Rate Constants for the Gas-Phase Reactions of OH Radicals with a Series of Unsaturated Alcohols

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ABSTRACT: Using a relative rate method, rate constants for the gas-phase reactions of OH radicals with allyl alcohol, 3-buten-1-ol, 3-buten-2-ol, and 2-methyl-3-buten-2-ol have been measured at 296 ± 2 K and atmospheric pressure of air. Using 1,3,5-trimethylbenzene as the reference compound, the rate constants (in units of 10^{-11} cm^3 molecule^{-1} s^{-1}) were: allyl alcohol, 5.46 ± 0.35; 3-buten-1-ol, 5.50 ± 0.20; 3-buten-2-ol, 5.93 ± 0.23; and 2-methyl-3-buten-2-ol, 5.67 ± 0.13; where the indicated errors are two least-squares standard deviations and do not include the uncertainty in the rate constant for 1,3,5-trimethylbenzene. The H-atom abstraction products acrolein and methyl vinyl ketone were observed from the allyl alcohol and 3-buten-2-ol reactions, respectively, with respective yields of 5.5 ± 0.7 and 4.9 ± 1.4%. No evidence for formation of acrolein from 3-buten-1-ol or 3-buten-2-ol was obtained, with upper limits to the acrolein yields of $\leq$1.2 and $\leq$0.5%, respectively, being determined. Reaction mechanisms are discussed. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 33: 142–147, 2001

INTRODUCTION

2-Methyl-3-buten-2-ol [$(CH_3)_2C(OH)CH{=}CH_2$] is emitted into the atmosphere in large quantities from vegetation [1–3], and allyl alcohol [$CH_2{=}CHCH_2OH$] is used as an intermediate in the manufacture of a number of chemicals [4]. In the troposphere, these and other unsaturated alcohols react with OH radicals [5–8], NO_3 radicals [7,9,10], and O_3 [7,11–13], with the O_3 and daytime OH radical reactions being calculated to dominate as the tropospheric loss processes for 2-methyl-3-buten-2-ol [14]. To date, rate constants for the OH radical reactions with unsaturated alcohols are available only for allyl alcohol [5] and 2-methyl-3-buten-2-ol [6–8], with the available rate constant for allyl alcohol being at 440 K. In this work, we have used a relative rate method to measure rate constants at 296 ± 2 K for allyl alcohol, 3-buten-1-ol [$CH_2{=}CHCH_2CH_2OH$], 3-buten-2-ol [$CH_2{=}CHCH(OH)CH_3$], and 2-methyl-3-buten-2-ol. In addition, we have investigated the formation of products that arise after initial H-atom abstraction from the allylic C—H bonds in these alcohols.

EXPERIMENTAL

The experimental methods were similar to those used previously [15]. Experiments were carried out in a 7000-l Teflon chamber at 296 ± 2 K and 740 Torr

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total pressure of purified air at ~5% relative humidity. The chamber is equipped with two parallel banks of black lamps for irradiation and a Teflon-coated fan to ensure rapid mixing of reactants during their introduction into the chamber. Rate constants were measured using a relative rate method in which the relative disappearance rates of the alcohols and a reference compound, whose OH radical reaction rate constant is reliably known, were measured in the presence of OH radicals [15]. Providing that the alcohols and the reference compound reacted only with OH radicals, then [15],

$$\ln\left(\frac{[\text{alcohol}]_{t_0}}{[\text{alcohol}]_t}\right) = \frac{k_1}{k_2}\ln\left(\frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t}\right) \qquad \text{(I)}$$

where $[\text{alcohol}]_{t_0}$ and $[\text{reference organic}]_{t_0}$ are the concentrations of the alcohol and the reference compound, respectively, at time t_0, $[\text{alcohol}]_t$ and $[\text{reference organic}]_t$ are the corresponding concentrations at time t, and k_1 and k_2 are the rate constants for reactions (1) and (2), respectively:

$$\text{OH} + \text{alcohol} \longrightarrow \text{products} \qquad (1)$$

$$\text{OH} + \text{reference organic} \longrightarrow \text{products} \qquad (2)$$

Therefore, plots of $\ln([\text{alcohol}]_{t_0}/[\text{alcohol}]_t)$ against $\ln([\text{reference organic}]_{t_0}/[\text{reference organic}]_t)$ should be straight lines with slope k_1/k_2 and zero intercept.

OH radicals were generated by the photolysis of methyl nitrite (CH_3ONO) in air at wavelengths >300 nm [16], and NO was added to the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals [16]. The initial reactant concentrations (in molecule cm^{-3} units) were: CH_3ONO, $\sim 2.4 \times 10^{14}$; NO, $\sim 2.4 \times 10^{14}$; and alcohols and reference compound, $\sim 2.4 \times 10^{13}$ each. 1,3,5-Trimethylbenzene and *m*-xylene were used as reference compounds because their OH radical reaction rate constants [17–20] are similar to those reported for allyl alcohol (at 440 K) [5] and 2-methyl-3-buten-2-ol [6–8], and they could be analyzed by gas chromatography using the same sampling procedure and gas chromatographic column as the alcohols. Irradiations were carried out for 7–33 min, resulting in up to 45–84% reaction of the initially present alcohols, *m*-xylene and 1,3,5-trimethylbenzene.

To check on the importance of photolysis of the unsaturated alcohols during the CH_3ONO—NO—alcohol–1,3,5-trimethylbenzene–*m*-xylene–air irradiations, a mixture containing the alcohols ($\sim 2.4 \times 10^{13}$ molecule cm^{-3} each) and *n*-octane (1.0×10^{16} molecule cm^{-3}) in air was irradiated for up to 40 min at the same light intensity as used in the rate constant determinations. The excess of *n*-octane was present to scavenge any OH radicals formed during the irradiation. To investigate the formation of selected products and to ascertain that reaction products did not interfere with the analysis of the other reactants, irradiations of CH_3ONO—NO—individual alcohol–air mixtures were also carried out using similar initial concentrations as in the rate constant determinations.

The concentrations of the alcohols and reference compounds were measured using gas chromatography with flame ionization detection (GC-FID). 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 −40°C and then temperature programmed to 240°C at 8°C min^{-1}. Based on replicate analyses in the dark, the GC-FID measurement uncertainties for the alcohols and reference compounds were typically 1–2%. GC-FID response factors for the alcohols and selected potential products were determined by introducing measured amounts of the compounds into the chamber and conducting several replicate analyses [21]. Products were confirmed by combined gas chromatography–mass spectrometry (GC–MS) analyses, with collection of pre- and post-reaction samples onto Tenax-TA solid adsorbent with subsequent thermal desorption onto a DB-1701 column in a Hewlett-Packard (HP) 5890 GC interfaced to an HP 5971A Mass Selective Detector. Confirmation of products involved matching of GC retention times and mass spectra with those of authentic standards. The NO and initial NO_2 concentrations were measured using a Thermo Environmental Instruments, Inc. Model 42 chemiluminescence NO–NO_2–NO_x analyzer.

The chemicals used, and their stated purities, were: allyl alcohol (99+%), AcrosOrganic; acrolein (90%), 3-buten-1-ol (98+%), 3-buten-2-ol (97%), 2-methyl-3-buten-2-ol (98%), methyl vinyl ketone (99%), *n*-octane (99+%), and *m*-xylene (99+%), Aldrich Chemical Company; 1,3,5-trimethylbenzene, Eastman Chemical Company; and NO (≥99%), Matheson Gas Products. Methyl nitrite was prepared and stored as described previously [16].

RESULTS

Irradiation of an alcohols–*n*-octane–air mixture for up to 40 min showed <5% loss of any of the alcohols,

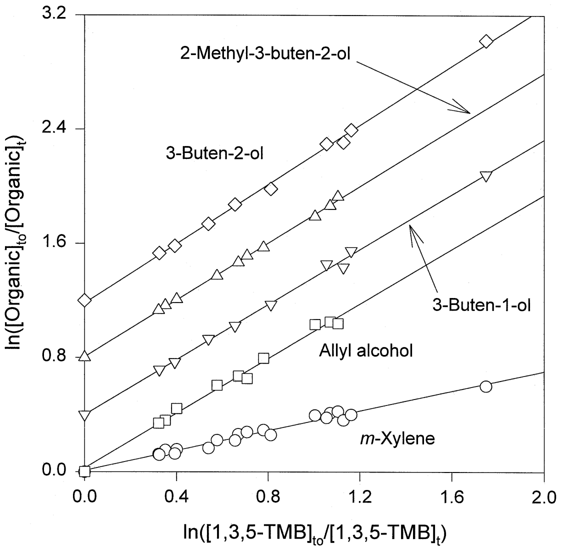

Figure 1 Plots of Eq. (I) for the gas-phase reactions of the OH radical with allyl alcohol, 3-buten-1-ol, 3-buten-2-ol, 2-methyl-3-buten-2-ol, and *m*-xylene, with 1,3,5-trimethylbenzene (1,3,5-TMB) as the reference compound. The data for 3-buten-1-ol, 3-buten-2-ol, and 2-methyl-3-buten-2-ol have been displaced vertically by 0.4, 0.8, and 1.2 units, respectively, for clarity.

indicating that photolysis of the alcohols during the OH radical rate constant determinations was of no importance. Furthermore, over the ~6-h duration of the photolysis experiment the concentrations of the alcohols changed by <5%, showing that wall losses of the alcohols were also negligible. The lack of photolysis of these alcohols at wavelengths >300 nm is consistent with the measured, very weak absorption of 2-methyl-3-buten-2-ol above 290 nm [6]. A series of $CH_3ONO-NO-$alcohol-1,3,5-trimethylbenzene-*m*-xylene-air irradiations was carried out, and the experimental data obtained are plotted in accordance with Eq. (I) in Figure 1. Straight-line plots are observed, and the rate constant ratios k_1/k_2 obtained by least-squares analyses of the data are given in Table I. These rate constant ratios k_1/k_2 are placed on an absolute basis by use of a rate constant k_2 for the reaction of the OH radical with 1,3,5-trimethylbenzene of $k_2 = 5.70 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 296 K (with an estimated overall uncertainty of ±10%), this being an average of the rate constants obtained from the relative rate studies of Atkinson and Aschmann [18] (5.75×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 ± 2 K) and Kramp and Paulson [20] (5.64×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 ± 2 K, after reevaluation using the most recent recommendations [19,22] for the rate constants of the reference compounds used). 1,3,5-Trimethylbenzene

Table I Rate Constant Ratios k_1/k_2 and Rate Constants k_1 for the Gas-Phase Reactions of OH Radicals with Unsaturated Alcohols at 296 ± 2 K and Atmospheric Pressure of Air

		$10^{11} \times k_1$ (cm^3 molecule^{-1} s^{-1})		
Alcohol	k_1/k_2[a]	This Work[b]	Literature	Reference
Allyl alcohol	0.958 ± 0.060	5.46 ± 0.35	2.59 ± 0.34 (at 440 K)	Gordon and Mulac [5]
3-Buten-1-ol	0.965 ± 0.035	5.50 ± 0.20		
3-Buten-2-ol	1.04 ± 0.04	5.93 ± 0.23		
2-Methyl-3-buten-2-ol	0.995 ± 0.022	5.67 ± 0.13	6.4 ± 0.6	Rudich et al. [6]
			4.27 ± 1.80[c]	Fantechi et al. [7]
			3.85 ± 0.80[d]	Fantechi et al. [7]
			7.35 ± 0.79[e]	Ferronato et al. [8]
			6.43 ± 0.54[f]	Ferronato et al. [8]
m-Xylene	0.347 ± 0.027	1.98 ± 0.16	2.30 ± 0.06[g]	Atkinson and Aschmann [18]
			2.18 ± 0.19[g]	Kramp and Paulson [20]
			2.09 ± 0.14[g]	Aschmann and Atkinson [39]

[a] Indicated errors are two least-squares standard deviations.

[b] Placed on an absolute basis using a rate constant for the reaction of the OH radical with 1,3,5-trimethylbenzene of $k_2 = 5.70 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 296 K [18,20]. The indicated errors are two least-squares standard deviations and do not take into account uncertainties in the rate constant k_2 (estimated to be approximately ±10% [20]).

[c] At 298 ± 2 K, relative to k_2(isoprene) = 1.01×10^{-10} cm^3 molecule^{-1} s^{-1} [22].

[d] At 298 ± 2 K, relative to k_2(propene) = 2.63×10^{-11} cm^3 molecule^{-1} s^{-1} [22].

[e] At 295 ± 1 K, relative to k_2(ethene) = 8.65×10^{-12} cm^3 molecule^{-1} s^{-1} [22].

[f] At 295 ± 1 K, relative to k_2(propene) = 2.68×10^{-11} cm^3 molecule^{-1} s^{-1} [22].

[g] Relative rate studies at 296 ± 2 K. The rate constant of Kramp and Paulson [20] has been reevaluated to be consistent with the most recent recommendations [17,19,22] for the reference compounds used.

was used as the reference compound rather than *m*-xylene because the alcohols studied here are very similar to 1,3,5-trimethylbenzene in their reactivity towards the OH radical, but are a factor of ~3 more reactive than is *m*-xylene. The resulting rate constants k_1 are given in Table I.

GC-FID analyses of irradiated CH_3ONO–NO–alcohol–air mixtures suggested the formation of acrolein from allyl alcohol and methyl vinyl ketone from 3-buten-2-ol, and these products were confirmed by GC-MS analyses. There was no evidence for the formation of acrolein from 3-buten-1-ol or from 3-buten-2-ol (products of the OH radical reaction with 2-methyl-3-buten-2-ol have previously been studied by Fantechi et al. [23], Ferronato et al. [8], and Alvarado et al. [24] and were hence not studied here). Acrolein and methyl vinyl ketone also react with the OH radical [17,19], and in the product yield determinations secondary reactions with the OH radical were taken into account as described previously [25]. Corrections to account for secondary reactions with OH radicals increase with the rate constant ratio $k(\mathrm{OH} + \mathrm{product})/k(\mathrm{OH} + \mathrm{alcohol})$ and with the extent of reaction [25] and are expressed as multiplicative correction factors F [25]. For each experimental data point the multiplicative factor F was calculated using the analytical expression given by Atkinson et al. [25], using rate constants for reactions of OH radicals with acrolein and methyl vinyl ketone at 296 K of 1.99×10^{-11} cm^3 molecule^{-1} s^{-1} [19] and 2.06×10^{-11} cm^3 molecule^{-1} s^{-1} [26,27], respectively. The maximum values of F were 1.25 for formation of acrolein from allyl alcohol, 1.45 for the potential formation of acrolein from 3-buten-1-ol, 1.48 for formation of methyl vinyl ketone from 3-buten-2-ol, and 1.20 for the potential formation of acrolein from 3-buten-2-ol. Least-squares analyses of the amounts of product formed, corrected for reaction with the OH radical, against the amounts of alcohol reacted lead to formation yields of acrolein from allyl alcohol of $5.5 \pm 0.7\%$, of acrolein from 3-buten-1-ol of $\leq 1.2\%$, and of methyl vinyl ketone and acrolein from 3-buten-2-ol of $4.9 \pm 1.4\%$ and $<0.5\%$, respectively, where the indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for the products and alcohols of $\pm 5\%$ each.

DISCUSSION

The rate constants measured here for reaction of OH radicals with unsaturated alcohols are compared with the literature values in Table I. Our rate constant for 2-methyl-3-buten-2-ol agrees to within 11% with the absolute room-temperature rate constant reported by Rudich et al. [6] and is between the rate constants obtained in the relative rate studies of Fantechi et al. [7] and Ferronato et al. [8]. Rudich et al. [6] observed formation of OH radicals from 2-methyl-3-buten-2-ol in the absence of O_2, presumably from elimination of the hydroxyl group at the 2-position. The rate constant of Rudich et al. [6] cited in Table I was obtained from experiments using OH radicals in the presence of O_2 and from experiments using OD radicals [6].

The only rate constant available for allyl alcohol was obtained by Gordon and Mulac [5] at 440 K (Table I). The rate constant for reaction of the OH radical with 2-methyl-3-buten-2-ol has a temperature dependence of B (in $k = Ae^{-B/T}$) $= -610$ K [6] (similar to the temperature dependencies for reactions of the OH radical with alkenes [17,19], which typically have $B \sim -500$ K). Hence, a 296 K rate constant for allyl alcohol of $\sim(4.5–5.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} is anticipated from the 440 K rate constant measured by Gordon and Mulac [5], in reasonable agreement with our measured value (Table I). No rate constants have been reported to date for the reactions of the OH radical with 3-buten-1-ol or 3-buten-2-ol. The rate constant measured here for *m*-xylene is in reasonable agreement with the literature values [17–20,28–40] and especially with the more recent relative rate studies [18,20,39].

The reactions of the OH radical with the four unsaturated alcohols studied here are expected [17,19,24,41] to proceed mainly by initial addition of the OH radical to the carbon atoms of the $>C{=}C<$ bond. The first-generation products anticipated to be formed from OH radical addition to allyl alcohol, 3-buten-1-ol, and 3-buten-2-ol in the presence of NO are $HOCH_2CHO + HCHO$ from allyl alcohol, $HOCH_2CH_2CHO + HCHO$ from 3-buten-1-ol, and $HOCH_2CHO + CH_3CHO$ and $HCHO + CH_3CH(OH)CHO$ from 3-buten-2-ol [19,22]. Unfortunately, apart from acetaldehyde, these products are not expected to be amenable to analysis by gas chromatography without prior derivatization [24,42,43] and were not observed in the present study.

H-atom abstraction from the C—H bonds of the substituent groups is anticipated to be relatively minor compared to OH radical addition to the $>C{=}C<$ bonds [17,19] (note that H-atom abstraction from vinylic C—H bonds and from O—H bonds is of negligible importance [17,19,41]). H-atom abstraction from the allylic C—H bonds of allyl alcohol leads to the α-hydroxy radical $CH_2{=}CHC^{\bullet}HOH$,

$$\mathrm{OH + CH_2{=}CHCH_2OH \longrightarrow H_2O + CH_2{=}CHC^{\bullet}HOH} \tag{3}$$

which is expected to react with O_2 [19] to form acrolein:

$$\mathrm{CH_2{=}CHC^{\bullet}HOH + O_2 \longrightarrow CH_2{=}CHCHO + HO_2} \tag{4}$$

This is the only route to acrolein formation from allyl alcohol, and our measured formation yield of acrolein from allyl alcohol of 5.5 ± 0.7% therefore refers to the fraction of the reaction proceeding via initial H-atom abstraction from the allylic C—H bonds in the CH_2OH group.

H-atom abstraction from the allylic C—H bond of 3-buten-2-ol results in the formation of methyl vinyl ketone by analogous reactions:

$$\mathrm{OH + CH_2{=}CHCH(OH)CH_3 \longrightarrow H_2O + CH_2{=}CHC^{\bullet}(OH)CH_3} \tag{5}$$

$$\mathrm{CH_2{=}CHC^{\bullet}(OH)CH_3 + O_2 \longrightarrow CH_2{=}CHC(O)CH_3 + HO_2} \tag{6}$$

while H-atom abstraction from the CH_3 group is expected to lead to formation of acrolein because the intermediate alkoxy radical $CH_2{=}CHCH(OH)CH_2O^{\bullet}$ will undergo decomposition [22]:

$$\mathrm{CH_2{=}CHCH(OH)CH_2O^{\bullet} \longrightarrow CH_2{=}CHC^{\bullet}HOH + HCHO} \tag{7}$$

$$\mathrm{CH_2{=}CHC^{\bullet}HOH + O_2 \longrightarrow CH_2{=}CHCHO + HO_2} \tag*{(4)}$$

Therefore, our measured formation yield of methyl vinyl ketone from 3-buten-2-ol of 4.9 ± 1.4% refers to the fraction of the reaction proceeding via initial H-atom abstraction from the allylic C—H bond of 3-buten-2-ol. The upper limit to the acrolein yield from 3-buten-2-ol places an upper limit of 0.5% for the contribution of H-atom abstraction from the methyl group to the overall OH radical reaction.

For 3-buten-1-ol, H-atom abstraction from the allylic C—H bonds leads initially to the $CH_2{=}CHC^{\bullet}HCH_2OH$ radical, which is expected to exist mainly as $^{\bullet}CH_2CH{=}CHCH_2OH$ and ultimately form $HC(O)CH{=}CHCH_2OH$ [22]. The $CH_2{=}CHC^{\bullet}HCH_2OH$ radical would lead to formation of acrolein through the intermediary of the $CH_2{=}CHCH(O^{\bullet})CH_2OH$ radical:

$$\mathrm{CH_2{=}CHCH(O^{\bullet})CH_2OH \longrightarrow CH_2{=}CHCHO + {}^{\bullet}CH_2OH} \tag{8}$$

Our upper limit to the formation yield of acrolein from 3-buten-1-ol of ≤1.2% is consistent with the expectation that $^{\bullet}CH_2CH{=}CHCH_2OH$ is the dominant radical after H-atom abstraction from the allylic C—H bonds of 3-buten-1-ol. H-atom abstraction from the C—H bonds of the CH_2OH group in 3-buten-1-ol is expected to result in the formation of $CH_2{=}CHCH_2CHO$, which was not observed in this work (note, however, that no standard of this product was available).

The 296 K rate constants for reaction of OH radicals with allyl alcohol, 3-buten-1-ol, 3-buten-2-ol, and 2-methyl-3-buten-2-ol are all similar at $(5.5-5.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and are a factor of 2.1–2.2 higher than the 296 K rate constant for propene (2.66×10^{-11} cm^3 molecule^{-1} s^{-1} [17,19,22]). Because H-atom abstraction from the reactions of 2-methyl-3-buten-2-ol [24] (which contains no allylic C—H bonds), allyl alcohol, and 3-buten-2-ol is predicted [17,41] and observed to be of minor or negligible importance, then the substituent $C(OH)(CH_3)_2$, CH_2OH, and $CH(OH)CH_3$ groups must activate the $CH_2{=}CH{-}$ bond by a factor of ~2 towards OH radical addition, relative to propene. While it is possible that H-atom abstraction from the CH_2 and CH_2OH groups in 3-buten-1-ol is significantly higher than that observed from allyl alcohol and 3-buten-2-ol (i.e., >5%), the observed OH radical reaction rate constant for 3-buten-1-ol suggests that the CH_2CH_2OH group also activates the $CH_2{=}CH{-}$ bond towards OH radical addition by a factor of ~2.

Finally, all four of the unsaturated alcohols studied here are calculated to have tropospheric lifetimes due to gas-phase reaction with the OH radical of 2.5 h for a 12-h average daytime OH radical concentration of 2.0×10^6 molecule cm^{-3} [44,45].

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