall, R.; Karl, T.; Jordan, A.; Lindinger, W. *Atmos. Environ.* **2001**, submitted.

(13) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215.

(14) Grosjean, E.; Grosjean, D. *Int. J. Chem. Kinet.* **1994**, *26*, 1185.

(15) Shetter, R. E.; Davidson, J. A.; Cantrell, C. A.; Calvert, J. G. *Rev. Sci. Instrum.* **1987**, *58*, 1427.

(16) Ferronato, C.; Orlando, J. J.; Tyndall, G. S. *J. Geophys. Res.* **1998**, *103*, 25579.

(17) Niki, H.; Maker, P. D.; Savage, C. M.; Hurley, M. D. *J. Phys. Chem.* **1987**, *91*, 2174.

(18) Tuazon, E. C.; Atkinson, R. *Int. J. Chem. Kinet.* **1989**, *21*, 1141.

(19) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, *26*, 521.

(20) Bacher, C.; Tyndall, G. S.; Orlando, J. J. *J. Atmos. Chem.* **2001**, in press.

(21) Taylor, W. D.; Allston, T. D.; Moscato, M. J.; Fazekas, G. B.; Kozlowski, R.; Takacs, G. C. *Int. J. Chem. Kinet.* **1980**, *12*, 231.

(22) Atkinson, R. *Int. J. Chem. Kinet.* **1997**, *29*, 99.

(23) Vereecken, L.; Peeters, J.; Orlando, J. J.; Tyndall, G. S.; Ferronato, C. *J. Phys. Chem. A* **1999**, *103*, 4693.

(24) Papagni, C.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **2001**, *33*, 142.

(25) Gordon, S.; Mulac, W. A. *Int. J. Chem. Kinet.*, *Symp.1* **1975**, 289.

(26) Rudich, Y.; Talukdar, R.; Burkholder, J. B.; Ravishankara, A. R. *J. Phys. Chem.* **1995**, *99*, 12188.

(27) Fantechi, G.; Jensen, N. R.; Hjorth, J.; Peeters, J. *Int. J. Chem. Kinet.* **1998**, *30*, 589.

(28) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685.

(29) Rudich, Y.; Talukdar, R.; Fox, R. W.; Ravishankara, A. R. *J. Phys. Chem.* **1996**, *100*, 5374.

(30) Hallquist, M.; Langer, S.; Ljungstrom, E.; Wangberg, I. *Int. J. Chem. Kinet.* **1996**, *28*, 467.

(31) Grosjean, D.; Williams II, E. L.; Grosjean, E. *Environ. Sci. Technol.* **1993**, *27*, 979.

(32) Roberts, J. M.; Bertman, S. B.; Parrish, D. D.; Fehsenfeld, F. C. *J. Geophys. Res.* **1998**, *103*, 13569.