Kinetics of the Gas-Phase Reaction of Some Unsaturated Alcohols with the Nitrate Radical

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Rate coefficients for the gas-phase reaction between nitrate radicals and the unsaturated alcohols 2-buten-1-ol (crotyl alcohol, a mixture of *cis* and *trans*), 3-methyl-2-buten-1-ol (MBO321), and 3-methyl-3-buten-1-ol (MBO331) and the alkenes 2-methyl-1-butene and 3-methyl-1-butene have been determined. The values that are found are $(4.1 \pm 0.4) \times 10^{-13}$, $(1.0 \pm 0.1) \times 10^{-12}$, $(2.7 \pm 0.2) \times 10^{-13}$, $(5 \pm 1) \times 10^{-13}$, and $(1.4 \pm 0.2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, respectively. In addition, the rate coefficients for 2-propen-1-ol (allyl alcohol), 3-buten-2-ol, 2-methyl-3-buten-2-ol (MBO232), and 2-methyl-2-butene were redetermined. The experiments were performed using the relative rate technique. One set of experiments was carried out using a glass reactor and long-path FTIR spectroscopy. A second set of experiments was carried out with a collapsible sampling bag as the reaction chamber, employing solid-phase micro extraction (SPME) for sampling and gas chromatography/flame ionization detection for analysis of the reaction mixtures. The results from the two experimental methods showed good correspondence. All experiments were carried out at 297 ± 2 K and 1020 ± 10 mbar and using both synthetic air and nitrogen as the bath gas. The energy of the highest occupied molecular orbital (E_{HOMO}) of the investigated organic compounds was calculated using the PM3 semiempirical approach, and a relation to $\ln(k)$ was observed. A similar relation, available from the literature developed for alkenes, would underestimate the unsaturated alcohol rate coefficients slightly. The measured values of the rate coefficients for the unsaturated alcohols are in reasonable agreement with those predicted by a structure−activity relationship (SAR) available in the literature. However, the SAR slightly overestimates the rate coefficients. The presence of the OH group in the examined alcohols does not affect the NO_3 rate coefficient compared to that of the parent alkene, except in the case of MBO321 and MBO331 where steric effects may be responsible for lowering the reactivity.

Introduction

Emission of biogenic volatile organic compounds (BVOC) greatly exceeds that of anthropogenically generated volatile organic compounds (VOC) and is estimated to be more than 1000 Tg C/year[1] on a global scale. The BVOC that are emitted are mainly isoprene and monoterpenes, but a wide range of other compounds of biogenic origin, including oxygenated compounds such as aldehydes and alcohols, have been found in the troposphere (e.g., see refs 2−6). One important characteristic of many BVOC is their high reactivity toward the main atmospheric oxidants, compared to many anthropogenic VOC.[7] Thus, they possess a potential to contribute to such adverse effects as photochemical oxidant formation and haze.

One biogenic compound, pointed out in the literature as an abundant species, is the unsaturated alcohol 2-methyl-3-buten-2-ol (MBO232).[8,9] Other studies have presented the leaf level and canopy fluxes of MBO232 over pine forest.[10,11] The flux of MBO232 has the same temperature and photosynthetically active radiation behavior as isoprene.[12] In addition, emission of two structurally similar compounds, 3-methyl-2-buten-1-ol (MBO321) and 3-methyl-3-buten-1-ol (MBO331), has been observed.[4]

Both the kinetics[13−17] and the mechanisms[16−21] for the reaction of MBO232 with the atmospheric free radicals OH, NO_3, and Cl, and ozone, have been studied using various experimental techniques. Some other unsaturated alcohols, structurally similar to MBO232, have also been studied with respect to kinetics[13] and reaction mechanisms.[21]

Effort has been put into developing various ways to predict the rate coefficient for a particular reaction based on the chemical structure of the organic compounds, so-called structure−activity relationships (SARs). This approach typically employs combination of group-specific rate coefficients and neighboring group factors for predicting an unknown rate coefficient. SARs have been developed for Cl- and NO_3-initiated reaction of alkanes,[22−24] and for OH reactions with various hydrocarbons, including substituted and unsaturated ones.[7,25] Another way to predict rate coefficients is to use linear free energy relations. Such a relation is based on the rate coefficient ratio for a substance reacting with two reactants, e.g., NO_3 and OH radicals. This ratio is approximately constant regardless of the substance as long as the mechanism is the same. Once the ratio has been established and one rate coefficient is known, the other may be estimated.

Recently, correlations between the energy of the highest occupied molecular orbital E_{HOMO} of alkenes and dienes and the corresponding rate coefficient for reaction with NO_3, OH, and O_3 were presented.[26] This approach needs no experimental information, but it requires the calculation of E_{HOMO} for estimation of a rate coefficient. Also, a SAR for predicting the rate coefficients for the reaction of NO_3, OH, and O_3 with alkenes and dienes, based on their HOMO energies, has been published.[27]

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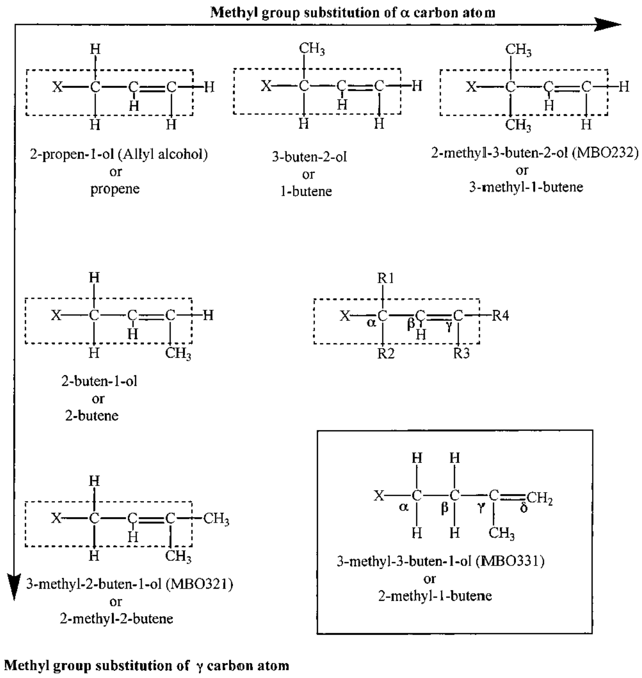

Figure 1. Schematic structure of the investigated compounds. The common carbon skeleton is denoted by the dashed lines. X = −H for the parent alkene, and X = −OH for the corresponding alcohol.

The work presented here gives the first experimental determination of rate coefficients for the reaction between nitrate radicals and 2-buten-1-ol (crotyl alcohol), 3-methyl-2-buten-1-ol (MBO321), 3-methyl-3-buten-1-ol (MBO331), 2-methyl-1-butene, and 3-methyl-1-butene. Further, the rate coefficients for the NO_3 reaction with 2-propen-1-ol (allyl alcohol), 3-buten-2-ol, 2-methyl-3-buten-2-ol (MBO232), and 2-methyl-2-butene were redetermined and compared with previously published data to assess the performance of an experimental method that is described below.

The atmospheric oxidation of unsaturated alcohols is of interest because of the potentially high rates of emission of such compounds and their high reactivities. The alcohols selected for investigation are illustrated in Figure 1 and may, with the exception of MBO331, be regarded as methyl-substituted derivatives of 2-propen-1-ol. The rate coefficients of the alcohols were compared to those of the parent alkene to assess the influence of the OH group on reactivity.

Experimental Setup and Procedures

The rate coefficients were determined in relative rate experiments, where the objective is to measure changes in concentration of two organic compounds reacting simultaneously with one reactive species (here NO_3). In this case, the nitrate radical reacts with an unsaturated alcohol or alkene (denoted organic in the following) with an unknown rate coefficient, k_{organic}, and with a reference compound with a known rate coefficient, $k_{\text{reference}}$, according to reactions 1 and 2.

$$\text{organic} + NO_3 \rightarrow \text{products} \qquad (1)$$

$$\text{reference} + NO_3 \rightarrow \text{products} \qquad (2)$$

Provided that both compounds are lost only due to reaction with NO_3 and that neither the organic compound nor the reference is reformed in any process, the loss of compounds is given by eq I.[28]

$$\ln\frac{[\text{organic}]_0}{[\text{organic}]_t} = \frac{k_{\text{organic}}}{k_{\text{reference}}} \times \ln\frac{[\text{reference}]_0}{[\text{reference}]_t} \qquad (\text{I})$$

Subscripts 0 and t indicate concentration at the beginning of an experiment and at time t, respectively. The rate coefficient is obtained from a linear regression, based on the least-squares method, where $\ln([\text{organic}]_0/[\text{organic}]_t)$ is plotted against $\ln([\text{reference}]_0/[\text{reference}]_t)$. The slope of the straight line gives the relative rate coefficient k_{rel} ($=k_{\text{organic}}/k_{\text{reference}}$), which, combined with the literature value of $k_{\text{reference}}$, yields the desired rate coefficient for reaction 1. The error limits for the final rate coefficients, given in Table 1, were calculated with a standard error propagation technique, using the statistical confidence interval (95%) for k_{rel} and the given error for $k_{\text{reference}}$. The following reference values (cm^3 molecule^{-1} s^{-1}), obtained from absolute rate determinations, were used: $k(\text{propene}+NO_3) = (9.3 \pm 1.2) \times 10^{-15}$ (Canosa-Mas et al.[29]), $k(\textit{trans}\text{-2-butene}+NO_3) = (4.06 \pm 0.33) \times 10^{-13}$ (Rudich et al.[14]), and $k(\text{butanal}+NO_3) = (1.1 \pm 0.1) \times 10^{-14}$ (Ullerstam et al.[30]). An advantage of the relative rate technique is that only the ratio of the concentrations is required, which allows any quantity proportional to the concentration to be used in eq I.

Two different experimental setups were employed to carry out the measurements. In both setups, the NO_3 radicals were generated by thermal decomposition of N_2O_5. The N_2O_5 was synthesized separately by the reaction of excess O_3 with NO_2 according to reaction 3 followed by reaction 4.[31] The product was collected in a trap, and stored at 195 K between runs.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (3)$$

$$NO_2 + NO_3 \Leftrightarrow N_2O_5 \qquad (4)$$

The two experimental techniques used to determine input data for eq I are described in the following two subsections.

FTIR Spectroscopy. The main features of the FTIR experimental procedure and equipment have been described previously,[32] and only the main points will be given here. The reactor is a 153 L cylindrical borosilicate glass vessel with a 2 m base-path White mirror system. Long optical path FTIR spectroscopy [Nicolet Magna 560 spectrometer equipped with an MCT (Hg−Cd−Te) detector] was employed to quantify the investigated and the reference compounds. Spectra were collected at $1.0\ \text{cm}^{-1}$ spectral resolution and with an optical path length of 40 m. The desired amounts of the organic compounds were metered using a vacuum line equipped with a barometric dilution system. The reactants were introduced into the reactor by a stream of bath gas (pure N_2 or synthetic air) via a Teflon line with nozzles, placed axially along the bottom of the reactor. One large single dose of N_2O_5 was introduced for the slowly reacting compounds, while for the rapidly reacting substances, repeated small doses of N_2O_5 were used, with measurements taken between the doses.

The concentration of the reacting compounds was determined by the scaled subtraction technique. Prior to the kinetic experiments, reference spectra were collected using known concentrations of the examined compounds, and the validity of Beer's law was confirmed for the concentrations that were used.

SPME−GC. The solid-phase micro extraction (SPME) sampling technique, combined with gas chromatography (GC), has found many applications in various environmental analyses.[33] Recently, it has been used for relative rate[34,35] and photolytic loss rate[36] investigations.

TABLE 1: Rate Coefficients for the NO_3 Reaction with Some Unsaturated Alcohols and Alkenes Determined by the Relative Rate Technique[a]

compound	reference compound	method	bath gas	combined k_{rel}	k (cm^3 molecule^{-1} s^{-1})	combined k (cm^3 molecule^{-1} s^{-1})	ref
2-propen-1-ol	propene	SPME−GC	N_2, air		$(1.0 \pm 0.3) \times 10^{-14}$		this work
	propene	FTIR	N_2, air		$(1.1 \pm 0.2) \times 10^{-14}$	$(1.1 \pm 0.2) \times 10^{-14}$	this work
		FFD			$(1.3 \pm 0.2) \times 10^{-14}$		Hallquist et al.[13]
3-buten-2-ol	propene	SPME−GC	N_2, air		$(1.2 \pm 0.3) \times 10^{-14}$		this work
		FTIR	N_2, air		$(1.0 \pm 0.2) \times 10^{-14}$	$(1.2 \pm 0.2) \times 10^{-14}$	this work
		FFD	He		$(1.2 \pm 0.3) \times 10^{-14}$		Hallquist et al.[13]
MBO232	butanal	SPME−GC	N_2, air	1.001 ± 0.054	$(1.1 \pm 0.1) \times 10^{-14}$		this work
	propene	FTIR	N_2, air		$(1.0 \pm 0.2) \times 10^{-14}$	$(1.1 \pm 0.2) \times 10^{-14}$	this work
		FTIR			$(0.86 \pm 0.29) \times 10^{-14}$		Fantechi et al.[15]
		FFD			$(1.2 \pm 0.09) \times 10^{-14}$		Rudich et al.[14]
		FFD			$(2.1 \pm 0.3) \times 10^{-14}$		Hallquist et al.[13]
2-buten-1-ol	*trans*-2-butene	SPME−GC	N_2, air		$(4.1 \pm 0.4) \times 10^{-13}$		this work
		FTIR	N_2, air	1.011 ± 0.047	$(4.1 \pm 0.5) \times 10^{-13}$	$(4.1 \pm 0.4) \times 10^{-13}$	this work
MBO321	*trans*-2-butene	SPME−GC	N_2, air		$(1.0 \pm 0.2) \times 10^{-12}$		this work
		FTIR	N_2, air	2.486 ± 0.228	$(1.0 \pm 0.2) \times 10^{-12}$	$(1.0 \pm 0.1) \times 10^{-12}$	this work
MBO331	*trans*-2-butene	SPME−GC	N_2, air		$(2.6 \pm 0.5) \times 10^{-13}$		this work
		FTIR	N_2, air	1.289 ± 0.274	$(2.6 \pm 0.3) \times 10^{-13}$	$(2.7 \pm 0.2) \times 10^{-13}$	this work
3-methyl-1-butene	butanal	SPME−GC	N_2, air	1.286 ± 0.099	$(1.4 \pm 0.2) \times 10^{-14}$	na[b]	this work
2-methyl-1-butene	*trans*-2-butene	SPME−GC	N_2, air	0.652 ± 0.055	$(5.2 \pm 1.2) \times 10^{-13}$	na[b]	this work
2-methyl-2-butene	*trans*-2-butene	SPME−GC	N_2, air	7.760 ± 0.239	$(3.2 \pm 0.5) \times 10^{-12}$	na[b]	this work
propene					$(9.3 \pm 1.2) \times 10^{-15}$		Canosa-Mas et al.[29]
1-butene					1.35×10^{-14}		Atkinson[7]
cis-2-butene					3.50×10^{-13}		Atkinson[7]
trans-2-butene					$(4.06 \pm 0.33) \times 10^{-13}$		Rudich et al.[14]

[a] Previous values, determined by FTIR or the fast flow discharge (FFD) technique, are included for comparison as are some other values that are relevant to the discussion. "Combined" indicates that all data available for a certain reaction were combined to produce the entry. [b] Not applicable.

The experiments were carried out at 297 ± 2 K and 1010 ± 10 mbar using a collapsible 100 L polyvinyl fluoride bag (Tedlar, DuPont) as the reactor. The bag was covered with black plastic film to exclude light. The compound to be investigated and the reference were introduced into the bag via a barometric dilution system. Sampling was accomplished by inserting the SPME protection needle into the bag through a septum. The SMPE fiber was then exposed to the reaction mixture for an appropriate, constant amount of time. The exposure time is important since the clean fiber initially adsorbs substances at a constant rate; i.e., the amount of adsorbed substance is a linear function of time. However, after some time, the apparent rate drops as the gas−solid phase equilibrium is approached. The practical adsorption characteristics of a compound are also dependent on which other substances are present in the gas mixture. This work was carried out in the linear region, and the fiber was exposed for a constant sampling time, typically between 1 and 5 min. The region of linearity was established for each reaction mixture by separate experiments. After exposure, the fiber was retracted into the protection needle, the SPME assembly detached from the sampling bag, and the needle immediately inserted into the heated GC injection port for subsequent chromatographic analysis.

The SPME adsorbent selected for this study was Carboxen/polydimethylsiloxane (CAR/PDMS, Supelco). The analyses were carried out using a Finnigan 9001 gas chromatograph equipped with a flame ionization detector (FID) and a GS-Q, 30 m, 0.32 mm i.d. (J&W Scientific) capillary column. The carrier gas was ultra-high purity helium. The injector port and detector temperatures were set to 240 and 245 °C, respectively. The GC oven temperature was kept at 130 °C for 1 min, then ramped at a rate of 40 °C/min to 180 °C, and held at that temperature for 9 min. For MBO321 and MBO331, the same program was used initially; however, a final temperature of 210 °C was employed. The experiments with 2-methyl-2-butene were analyzed with an HP-PLOT Q, 30 m, 0.53 mm i.d. (Agilent Technologies) column and a program where the oven temperature was kept at 80 °C for 3 min, then ramped at a rate of 50 °C/min to 220 °C, and held for 6 min. The concentrations of reactants in the bag were expressed as the integrated peak areas, a quantity that could be used directly in eq I.

The experiments were conducted by first introducing the reference and the organic compound into the bag and determining their initial concentrations. Stable concentrations of the investigated compounds in the mixture were confirmed by at least three measurements made over the course of 1 h and giving less than 5% standard deviation of the mean integrated peak area. Then, 5−10 mL of N_2, saturated with N_2O_5 and corresponding to a bag concentration of $4{-}8 \times 10^{13}$ molecule cm^{-3} of N_2O_5, was injected into the bag using a syringe. To reduce losses by hydrolysis of N_2O_5 in the syringe, it was conditioned by repeated filling prior to the injections. After the introduction of N_2O_5, the bag was kneaded vigorously to promote mixing. Then sampling of the gas mixture was conducted as described above. The injection step was repeated several times. The total volume increase due to the injections of N_2O_5 was less than 0.1% of the total bag volume and was considered to be negligible.

The initial concentrations of the organic compounds in both experimental setups were $1.2{-}5.1 \times 10^{14}$ molecule cm^{-3} for the unsaturated compounds that were being investigated and $1.2{-}4.5 \times 10^{14}$ molecule cm^{-3} for the reference compounds. The initial (or the total in the case of stepwise addition) amount of N_2O_5 added was $3{-}10 \times 10^{14}$ molecule cm^{-3}.

The following chemicals were used: 2-propen-1-ol (>95%, Merck), 3-buten-2-ol (>97%, Merck), MBO232 (>98%, Aldrich), 2-buten-1-ol (>97%, mixture of *cis* and *trans*, Aldrich), MBO321 (>99%, Aldrich), MBO331 (>97%, Aldrich), 2-methyl-1-butene (98%, Aldrich), 3-methyl-1-butene (95%, Aldrich), 2-methyl-2-butene (>95%, Merck), butanal (>99%, Aldrich), propene (99.5%, AGA Gas AB), and *trans*-2-butene (99.0%, AGA Gas AB). Synthetic air (20% O_2 in 99.996% N_2, AGA Gas AB) and Nitrogen Plus (99.996%, AGA Gas AB) were employed as bath gases for the experiments, and helium

(99.9995%, AGA Gas AB) was used as the GC carrier gas. For all investigated liquid compounds, freeze−pump−thaw cycles were repeated several times to eliminate dissolved gases before use in the dilution system.

Computational Aspects. On the basis of perturbation frontier molecular orbital theory, the reactivity of a series of structurally similar organic compounds, expressed as ln(k), can be correlated to the energy level of their frontier molecular orbitals.[37−40] A useful relationship can be expressed as eq II

$$\ln(k) = m/(E_{\mathrm{SOMO}} - E_{\mathrm{HOMO}}) + c \qquad \text{(II)}$$

where m and c are obtained from linear-least-squares regression and E_{HOMO} is the energy of the highest occupied molecular orbital from the calculations. E_{SOMO} is the energy of the singly occupied orbital for a radical and the energy of the lowest unoccupied orbital for other species.

In the recent work by King et al.,[26] this correlation has been investigated for a series of monoalkenes and conjugated dienes. King et al.[26] also investigated a simpler correlation given by eq III, which was found to work equally well for the investigated reactions. In this study, the capability of eq III to describe the reactivity between NO_3 and the unsaturated alcohols was investigated.

$$\ln(k) = mE_{\mathrm{HOMO}} + c \qquad \text{(III)}$$

King et al.[26] used two methods to obtain values for E_{HOMO}. In one approach, they performed Hartree−Fock self-consistent field (HF-SCF) calculations with a 6-31G** basis set employing the Gaussian94[41] program package. In the second approach, they investigated the same compounds with semiempirical PM3 calculations using the MOPAC6.0[42] program package. The absolute values calculated for E_{HOMO} for the various compounds differ between the HF-SCF and PM3 calculations. Still, King et al.[26] found the two relationships given above to hold essentially equally well for both the HF-SCF and PM3 calculations. The PM3 calculations are much faster to perform, and following the suggestion by King et al.,[26] this approach was chosen here. The PM3 calculations were performed using the HyperChem program suite.[43]

Results and Discussion

Experimental Part. Table 1 presents the rate coefficients determined for 2-buten-1-ol, MBO321, MBO331, 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene reacting with NO_3. Table 1 also gives the redetermined values and a summary of the previously determined rate coefficients for 2-propen-1-ol, 3-buten-2-ol, and MBO232. The methylbutenes were investigated only by the SPME−GC method because we had serious problems resolving the FTIR spectra in terms of contributions from the individual compounds in the reactor. Figures 2−5 show examples of relative rate plots according to eq I. The scatter on the plots illustrates the difficulties in the FTIR evaluation, while for the SPME−GC technique, it may be sampling artifacts originating from unexpected nonlinear adsorption processes and the presence of reaction products in chromatograms that cannot be distinguished by the flame ionization detector.

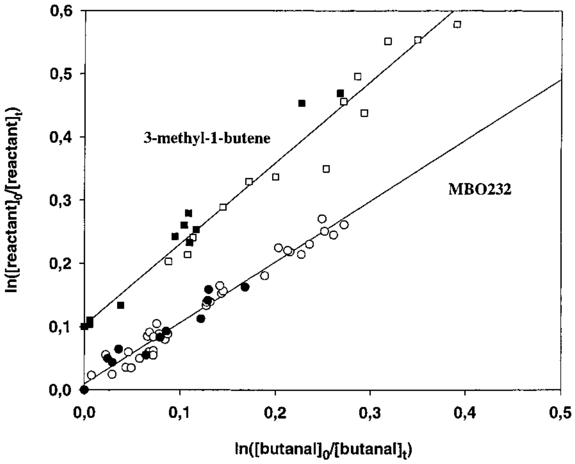

Figure 2. Relative rate plots of MBO232 (circles) and 3-methyl-1-butene (squares) with butanal as the reference compound from SPME−GC experiments. The data points for 3-methyl-1-butene were shifted by 0.1 y-unit for clarity: (black symbols) air as the bath gas and (white symbols) nitrogen as the bath gas.

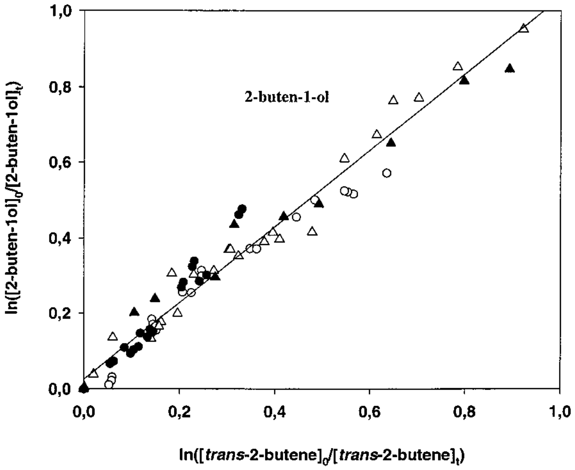

Figure 3. Relative rate plot of 2-buten-1-ol with *trans*-2-butene as the reference compound. The circles and triangles show data from SPME−GC and FTIR measurements, respectively: (black symbols) air as the bath gas and (white symbols) nitrogen as the bath gas.

Data from the two experimental methods were plotted separately, and straight lines according to eq I were fitted by the least-squares method. No systematic difference in the results between the FTIR and SPME−GC methods could be seen; instead, the agreement was very good. Therefore, it was decided to use both data sets for a compound to obtain the relative rate coefficient. This procedure generated the rate coefficients mentioned in Table 1 as “combined”. For the experiments with MBO232, the combined plot could not be generated because different reference compounds were used. Instead, the combined rate coefficient was calculated as an average of the FTIR and SPME−GC determinations. Also, the rate coefficients determined using nitrogen and synthetic air as the bath gas agree well for the reactions that were investigated, indicating that there is no serious influence on the rate determination by secondary reactions.

As can be seen in Table 1, the rate coefficients for the NO_3 radical reaction with 2-propen-1-ol and 3-buten-2-ol are in good agreement with the values from previous absolute rate determinations.[13] The rate coefficient for MBO232 has also been reported before, and the results presented here are in a good agreement with the works of Fantechi et al.[15] and Rudich et al.[14] However, the value reported by Hallquist et al.[13] is a factor of 2 higher than the other determinations. The rate coefficient for 2-methyl-2-butene found here is a factor of 3 lower than the value recommended by Atkinson.[7] We do not have an explanation for the discrepancy.

The rate coefficient increases in the order 2-propen-1-ol, 2-buten-1-ol, and MBO321 (top to bottom in Figure 1), i.e.,

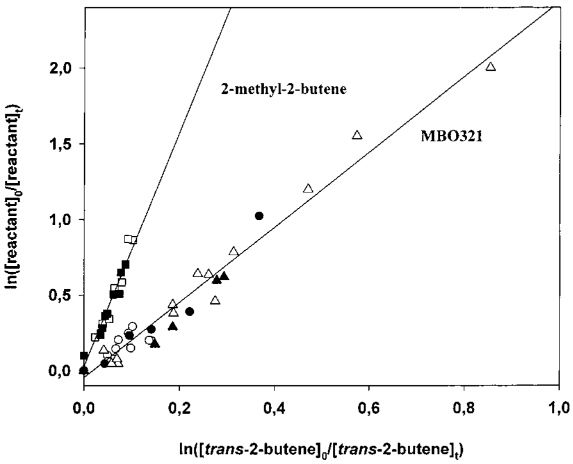

Figure 4. Relative rate plots of MBO321 and 2-methyl-2-butene with *trans*-2-butene as the reference compound. For MBO321, circles and triangles show data from SPME−GC and FTIR measurements, respectively. The data points for 2-methyl-2-butene (squares) were shifted by 0.1 *y*-unit for clarity: (black symbols) air as the bath gas and (white symbols) nitrogen as the bath gas.

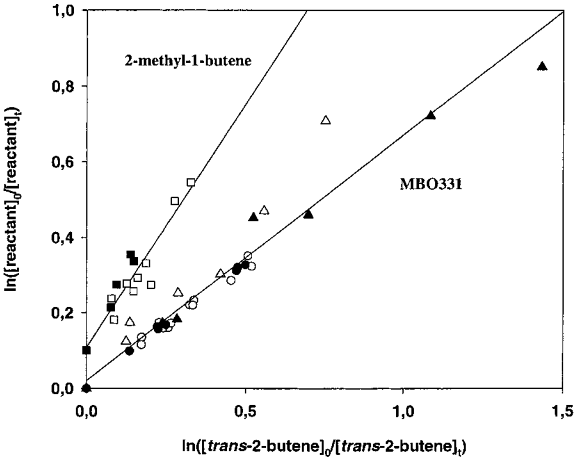

Figure 5. Plot of MBO331 and 2-methyl-1-butene with *trans*-2-butene as the reference compound. For MBO331, circles and triangles show data for SPME−GC and FTIR measurements, respectively. The data points for 2-methyl-1-butene (squares) were shifted by 0.1 *y*-unit for clarity: (black symbols) air as the bath gas and (white symbols) nitrogen as the bath gas.

with an increasing number of methyl groups at the γ-carbon atom participating in the double bond. This is in accordance with the stabilization theory for leaving groups mentioned by Atkinson[44] and Noda et al.[21] As expected, the rate coefficients do not change significantly when the number of methyl substituents is increased from 0 to 2 at the α-carbon atom in the order 2-propen-1-ol (0), 3-buten-2-ol (1), and MBO232 (2) (left to right in Figure 1).

Correlation between Rate Coefficients for Alcohols and Parent Alkenes. The nitrate radical attack on unsaturated substances is expected to take place at one of the carbon atoms participating in the double bond. The attack is controlled by the substitution pattern at the double bond, expressed here as the number of neighboring carbon atoms. The preferred site is the least substituted carbon atom, i.e., the one with lowest number of neighboring carbon atoms, producing the more stable radical (Wayne et al.[45]). The number of neighboring carbon atoms, listed in Table 2, identifies the likely point of NO_3 attack. A substituent, not attached to one of the double bond carbon atoms, is not expected to directly affect the reaction rate.

TABLE 2: Rate Coefficient Ratios between the Examined Alcohols and the Corresponding Alkenes Obtained from the Experimental Data[a]

alcohol	parent alkene	$k_{alcohol}$/ k_{alkene}	no. of neighboring carbon atoms α	β	γ	δ
2-propen-1-ol	propene	1.2	1	2	1	na[b]
3-buten-2-ol	1-butene	0.9	2	2	1	na[b]
MBO232	3-methyl-1-butene	0.8	3	2	1	na[b]
2-buten-1-ol	*trans*-2-butene	1.0	1	2	2	na[b]
MBO321	2-methyl-2-butene	0.3	1	2	3	na[b]
MBO331	2-methyl-1-butene	0.5	1	2	3	1

[a] The number of neighboring carbon atoms for different carbon atom positions is also given. The carbon atom notation refers to Figure 1. [b] Not applicable.

Table 2 gives the $k_{alcohol}/k_{alkene}$ ratios for the unsaturated alcohol and the corresponding parent compound without the OH substituent. The rate coefficient ratios were approximately unity, confirming that the OH substituent does not cause any great change in the reaction rate. The exceptions from this behavior are MBO331 and MBO321, where the alcohol reacted between 2 and 3 times slower than the corresponding alkene. The reason for this may be steric hindrance. In the case of MBO331, we found in PM3 calculations that the structure is bent such that the molecules partially shield its double bond.

The similarity of the rate coefficients for 2-buten-1-ol and *trans*-2-butene indicates a lack of steric hindrance by the OH substitution. However, in this case, the β- and γ-carbon atoms have equal chances of being attacked by the NO_3 radical and the difference between the parent alkene and the alcohol may not be significant. The other alcohols that were investigated have the OH group still further away from the site of the expected NO_3 attack (γ-position) and do not exhibit any anomalous behavior.

Correlation between the Rate Coefficients and E_{HOMO}. Our PM3 results for the HOMO energy obtained with HyperChem were compared to some results obtained by King et al.[26] using MOPAC6.0.[42] The agreement is good as can be seen in Table 3. The reported E_{HOMO}(alcohol) values correspond to the molecular conformations found that gave the minimum total electronic energy. On average, a difference of −0.3 eV between the E_{HOMO} values for the alcohol and its parent alkene was found for the six structurally related alcohols that were studied (cf. Figure 1). Figure 6 shows a plot, according to eq III, of $-\ln(k)$ versus $-E_{HOMO}$. The solid line is obtained from a regression analysis of the 30 alkene data by King et al.[26] which gave an m of 8.0 ± 0.8 eV^{-1} and a c of 49 ± 8.

Figure 6 also shows the 95% confidence interval from the regression, represented by dashed lines. The three measured alkene values from this work were included in the regression (a total of 33 data points), and a similar analysis provided an m of 7.8 ± 0.8 eV^{-1} and a c of 48 ± 8. As expected, adding three data points does not significantly alter the original correlation. Data for the six unsaturated alcohols are shown with empty circles, and data for the six corresponding alkenes are shown with diamonds. Three of the alcohols fall within the 95% confidence interval, while MBO232, 3-buten-2-ol, and MBO331 are slightly outside. The alcohols systematically appear below the solid line, and thus, if the correlation was used to predict the rate coefficients from calculated E_{HOMO} values, they would be underestimated. As was noted in the previous section, the measured parent alkene and alcohol rate coefficients are identical in most cases. The parent alkene E_{HOMO} would therefore also be the choice for predicting the rate coefficient for the alcohol.

TABLE 3: Summary of the PM3 Calculations for the Energy of the Highest Occupied Molecular Orbital

ID	alcohol	E_{HOMO}	ID	alkene	E_{HOMO}[a]	difference[c]	alkene (King et al.[26])
1	2-propen-1-ol	−10.364	7	propene	−10.105	−0.26	−10.105
2	3-buten-2-ol	−10.497	8	1-butene	−10.149	−0.35	−10.145
3	MBO232	−10.470	9	3-methyl-1-butene	−10.264	−0.21	−10.264
4	*cis*-2-buten-1-ol	−9.932	10	*cis*-2-butene	−9.663[b]	−0.27	−9.690
4	*trans*-2-buten-1-ol	−10.005	10	*trans*-2-butene	−9.656	−0.35	−9.655
5	MBO321	−9.714	11	2-methyl-2-butene	−9.392	−0.32	−9.387
6	MBO331	−10.101	12	2-methyl-1-butene	−9.855	−0.25	−9.854

[a] Three decimal places are provided; however, the third one is not to be considered significant. [b] We obtained a local minimum giving a HOMO energy of −9.691 eV, which is close to the value of King et al. This minimum disappeared in ab initio calculations. [c] Difference between E_{HOMO}(alcohol) and E_{HOMO}(alkene) from this work.

TABLE 4: Rate Coefficients Obtained from the SAR Calculations and Experiments

ID	alcohol or alkene	*k* calculated with the SAR (cm^3 $molecule^{-1}$ s^{-1})	*k* measured (cm^3 $molecule^{-1}$ s^{-1})	ref	k_{SAR}/k_{meas}
1	2-propen-1-ol	2.95×10^{-14}	1.1×10^{-14}	this work	2.7
2	3-buten-2-ol	3.45×10^{-14}	1.2×10^{-14}	this work	2.9
3	MBO232	4.73×10^{-14}	1.1×10^{-14}	this work	4.3
4	2-buten-1-ol	4.87×10^{-13}	4.1×10^{-13}	this work	1.2
5	MBO321	3.60×10^{-12}	1.0×10^{-12}	this work	3.6
6	MBO331	2.47×10^{-13}	2.7×10^{-13}	this work	0.9
7	propene	2.50×10^{-14}	0.95×10^{-14}	Atkinson[7]	2.6
8	1-butene	2.95×10^{-14}	1.35×10^{-14}	Atkinson[7]	2.2
9	3-methyl-1-butene	3.45×10^{-14}	1.3×10^{-14}	this work	2.7
10	*trans*-2-butene	4.13×10^{-13}	4.06×10^{-13}	Rudich et al.[14]	1.0
11	2-methyl-2-butene	3.05×10^{-12}	3.2×10^{-12}	this work	1.0
12	2-methyl-1-butene	2.47×10^{-13}	5.2×10^{-13}	this work	0.5

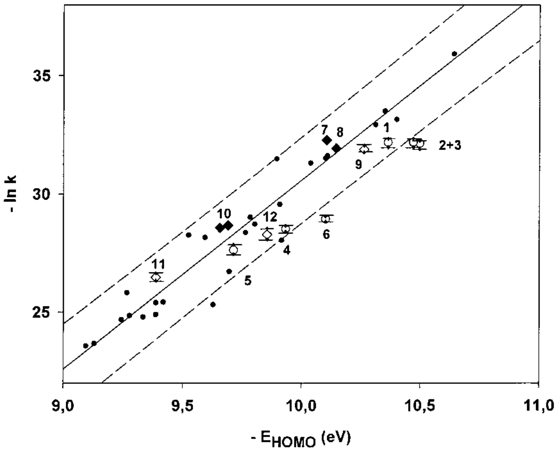

Figure 6. Plot of $-\ln(k)$ vs $-E_{HOMO}$. Black circles represent the data from King et al.[26] with the corresponding regression line and 95% confidence interval. The white circles and diamonds represent data for alcohols and alkenes, respectively, from this work. The black diamonds are alkene values from the literature. The numbering refers to Table 3.

Correlation between the SAR and Measured Rate Coefficients. The rate coefficients for the compounds that were studied can be calculated by the SAR developed by King et al.[27] The numbers are presented in Table 4. The effect of the OH group in the SAR is to increase the predicted rate coefficient. The increase is a factor of 1.18 when the $-CH_3$ groups are changed to $-CH_2-$ groups when substituting the alkene for the alcohol, and 1.38 when CH_2 groups are changed to $>CH-$ groups. The SAR suggests that the alcohols should react equally fast or slightly faster than the corresponding alkene. These small differences could not be observed in the measured data, although the errors in the measurements make this type of analysis difficult. For the nitrate radical reactions, King et al. state that for the reactions they studied 44% of the values calculated by the SAR fall in the range of $0.5 < r < 2$, where $r = k_{SAR}/k_{measured}$. The same analysis applied to the present values gives 50, 33, and 42% for the alkenes, alcohols, and all values, respectively. Although the agreement between predicted and measured rate coefficients is not excellent, it can still be considered to be a good method for estimating unknown rate coefficients. The SAR has the advantage of not requiring any computations.

Conclusions

SPME−GC is a useful technique for relative rate measurements. It offers an alternative to FTIR spectroscopy, e.g., when reactants and products contain identical functional groups that would not be resolved by the latter method. However, SPME−GC is experimentally more demanding and time-consuming than FTIR spectroscopy for performing relative rate determinations.

The rate coefficients for the nitrate radical reaction with 2-buten-1-ol, MBO321, MBO331, 2-methyl-1-butene, and 3-methyl-1-butene were determined for the first time. The rate coefficients for 2-propen-1-ol, 3-buten-2-ol, MBO232, 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene were redetermined with good agreement with previously determined values except for that for 2-methyl-2-butene where a difference of a factor of 3 was noted.

Comparison of six unsaturated alcohols with their parent alkenes indicates that the presence of an OH group in the molecule does not influence the rate coefficients. Exceptions are MBO321 and MBO331 where the alcohols react slower than the corresponding alkene.

The alkene rate coefficients determined here fit well to a relation between E_{HOMO} and $\ln(k)$ from the literature, even though the rate coefficients for the unsaturated alcohols are underestimated by this relation. This is because the calculated E_{HOMO} values of the alcohols lie lower in energy by 0.3 eV.

A SAR from the literature predicted the rate coefficients determined here for the alkenes quite well but slightly less well for the alcohols. In the PM3 calculations, the most critical and sensitive step is determination of the most stable conformation which also has some bearing on the E_{HOMO} values.

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