Rate Coefficients for the Reaction of OH with a Series of Unsaturated Alcohols between 263 and 371 K

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Rate coefficients for the gas-phase reactions of OH radicals with four unsaturated alcohols, 3-methyl-3-buten-1-ol (k_1), 2-buten-1-ol (k_2), 2-methyl-2-propen-1-ol (k_3) and 3-buten-1-ol (k_4), were measured using two different techniques, a conventional relative rate method and the pulsed laser photolysis-laser induced fluorescence technique. The Arrhenius rate coefficients (in units of cm^{3}molecule^{-1} s^{-1}) over the temperature range 263−371 K were determined from the kinetic data obtained as $k_1 = (5.5 \pm 1.0) \times 10^{-12}$ exp [(836 ± 54)/T]; $k_2 = (6.9 \pm 0.9) \times 10^{-12}$ exp [(744 ± 40)/T]; $k_3 = (10 \pm 1) \times 10^{-12}$ exp [(652 ± 27)/T]; and $k_4 = (4.0 \pm 0.4) \times 10^{-12}$ exp [(783 ± 32)/T]. At 298 K, the rate coefficients obtained by the two methods for each of the alcohols studied were in good agreement. The results are presented and compared with those obtained previously for the same and related reactions of OH radicals. Reactivity factors for substituent groups containing the hydroxyl group are determined. The atmospheric implications for the studied alcohols are considered briefly.

1. Introduction

Unsaturated alcohols are emitted into the atmosphere as primary pollutants from a wide number of anthropogenic and biogenic sources. For example, 3-methyl-3-buten-1-ol (MBO331) is emitted by vegetation,[1,2] and 2-buten-1-ol (BO21), 2-methyl-2-propen-1-ol (MPO221), and 3-buten-1-ol (BO31) are used as starting materials in several plastic industries and polymer synthesis. The main gas phase removal process of unsaturated alcohols is the reaction with the OH radical, with the oxidation with O_3 and NO_3 radicals being other important degradation pathways.[3–7] In order to assess the impact of these chemical species on air quality, a detailed understanding of the kinetics and mechanisms of their atmospheric degradation is required.

In this work, we report the rate coefficients for OH radical reactions with MBO331 (k_1), BO21 (k_2), MPO221 (k_3) and BO31 (k_4):

$$OH + CH_2{=}C(CH_3)CH_2CH_2OH \rightarrow \text{products} \quad (k_1) \quad (1)$$

$$OH + CH_3CH{=}CHCH_2OH \rightarrow \text{products} \quad (k_2) \quad (2)$$

$$OH + CH_2{=}C(CH_3)CH_2OH \rightarrow \text{products} \quad (k_3) \quad (3)$$

$$OH + CH_2{=}CHCH_2CH_2OH \rightarrow \text{products} \quad (k_4) \quad (4)$$

The kinetic study of the above reactions was performed in the temperature range 263−371 K and pressure of 100 Torr, using the pulsed laser photolysis-laser induced fluorescence (PLP-LIF) technique and also by using a relative method at 298 K and atmospheric pressure.

To the best of our knowledge, this work provides the first temperature dependence studies for the four reactions. The only existing data reported in the literature are those at 298 K of Imamura et al.[8] for MBO331 and Papagni et al.[9] for BO31.

The kinetics results obtained are presented and discussed in terms of the influence of the OH group on the reactivity of these alcohols compared to the parent alkenes. They contribute to extend the kinetic database which is necessary to develop structure−activity relationships for OH reactions with oxygenated volatile organic compounds. Also, the tropospheric lifetimes of the four alcohols are estimated.

2. Experimental Section

The experiments were conducted partly at ICARE/CNRS (Orléans, France) where an absolute method, pulsed laser photolysis-laser induced fluorescence (PLP-LIF), was used to determine the rate coefficients for the above reactions in the temperature range 263−371 K at around 100 Torr, and partly at INFIQC (Córdoba, Argentina) where the k_1−k_4 rate coefficients were measured with a conventional relative rate technique using collapsible bags at room temperature and atmospheric pressure. This last method was also used to measure $k_2$at ICARE/CNRS.

2.1. Relative Measurements. The INFIQC experimental setup used to measure the relative rate coefficients consisted of a greaseless vacuum system, an 80 L collapsible Teflon bag, and a gas chromatograph (Shimadzu GC-14B) coupled with flame ionization detection (GC-FID). Measured amounts of the reagents were flushed from calibrated Pyrex bulbs into the collapsible reaction chamber by a stream of synthetic air, and it was then filled to its full capacity at atmospheric pressure with synthetic air. The Teflon bag was surrounded by germicide lamps (Philips 30W) which provided UV radiation with a λ maximum around 254 nm. In the present

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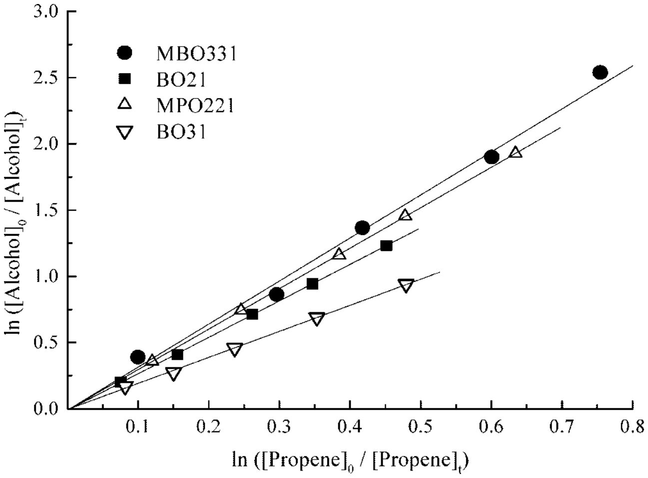


Figure 1. Relative rate data for the OH reaction with 3-methyl-3-buten-1-ol (MBO331), 2-buten-1-ol (BO21), 2-methyl-2-propen-1-ol (MPO221), and 3-buten-1-ol (BO31) using propene as a reference compound.

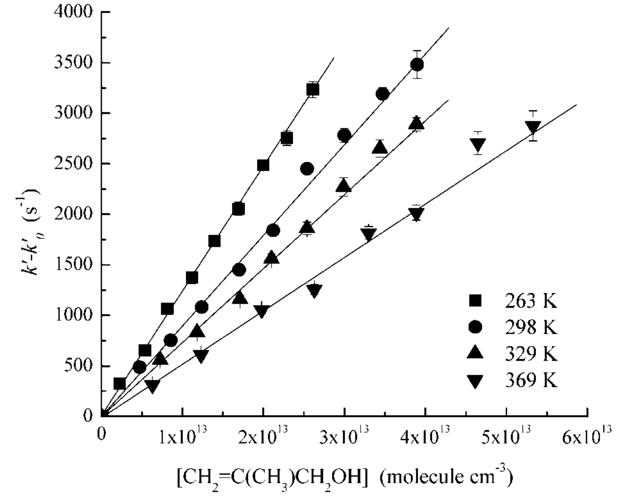


Figure 2. Absolute rate data for the OH reaction with 2-methyl-2-propen-1-ol (MPO221) at different temperatures.

study, these lamps were used to produce OH radicals by the photolysis of H_2O_2. Periodically, gas samples were removed from the Teflon bag using calibrated gas syringes (Hamilton gastight) and analyzed using the GC-FID. An Elite-1 capillary column (Perkin-Elmer, 30 m, 0.32 mm i.d.) was used and maintained at 308 K during the chromatographic runs. N_2 was used as the carrier gas.

The experimental system of ICARE-CNRS used to measure $k_2$by the relative method consisted of 120 L Teflon bag located in a wooden box with the internal walls covered by aluminum foil. Measured amounts of the organic reactants were flushed from calibrated bulbs into the Teflon bag through a stream of ultra-pure air. The bag was then filled to its full capacity at atmospheric pressure with ultra-pure air. H_2O_2, introduced into the bag by a Hamilton syringe, was used to generate OH radicals by direct UV photolysis with lamps emitting at 254 nm (Sylvania G30W). The concentrations of the organics were monitored, over the course of the reaction. Gas samples were automatically collected from the chamber and introduced via a heated sampling loop of 0.25 mL capacity by gas chromatography using a gas chromatograph equipped with flame ionization detection (GC-FID, Star 3600 CX, Varian). Chromatographic separation was achieved by using a DB-1 capillary column (J&W Scientific, 30 m, 0.25 mm id, 5μm film). The column was operated at the temperature of 353 K, and helium was used as the carrier gas.

Relative rate coefficients were determined by comparing the rate coefficients for the reaction of OH radicals with the unsaturated alcohols to that with reference compounds:

$$\mathrm{OH} + \mathrm{alcohol} \rightarrow \mathrm{products} \qquad k_i$$

$$\mathrm{OH} + \mathrm{reference} \rightarrow \mathrm{products} \qquad k_{\mathrm{Ref}}$$

Provided that both reactant and reference compounds are lost only by reaction with OH, it can be shown that

$$\ln([\mathrm{alcohol}]_0/[\mathrm{alcohol}]_t) = (k_i/k_{\mathrm{Ref}}) \times \ln([\mathrm{Ref}]_0/[\mathrm{Ref}]_t)$$

where $[\mathrm{alcohol}]_0$ and $[\mathrm{alcohol}]_t$are the concentrations of the unsaturated alcohol at times 0 and t, respectively, $[\mathrm{Ref}]_0$ and $[\mathrm{Ref}]_t$ are the concentrations of the reference compound at times 0 and t, respectively, k_i ($i = 1-4$) are the second-order rate coefficients for reactions 1−4, and k_{Ref} is the second-order rate coefficient for the reaction of the reference compound with OH radicals.

The rate coefficients for the reactions of OH with four unsaturated alcohols were measured at (298 ± 2) K and atmospheric pressure (~750 Torr), relative to the rate coefficient of OH with cyclohexene, propene, and 3-buten-2-ol (BO32) in the experiments conducted at INFIQC. The experiments carried out at ICARE for k_2 determination used 2-propen-1-ol (allyl

TABLE 1: Rate Coefficient Ratios, k_i/k_{Ref}, and the Obtained Second-Order Rate Coefficients for the Reactions of OH with the Studied Unsaturated Alcohols at (298 ± 2) K and Atmospheric Pressure

unsaturated alcohol	reference compound	number of runs	k_i/k_{ref}	k_i (cm^3 molecule^{-1} s^{-1})
3-methyl-3-buten-1-ol $CH_2{=}C(CH_3)CH_2CH_2OH$	propene	2	3.19 ± 0.14	$(9.6 \pm 1.8) \times 10^{-11}$
	3-buten-2-ol	2	1.64 ± 0.06	$(9.7 \pm 0.8) \times 10^{-11}$
		average		$\mathbf{(9.7 \pm 1.8) \times 10^{-11}}$
2-buten-1-ol $CH_3CH{=}CHCH_2OH$	propene	2	2.78 ± 0.10	$(8.3 \pm 1.5) \times 10^{-11}$
	3-buten-2-ol	2	1.49 ± 0.09	$(8.8 \pm 0.9) \times 10^{-11}$
	3-buten-2-ol[a]	3	1.97 ± 0.03	$(11 \pm 1) \times 10^{-11}$
	2-propen-1-ol[a]	3	2.14 ± 0.04	$(11 \pm 1) \times 10^{-11}$
	propyl vinyl ether[a]	4	0.98 ± 0.03	$(10 \pm 1) \times 10^{-11}$
		average		$\mathbf{(9.8 \pm 1.5) \times 10^{-11}}$
2-methyl-2-propen-1-ol $CH_2{=}C(CH_3)CH_2OH$	propene	2	3.05 ± 0.02	$(9.2 \pm 1.3) \times 10^{-11}$
	3-buten-2-ol	2	1.53 ± 0.02	$(9.1 \pm 0.5) \times 10^{-11}$
		average		$\mathbf{(9.2 \pm 1.3) \times 10^{-11}}$
3-buten-1-ol $CH_2{=}CHCH_2CH_2OH$	propene	2	1.96 ± 0.03	$(5.9 \pm 0.9) \times 10^{-11}$
	cyclohexene	2	0.87 ± 0.01	$(5.9 \pm 0.2) \times 10^{-11}$
		average		$\mathbf{(5.9 \pm 0.9) \times 10^{-11}}$

[a] Experiments conducted at ICARE-CNRS.

TABLE 2: Summary of Experimental Conditions and the Measured OH Reaction Rate Coefficient with 3-Methyl-3-buten-1-ol (MBO331), 2-Buten-1-ol (BO21), 2-Methyl-2-propen-1-ol (MPO221), and 3-Buten-1-ol (BO31) in the Temperature Range 263−371 K

T (K)	[MBO331][a]	k_1[b]	[BO21][a]	k_2[b]	[MPO221][a]	k_3[b]	[BO31][a]	k_4[b]
263	0.67−3.52	13.40 ± 0.80	0.53−2.71	12.02 ± 0.70	0.23−2.61	12.17 ± 0.27	1.37−4.90	7.42 ± 0.24
272	0.67−4.58	11.80 ± 0.80						
273			0.71−3.25	10.69 ± 0.29	0.59−4.45	10.81 ±v0.54	1.42−5.63	7.00 ± 0.43
			0.69−2.99	11.14 ± 0.70	0.50−2.69	11.00 ± 0.38		
282			0.83−3.05	9.15 ± 0.44			2.05−8.27	6.21 ± 0.20
283					0.73−2.66	10.46 ± 0.45	1.98−7.36	6.37 ± 0.25
294	1.27−6.22	9.05 ± 0.84						
298	0.67−4.44	9.72 ± 0.68	1.56−6.38	8.03 ± 0.48	0.47−3.90	9.12 ± 0.41	2.38−10.20	5.60 ± 0.23
	0.60−3.10	9.09 ± 0.10	0.79−3.42	8.56 ± 0.28	0.67−3.26	9.57 ± 0.48	1.97−9.51	5.83 ± 0.36
			0.64−3.57	7.81 ± 0.40	0.45−3.43	9.28 ± 0.58		
312	1.03−4.65	7.60 ± 0.26						
313			0.73−3.70	7.63 ± 0.30			2.34−8.65	4.99 ± 0.28
314					0.29−4.10	7.74 ± 0.20		
327	1.45−4.11	7.17 ± 0.29						
328							2.30−8.25	4.59 ± 0.15
329			0.62−5.17	6.31 ± 0.23	0.73−3.89	7.59 ± 0.31		
343							2.32−8.11	4.03 ± 0.22 ±
346			0.77−4.21	6.16 ± 0.40				
347	1.64−5.69	6.37 ± 0.46					2.17−9.09	3.73 ± 0.16
348					1.11−4.47	6.29 ± 0.46		
369	1.27−8.01	5.54 ± 0.60	1.02−5.70	5.24 ± 0.24	0.63−5.33	5.56 ± 0.38		
370			0.93−4.91	5.70 ± 0.40	1.04−5.71	5.52 ± 0.30	1.95−9.60	3.08 ± 0.16
371							1.66−9.90	3.18 ± 0.15

[a] Units of 10^{13} molecule cm^{-3}. [b] Units of 10^{-11} cm^{-3} molecule^{-1} s^{-1}. The uncertainties given for k_i are 2σ precision from the fit to the data and do not include systematic errors.

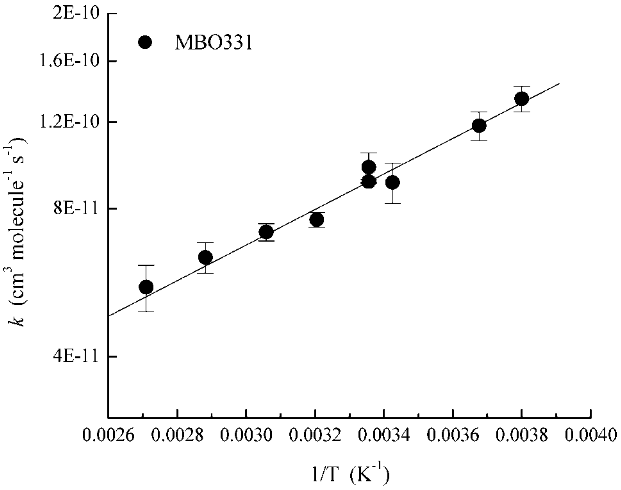


Figure 3. Plot of k_1 as function of $1/T$ for the OH reaction with 3-methyl-3-buten-1-ol (MBO331) in the temperature range 263−369 K.

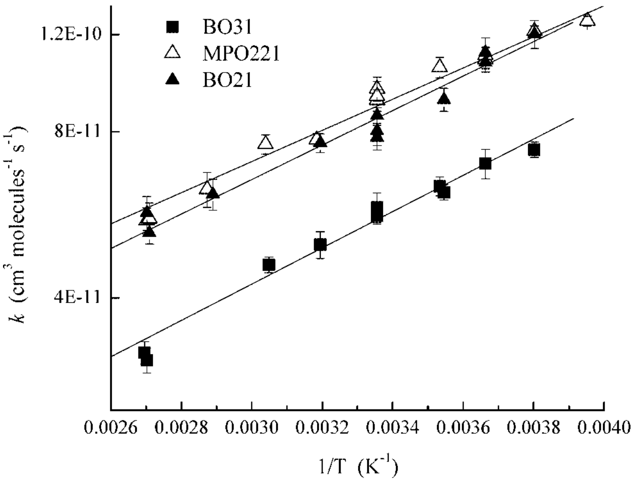


Figure 4. Plots of k_2, k_3, and k_4 as functions of $1/T$ for the OH reaction with 2-buten-1-ol (BO21), 2-methyl-2-propen-1-ol (MPO221), and 3-buten-1-ol (BO31) in the temperature range 263−371 K.

alcohol, PO21), propyl vinyl ether, and 3-buten-2-ol as reference compounds. The concentration range of the different alcohols and reference compounds was $(0.7-3.1) \times 10^{15}$ molecule cm^{-3}. The H_2O_2 concentrations used were in the range $(1.9-6.2) \times 10^{15}$ molecule cm^{-3}. The mixtures of alcohols and references with H_2O_2 were stable in the dark when left in the chamber for about 2 h. Moreover, no photolysis of both alcohols and references was observed when mixtures of the reactants in the absence of H_2O_2 and in air were irradiated for 20 min using the output of all of the germicide lamps. In the present work, photolysis was carried out in steps of 2 min, and the total time of photolysis varied from 2 to 12 min. Time between sampling of the gas mixture for analysis was about 5 min.

2.2. Absolute Measurements. The details of the PLP-LIF experimental setup and methodology used for studying these reactions have been described previously.[10] Therefore, the description below is limited to the features necessary to understand the current experiments.

OH radicals were generated by photolysis of H_2O_2 at $\lambda =$ 248 nm (KrF excimer laser). The concentration of OH radicals was monitored at various reaction times ranging from about 10 μs to 10 ms, by pulsed laser induced fluorescence (LIF). A frequency-doubled dye laser pumped by a Nd:YAG laser was used to excite the OH radicals at $\lambda = 282$ nm, and fluorescence from OH radicals was detected by a photomultiplier tube fitted with a 309 nm narrow bandpass filter. The output pulse from the photomultiplier was integrated for a preset period by a gated charge integrator. Typically, the fluorescence signal resulting from 100 probe laser shots was measured for 10 to 15 different delay times and averaged to generate OH concentration−time profiles over at least three lifetimes. H_2O_2 was introduced into the reaction cell by

TABLE 3: Summary of Arrhenius Parameters Obtained in This Work and Those from Previous Determinations

alcohol	k_{298K}[a]	A[b]	E/R (K)	T range (K)	method	reference
MBO331	9.4 ± 0.4	5.5 ± 1.0	−(836 ± 54)	263−369	PLP-LIF[c]	this work
	9.7 ± 1.8			298	RR[d]	this work
	9.7 ± 0.7			298	RR[d]	8
BO21	8.1 ± 0.4	6.9 ± 0.9	−(744 ± 40)	263−369	PLP-LIF[c]	this work
	9.8 ± 1.5			298	RR[d]	this work
MPO221	9.3 ± 0.2	10 ± 1	−(652 ± 27)	263−370	PLP-LIF[c]	this work
	9.2 ± 1.3			298	RR[d]	this work
BO31	5.7 ± 0.1	4.0 ± 0.4	−(783 ± 32)	263−371	PLP-LIF[c]	this work
	5.9 ± 0.9			298	RR[d]	this work
	5.5 ± 0.2			296	RR[d]	9

[a] Units of 10^{-11} cm^3 molecule^{-1} s^{-1}. [b] Units of 10^{-12} cm^3 molecule^{-1} s^{-1}. [c] Pulsed laser photolysis-laser induced fluorescence. [d] Relative rate.

TABLE 4: Substituent Group Factors C(X) at 298 K

substituent group X	group factor C(X)
$-CH_2OH$	1.7[a]
$-CH_2CH_2OH$	2.0[b]
$-CH(OH)CH_2CH_3$	2.5[c]
$-CH(OH)CH_3$	2.3[d]
$-C(CH_3)_2OH$	2.1[e]

[a] Derived from $k_{CH2=CHCH2OH} = 5.5 \times 10^{-11}$ (ref 9), $k_{CH2=C(CH3)CH2OH} = 9.3 \times 10^{-11}$ (this work), $k_{CH3CH=CHCH2OH} = 8.1 \times 10^{-11}$ (this work), $k_{Z\text{-}C2H5CH=CHCH2OH} = 10.6 \times 10^{-11}$ (ref 7), and $k_{(CH3)2C=CHCH2OH} = 15 \times 10^{-11}$ (ref 8). [b] Derived from $k_{CH2=CHCH2CH2OH} = 5.7 \times 10^{-11}$ (this work) and $k_{CH2=C(CH3)CH2CH2OH} = 9.4 \times 10^{-11}$ (this work). [c] Derived from $k_{CH2=CHCH(OH)CH2CH3} = 6.7 \times 10^{-11}$ (ref 7). [d] Derived from $k_{CH2=CHCH(OH)CH3} = 6.0 \times 10^{-11}$, which is the average value between 5.9×10^{-11} (ref 9) and 6.1×10^{-11} (ref 17). [e] Derived from $k_{CH2=CHC(CH3)2OH} = 5.5 \times 10^{-11}$ (ref 3). All of the k values are in units of 10^{-11} cm^3 molecule^{-1} s^{-1}.

passing a small flow of helium through a glass bubbler containing a solution of H_2O_2. Unsaturated alcohols were premixed with helium in a 10 L glass bulb to form a 0.1−0.4% mixture at total pressure of about 1000 Torr. The gas mixture, the photolytic precursor (H_2O_2), and the bath gas (He) were flowed through the cell with a linear velocity in the range 3−10 cm s^{-1}. Each photolysis/probe sequence interrogated a fresh gas mixture, and reaction products did not build up in the cell. The reactant concentrations were calculated from their mass flow rates, the temperature, and the pressure in the reaction cell. All flow rates were measured with mass flow meters calibrated by measuring the rate of pressure increase in a known volume. The pressure in the cell was measured with a capacitance manometer connected at the entrance of the cell.

Absolute rate coefficients were determined under pseudo-first-order conditions with the concentration of unsaturated alcohols in excess over that of the OH radicals ([alcohol]$_0$ > [OH]$_0$). Typically, the initial OH radical concentration ([OH]$_0$) was in the range (0.5−5.2) × 10^{11} molecule cm^{-3}. The rate of disappearance of the OH radical followed a simple exponential rate law:

$$[\mathrm{OH}]_t = [\mathrm{OH}]_0 e^{-k't} \qquad \text{where} \qquad k' = k_i[\text{alcohol}] + k'_0$$

and k_i represents the rate coefficient for the reaction of OH with the four alcohols, so that $i = 1-4$ and k'_0 is the first-order rate coefficient for OH removal in the absence of alcohol because of the diffusion of OH radicals out of the detection zone and the reaction between OH radicals and their precursor (H_2O_2).

Experiments were carried out in the temperature range 263−371 K and at total pressure between 101 and 107 Torr of helium. The unsaturated alcohol and H_2O_2 concentrations were in the range (0.2−10.2) × 10^{13} molecule cm^{-3} and (0.3−2.7) × 10^{14} molecule cm^{-3}, respectively.

2.3. Materials. The helium carrier gas (Alpha Gas UHP certified to >99.9995%), synthetic air (AGA 99.999%) and propene (99+%) were used without further purification. The 50 wt % H_2O_2 solution, from Prolabo, was concentrated by bubbling helium through the solution to remove water for several days prior to use and constantly during the experiment. MBO331 (97%), E/Z BO21 (97%), BO31 (96%), BO32 (97%), propyl vinyl ether (99%), and cyclohexene (99%) from Sigma-Aldrich, and MPO221 (98%) and PO21 (>99.5%) from Fluka were degassed by repeated freeze−pump−thaw cycles and purified by vacuum distillation before use.

3. Results and Discussion

3.1. Rate Coefficient Measurements. ***3.1.1. Relative Measurements.*** The second-order rate coefficients for reactions 1−4 were measured at (298 ± 2) K and atmospheric pressure and obtained from the relative loss of alcohols versus that of the reference compounds in the presence of OH. Figure 1 shows example plots of ln([alcohol]$_0$/[alcohol]$_t$) as a function of ln([Ref]$_0$/[Ref]$_t$). The rate coefficients of the reaction of OH (in cm^3 molecule^{-1} s^{-1}) with the references used in this work were taken as (6.74 ± 0.17) × 10^{-11} for cyclohexene,[11,12] (3.01 ± 0.42) × 10^{-11} for propene,[13] (5.46 ± 0.35) × 10^{-11} for 2-propen-1-ol,[9] (5.93 ± 0.23) × 10^{-11} for 3-buten-2-ol,[9] and (10 ± 1) × 10^{-11} for propyl vinyl ether[14] at 298 K. The linearity of the data points and the fact that the plots show practically zero intercepts suggest that the contribution of secondary reactions with the products of the reactions studied could be considered negligible. The obtained rate coefficient ratios and the corresponding rate coefficients for the reactions of OH radicals with the unsaturated alcohols are presented in Table 1. The value of k_2 obtained at ICARE was slightly higher than the one from INFIQC, $k_2 = (10.7 \pm 1.0) \times 10^{-11}$ and $(8.6 \pm 1.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. The recommended rate coefficients values obtained by averaging the values from different experiments were the following:

$$k_1 = (9.7 \pm 1.8) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

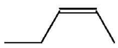
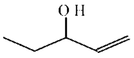
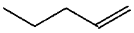
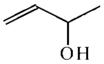
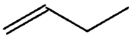
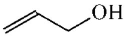
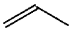
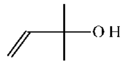
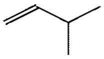
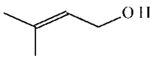
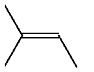
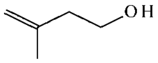
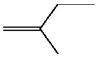
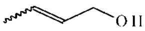
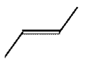
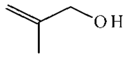
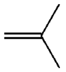
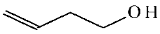
$$k_2 = (9.8 \pm 1.5) \times 10^{-11}\ \mathrm{cm^3 molecule^{-1} s^{-1}}$$

$$k_3 = (9.2 \pm 1.3) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1} s^{-1}}$$

$$k_4 = (5.9 \pm 0.9) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines and include the corresponding statistical error in the reference rate constant. The uncertainties in the rate coefficients do not take into account

TABLE 5: Rate Coefficient for the Reaction of OH Radicals with Unsaturated Alcohols and Homologous Alkenes at 298 K

alcohol	k_{298K}[a]	reference	alkene	k_{298K}[a]	reference
 Z-2-penten-1-ol	(10.6 ± 1.5)	7	 Z-2-pentene	(6.4 ± 0.2)	18
 1-penten-3-ol	(6.7 ± 0.9)	7	 1-pentene	(3.1 ± 0.1)	19
 3-buten-2-ol	(5.9 ± 0.2)	9	 1-butene	(3.1 ± 0.2)	19
 2-propen-1-ol	(5.5 ± 0.4)	9	 propene	(3.0 ± 0.4)	13
 2-methyl-3-buten-2-ol	(5.5 ± 0.5)	3	 3-methyl-1-butene	(3.2 ± 0.1)	19
 3-methyl-2-buten-1-ol	(15 ± 1)	8	 2-methyl-2-butene	(8.7 ± 0.3)	20
 3-methyl-3-buten-1-ol	(9.4 ± 0.4)	This work	 2-methyl-1-butene	(6.5 ± 0.1)	18
 (Z/E)-2-buten-1-ol	(8.1 ± 0.4)	This work	 E-2-butene	(6.1 ± 0.3)	20
 2-methyl-2-propen-1-ol	(9.3 ± 0.2)	This work	 2-methylpropene	(5.5 ± 0.1)	18
 3-buten-1-ol	(5.7 ± 0.1)	This work	 1-butene	(3.1 ± 0.2)	19

[a] Units of 10^{-11} cm^3 molecule^{-1} s^{-1}.

TABLE 6: Estimated Atmospheric Lifetimes of Unsaturated Alcohols Studied with OH and NO_3 Radicals and O_3 Molecules

alcohol	k_{OH}[a]	τ_{OH}[b]	k_{NO3}[a]	τ_{NO3}[c]	k_{O3}[a]	τ_{O3}[d]
MBO331	(9.4 ± 0.4) × 10^{-11}[e]	1.5 h	(2.7 ± 0.2) × 10^{-13}[f]	2.1 h		
BO21	(8.1 ± 0.4) × 10^{-11}[e]	1.7 h	(4.1 ± 0.4) × 10^{-13}[f]	1.4 h	(251 ± 41) × 10^{-18}[g]	1.6 h
MPO221	(9.3 ± 0.2) × 10^{-11}[e]	1.5 h				
BO31	(5.7 ± 0.1) × 10^{-11}[e]	2.4 h			(4.9 ± 0.4) × 10^{-18}[h]	3.4 d

[a] All of the k values are at 298 K and in units of cm^3 molecule^{-1} s^{-1}. [b] [OH] = 2 × 10^6 radicals cm^{-3} (ref 21), h = hours. [c] $[NO_3]$ = 5 × 10^8 radicals cm^{-3} (ref 22), h = hours. [d] $[O_3]$ = 7 × 10^{11} molecule cm^{-3} (ref 23), h = hours and d = days. [e] This work. [f] Reference 24. [g] Reference 5. [h] Reference 6.

potential systematic errors in the reference rate constants, which could be as high as 15−20%.

3.1.2. Absolute Measurements. The absolute rate coefficients k_1-k_4were measured in the temperature and pressure ranges 263−371 K and 101−107 Torr (of helium) under pseudo-first-order conditions in which the concentration of the unsaturated alcohols was at least 10 times that of the OH radicals. The OH decays were found to be exponential over at least three lifetimes while k'_0 and k' were in the ranges 132−554 s^{-1} and 627−7254 s^{-1}, respectively. The variation of the photolysis fluence (2.4−20 mJ cm^{-2}) had no effect on the determined rate coefficients indicating that there was no noticeable contribution of photofragments to the OH consumption. The alcohol samples were purified to better than 99%, and hence loss of OH radicals by reaction with impurities is expected to be insignificant.

Figure 2 shows as an example a plot of ($k'-k'_0$) as a function of MPO221 concentration at different temperatures. The experimental conditions and the values obtained for k_1-k_4 are presented in Table 2. The rate coefficients, taken as the average of all values obtained at (298 ± 2) K are

$$k_1 = (9.4 \pm 0.4)\ \mathrm{x}\ 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_2 = (8.1 \pm 0.4) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_3 = (9.3 \pm 0.2) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_4 = (5.7 \pm 0.1) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

The errors quoted for k_1-k_4 are 2σ from the linear least-squares fit to the data points and do not include systematic errors. These values are in good agreement with those obtained by the relative method. Figures 3 and 4 show the measured rate coefficients for the studied reactions plotted as a function of the reciprocal of temperature. A least-squares analysis of the ln k_i versus 1/T plot leads to the following expressions for the temperature dependence of k_1-k_4 in the temperature range 263−371 K (in units of cm^3 $molecule^{-1}$ s^{-1}):

$$k_1 = (5.5 \pm 1.0) \times 10^{-12} \exp\,[(836 \pm 54)/T]$$

$$k_2 = (6.9 \pm 0.9) \times 10^{-12} \exp\,[(744 \pm 40)/T]$$

$$k_3 = (10 \pm 1) \times 10^{-12} \exp\,[(652 \pm 27)/T]$$

$$k_4 = (4.0 \pm 0.4) \times 10^{-12} \exp\,[(783 \pm 32)/T]$$

Uncertainties are $2\sigma_{\ln A}$ and $2\sigma_{E/R}$ for A and E/R, respectively.

3.1.3. Discussion. Table 3 presents the OH reaction rate coefficients for the four alcohols obtained in this work at 298 K as well as the Arrhenius parameters and includes the values determined previously for MBO331 and BO31. As can be seen in Table 3, the values of the rate coefficients at 298 K for reactions 1 and 4 are in good agreement with those obtained by Imamura et al.[8] and Papagni et al.[9] using the relative method. The pressure independence of the rate coefficients at 298 K in the present study in the pressure range 100−760 Torr indicates that the measured values correspond to the high pressure limit. To our best knowledge, the rate coefficients for reactions 2 and 3 at 298 K and the temperature-dependence parameters for the four reactions have not been reported prior to this work. The results show negative temperature dependence for k_1-k_4consistent with the addition mechanism that is observed for the reaction of the OH radical with unsaturated compounds.[12]

In order to study the effect of the presence of substituents with a hydroxyl group on the reactivity of the OH radical with unsaturated alcohols, structure−activity relationship (SAR) calculations developed by Atkinson[15] were applied. For instance, for the alkene CH_2CHX containing the substituent group X, other than an alkyl group, the rate constant is given by $k(CH_2{=}CHX) = k(CH_2{=}CH-) \times C(X)$, where $k(CH_2{=}CH-)$ is the group rate constant for OH addition to $CH_2{=}CH-$ and C(X), the group factor for the substituent X. Group factors C(X) were calculated on the basis of the $k(CH_2{=}CH-)$ or $k(-CH{=}CH-)$ values, reported by Kwok and Atkinson[16] for OH + alkenes reactions, and k_{exp} values taken from this work and the literature.[3,7–9,17] The considered substituent groups and their corresponding factors calculated by SAR are shown in Table 4. This calculation implies a comparison between the reactivity of the unsaturated alcohols and the simple alkenes, that is, a basic structure with X = CH_3.

As can be seen in Table 4, C(X) factors for substituent groups containing the hydroxyl group are between 1.7 and 2.5, the reactivity of the unsaturated alcohols toward OH radicals being higher than that of the corresponding simple alkenes, for which the C(X) factor is taken as unity. This effect can be attributed to the strong electron donor character of the hydroxyl group which increases the charge density on the double bond as well as the polarizability of π electrons, leading to an increase in the rate constant value, which is consistent with the electrophilic character of the attaching OH radical.

The increase of reactivity, by a factor of about 2, as a result of the presence of the hydroxyl group in the unsaturated alcohols can be observed in Table 5, where $k_{298K}$of the unsaturated alcohols is compared with k_{298K} of the homologous alkenes (R has the same aliphatic structure as the substituent group but the hydroxyl group is changed to H).

3.2. Atmospheric Implications. In addition to reaction with OH, the unsaturated alcohols could be removed from the atmosphere by reaction with O_3, NO_3, and Cl atoms. Considering the gas-phase loss processes, the lifetimes toward reaction with OH, O_3, and NO_3 have been calculated for the four alcohols using an OH radical concentration (12 h daytime average) of 2 × 10^6 radicals cm^{-3},[21] a 12 h night time average of $[NO_3] = 5 \times 10^8$ radicals cm^{-3}, [22] and a 24 h average O_3 concentration of 7 × 10^{11} molecule cm^{-3}.[23] The lifetimes calculated using the relationship $\tau_x = 1/k_x[X]$ with X = OH, O_3, and NO_3 are summarized in Table 6.

Taking into account the UV spectrum of 2-methyl-3-buten-2-ol reported by Rudich et al.[3] and that its chemical structure is similar to this series of compounds, we can assume that the unsaturated alcohols studied in this work are photolytically stable in the actinic region of the solar spectrum, indicating that the tropospheric removal by photolysis can be considered negligible.

The studied alcohols are expected to be highly soluble (e.g., Henry's law coefficient for BO21 is estimated around 300 M atm^{-1} at 298 K[25]). Their lifetime for wet deposition is therefore of several months referring to calculations for fluoroalcohols.[26] These lifetimes are yet much higher than the lifetimes toward gas phase reactions, making wet deposition negligible for the studied alcohols.

The lifetime data shown in Table 6 indicate that the unsaturated alcohols are likely to be rapidly removed in the gas phase, that the losses by reaction with OH, NO_3, and O_3 are comparable, and that these compounds will be degraded near their emission sources. All of these values should be treated with caution because the OH, NO_3, and O_3 concentrations vary substantially depending on the environment, location, and season.

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