

# Kinetic and Mechanistic Study of the Gas-Phase Reactions of a Series of Vinyl Ethers with the Nitrate Radical

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NO<sub>3</sub> oxidation of methyl, ethyl, propyl, and butyl vinyl ethers has been studied under tropospheric conditions (atmospheric pressure and  $T = 293 \pm 3$  K) in the LISA indoor simulation chamber. NO<sub>3</sub> was produced inside the reactor by thermal decomposition of N<sub>2</sub>O<sub>5</sub> previously added to the air–VOC mixture, and concentrations were monitored using FTIR spectrometry. All the kinetic experiments were carried out by relative rate technique using isoprene as reference compound, leading to the rate constants  $k_1 = (7.2 \pm 1.5) \times 10^{-13}$ ,  $k_2 = (13.1 \pm 2.7) \times 10^{-13}$ ,  $k_3 = (13.3 \pm 3.0) \times 10^{-13}$ , and  $k_4 = (17.0 \pm 3.7) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for methyl, ethyl, propyl, and butyl vinyl ethers, respectively. Main oxidation products have been identified like being formaldehyde and respectively methyl, ethyl, propyl, and butyl formates. Production yields of oxidation products were close to 50%. Oxygenated nitrates and peroxy nitrates were also detected.

## 1. Introduction

Oxygenated volatile organic compounds are widely emitted into the troposphere by evaporation during their use in manufacturing as solvents in paints, pharmaceutical process synthesis, adhesives.<sup>1</sup> When released into the troposphere, they can undergo either photolysis or photochemical oxidation by OH radicals and ozone during daytime and by nitrate radicals (NO<sub>3</sub>) and ozone during nighttime. While OH radicals are produced by photochemical processes, NO<sub>3</sub> radicals are formed by reaction of NO<sub>2</sub> with ozone. Since the NO<sub>3</sub> photolysis is fast ( $\tau < 5$  s), it can only accumulate during the nighttime.<sup>2</sup>

These chemical processes may lead to the formation of environmentally and health damaging compounds such as photochemical oxidants which are involved in smog events. Reactions of VOCs with the nitrate radical produce nitro-substituted compounds,<sup>2</sup> whose most of them are likely to be toxic.<sup>3–5</sup> Furthermore, some solvents have direct damaging health effects (carcinogenic, mutagenic effects).

To reduce these damaging effects of solvents, new friendly solvents including vinyl ethers are used to replace traditional ones. Hence, as vinyl ethers emission may go increasingly, it appears particularly necessary to precisely evaluate their environmental impact. Thus, a good knowledge of their atmospheric lifetime and degradation products is needed. To date, few kinetic and mechanistic studies on the simplest and lightest vinyl ethers have been published. Hence, reactions of methyl, ethyl, *n*-propyl, and *n*-butyl vinyl ethers with OH and NO<sub>3</sub> radicals and with ozone have previously been reported in the literature.<sup>6–12</sup> Thiault et al.<sup>6,7</sup> have studied OH and O<sub>3</sub> oxidation kinetics of methyl, ethyl, *n*-propyl, and *n*-butyl vinyl ethers, and have reported both rate constants and activation energies in the temperature range 230–372 K and at 298 K. Perry et al.<sup>10</sup> have measured the OH oxidation rate constant of methyl vinyl ether at room temperature and over the temperature

range 299–427 K. Moreover, Klotz et al.<sup>8</sup> have studied the mechanisms of OH, O<sub>3</sub> and NO<sub>3</sub> oxidation of methyl vinyl ether. This last paper is the only mechanistic study on NO<sub>3</sub>-induced oxidation of vinyl ethers. Concerning the kinetic of NO<sub>3</sub> oxidation, three papers were reported in the literature. One is an estimation of the rate constant of methyl vinyl ether with NO<sub>3</sub>, from a structure activity relationship (SAR) by Grosjean et al.<sup>11</sup> which led to  $k = 4.68 \times 10^{-13}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at 298 K. This value remains to be experimentally confirmed. An other is a rate constant measurement of ethyl vinyl ether with NO<sub>3</sub> by Pfrang et al.<sup>9</sup> using relative rate method with GC–FID analysis, at room temperature and atmospheric pressure, leading to  $k = (1.7 \pm 1.3) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. According to the authors, a great uncertainty features this result, due to difficulty to control a wall-loss on the used PTFE bag. Recently Zhou et al.<sup>12</sup> have measured rate constants of ethyl, propyl, and butyl vinyl ethers, using relative rate method with FTIR spectroscopy device. Each rate constant was measured using two different reference compounds. Obtained averaged values were  $(1.40 \pm 0.35) \times 10^{-12}$ ,  $(1.85 \pm 0.53) \times 10^{-12}$ , and  $(2.10 \pm 0.54) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for ethyl, propyl, and butyl vinyl ethers, respectively.

Hence it appears that NO<sub>3</sub> oxidation rate constants of methyl, ethyl, propyl, and butyl vinyl ethers have to be measured again in order to confirm or precise previous measurements. Moreover, NO<sub>3</sub> oxidation products need to be more largely investigated, as only those of methyl vinyl ether have been previously studied. Study a complete series of vinyl ether is particularly interesting in order to investigate the reactivity change with the alkyl chain length.

So both complete kinetics and mechanisms of the reactions of an homologous series of vinyl ethers (i.e., methyl, ethyl, *n*-propyl, and *n*-butyl vinyl ethers) with the nitrate radical were investigated, and the obtained results are presented below.

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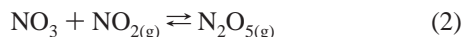
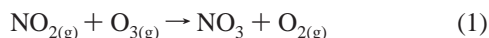
## 2. Experimental Section

**The Simulation Chamber.** Experiments were carried out in an environmental chamber, previously presented in detail by Doussin et al.,<sup>13</sup> and only a brief description is given here. The chamber is a large Pyrex reactor (6 m length, 0.45 m diameter, and 977 L volume) which is coupled to a Fourier transform infrared (FTIR) spectrometric device. The reactor contains a multireflection White cell which allows one to work with a long pathlength (i.e., 156 m for these experiments). This cell is coupled to a FTIR spectrometer BOMEM DA-8. Spectra were obtained by coadding 70 scans recorded at a resolution of 0.5 cm<sup>-1</sup> and with Hamming apodization. The scanning mirror speed allows one to record spectra every 200 s. The simulation chamber is also equipped with an UV–visible spectrometer (path length 72 m) but this device was not used for these experiments.

**Experimental Procedure.** All experiments were conducted in the dark at 293 ± 3 K and at atmospheric pressure, in synthetic air (80% N<sub>2</sub>, 20% O<sub>2</sub>). The acquired IR spectra allowed one to monitor concentrations of reactants and products inside the chamber through the time. After the studied VOC was introduced inside the chamber, it was checked that no significant wall-loss was observed on the time scale of an experiment. NO<sub>3</sub> oxidation experiments were performed by injecting N<sub>2</sub>O<sub>5</sub> in the gaseous mixture containing the studied organic compounds (i.e., N<sub>2</sub>O<sub>5</sub> + vinyl ether + isoprene for kinetic studies, and N<sub>2</sub>O<sub>5</sub> + vinyl ether for mechanistic studies). Then, as soon as N<sub>2</sub>O<sub>5</sub> was injected, reaction products were detected. As studied reactions were very fast, different methods were used to minimize the concentration of nitrate radicals and to slow the oxidation rate in order to ensure a satisfying monitoring of species concentrations. Namely, some kinetic experiments were carried out by stepwise injections of N<sub>2</sub>O<sub>5</sub>, while others were carried out by slow continuous N<sub>2</sub> flush of N<sub>2</sub>O<sub>5</sub> into the reactor and others were performed by injecting N<sub>2</sub>O<sub>5</sub> with an excess of NO<sub>2</sub> in order to shift the dissociation equilibrium to N<sub>2</sub>O<sub>5</sub>. All mechanistic experiments were carried out by stepwise injection of N<sub>2</sub>O<sub>5</sub> to vinyl ethers.

When the pressure inside the chamber exceeded 1020 mbar, it was pumped of few percents to maintain the atmospheric pressure. So some formation yields, i.e., those obtained at the end of the experiments (see below), which were slightly affected by this dilution, have been corrected.

Nitrate radicals were generated from the thermal decomposition of dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub> ⇌ NO<sub>2</sub> + NO<sub>3</sub>) which was synthesized in a vacuum line following a method adapted from Schott et al.<sup>14</sup> and Atkinson et al.<sup>15</sup>



In the first stage of the synthesis, NO<sub>2</sub> was trapped at 193 K in a cold tube. Ozone was then flushed onto the NO<sub>2</sub> crystals while the cold trap was moved to a second tube where formed dinitrogen pentoxide crystals were collected. At the end of the synthesis, the bulb containing dinitrogen pentoxide crystals was evacuated down to remove remaining NO<sub>2</sub> at room temperature. N<sub>2</sub>O<sub>5</sub> was hence purified by trap-to-trap distillation and could be kept for several weeks in the cold trap under vacuum.

Infrared spectra of reactants and products were calibrated by flushing known amounts of the vapor of these compounds (determined by measuring the pressure into a calibrated 0.55 L Pyrex bulb) into the chamber. Integrated bands intensities (IBI)

**TABLE 1: Integrated Broadband Intensities (IBI) of the Main Infrared Bands for the Different Studied Compounds**

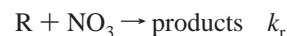
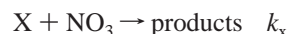
compounds	range (cm <sup>-1</sup> )	IBI, base e (cm molecule <sup>-1</sup> )
methyl vinyl ether <sup>a</sup>	1280–1163	(2.26 ± 0.23) × 10 <sup>-17</sup>
ethyl vinyl ether <sup>a</sup>	1255–1168	(2.53 ± 0.20) × 10 <sup>-17</sup>
propyl vinyl ether <sup>a</sup>	1250–1162	(2.19 ± 0.13) × 10 <sup>-17</sup>
butyl vinyl ether <sup>a</sup>	1260–1160	(2.21 ± 0.15) × 10 <sup>-17</sup>
methyl formate <sup>a</sup>	1290–1100	(5.33 ± 0.69) × 10 <sup>-17</sup>
ethyl formate <sup>a</sup>	1229–1126	(5.61 ± 0.20) × 10 <sup>-17</sup>
propyl formate <sup>a</sup>	1251–1089	(5.87 ± 0.16) × 10 <sup>-17</sup>
butyl formate <sup>a</sup>	1293–1099	(5.33 ± 0.32) × 10 <sup>-17</sup>
isoprene <sup>b</sup>	830–950	(1.03 ± 0.02) × 10 <sup>-17</sup>
formaldehyde <sup>c</sup>	1845–1625	(1.25 ± 0.13) × 10 <sup>-17</sup>
nitric acid <sup>d</sup>	840–930	(2.2 ± 0.2) × 10 <sup>-17</sup>
dinitrogen pentoxide <sup>e</sup>	710–790	(4.5 ± 0.5) × 10 <sup>-17</sup>
nitrogen dioxide <sup>f</sup>	1665–1540	(1.1 ± 0.1) × 10 <sup>-17</sup>

<sup>a</sup> Determined in this work. <sup>b</sup> See Klawatsch-Carrasco et al.<sup>42</sup> <sup>c</sup> See Klotz et al.<sup>8</sup> <sup>d</sup> See Hjorth et al.<sup>43</sup> <sup>e</sup> Averaged value of Cantrell et al.,<sup>44</sup> Cantrell et al.,<sup>45</sup> and Hjorth et al.<sup>46</sup> <sup>f</sup> Extracted from HITRAN database.

of the main infrared absorption band of vinyl ethers and their oxidation products are presented in Table 1.

**Chemicals.** Dry synthetic air was generated using N<sub>2</sub> (from liquid nitrogen evaporation, purity >99.995%, H<sub>2</sub>O < 5 ppm, Linde Gas) and O<sub>2</sub> (quality NUS, purity >99.995%, H<sub>2</sub>O < 5 ppm, Air Liquide). Organic reagents were obtained from commercial sources: methyl vinyl ether, methyl formate and ethyl formate were from Fluka (> 99%), ethyl vinyl ether and isoprene were from ACROS (> 99%), propyl vinyl ether, butyl vinyl ether, propyl formate, and butyl formate were from Aldrich (> 97%).

**Kinetic Method.** Time-resolved concentrations of reactants were monitored from their infrared spectral absorptions. The nitrate radical absorbs in the visible light at 662 nm.<sup>2</sup> Nevertheless, since NO<sub>3</sub> concentrations were very low due to the high reactivity of vinyl ethers and the high level of NO<sub>2</sub>, NO<sub>3</sub> remained below the detection limit of our UV–visible DOAS system. In consequence, it was impossible to determine an absolute rate constant and relative rate technique had to be used. The principle of this technique is to measure the decay rate of the selected compound (X) relative to a reference compound (R), through NO<sub>3</sub>-induced oxidation. The NO<sub>3</sub> oxidation rate constant of the reference must be well-known.



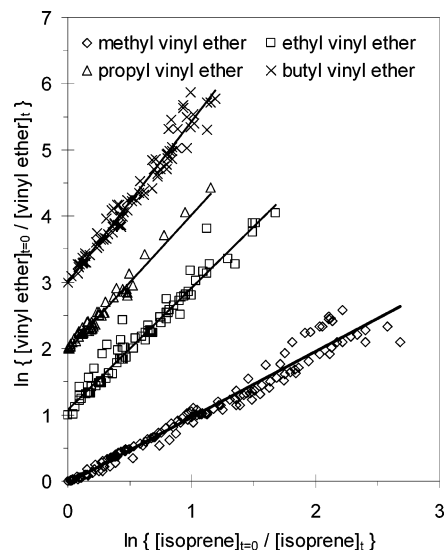
If the reaction with NO<sub>3</sub> radicals is the only sink for X and R compounds, the following relation is obtained from the integration of the kinetic equations:

$$\ln([X]_0/[X]_t) = (k_x/k_r) \ln([R]_0/[R]_t)$$

where [X]<sub>0</sub>, [R]<sub>0</sub>, [X]<sub>t</sub>, and [R]<sub>t</sub> are respectively the concentrations of the selected compound and the reference compound at times 0 and t. A plot of ln([X]<sub>0</sub>/[X]<sub>t</sub>) vs ln([R]<sub>0</sub>/[R]<sub>t</sub>) yields a straight line with a slope of k<sub>x</sub>/k<sub>r</sub> and a zero intercept. The chosen reference compound was isoprene, whose NO<sub>3</sub> oxidation rate constant has been measured by several studies over the last 20 years.<sup>15–23</sup> Despite some discrepancies, most recent papers are in good agreement.<sup>21–23</sup> The reviewed value proposed by IUPAC (k<sub>NO<sub>3</sub>+isoprene</sub> = (7.0 ± 1.4) × 10<sup>-13</sup> cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at 298 K,<sup>24</sup> February 2006) was used for this study.

## 3. Results

**Kinetic Study.** Plots of relative rate measurements for reactions of methyl, ethyl, propyl, and butyl vinyl ethers with



**Figure 1.** Plots of relative rate measurements for reactions of methyl, ethyl, propyl, and butyl vinyl ethers with nitrate radical (corresponding to all experiments for each ether). The ordinate scale is offset by 1 for EVE, by 2 for PVE, and by 3 for BVE.

the nitrate radical, using isoprene as reference compound are presented in Figure 1. For each vinyl ether, several experiments were carried out (3 or 4). The obtained rate constants are reported in the Table 2 and compared to previous studies. This study represents the first kinetic experimental determination for  $\text{NO}_3$  oxidation of methyl vinyl ether. One can notice that for each compound, rate constants deduced from different experiments are in good agreement (by taking into account the uncertainties) whatever the method used to generate  $\text{NO}_3$  radicals, which indicates that the used chemical system does not influence the results.

For each single experiment, the uncertainty was calculated using the method developed by Brauers and Finlayson-Pitts<sup>25</sup> which takes into account errors on both abscissa and ordinate scales (see Table 2). The uncertainty on the final averaged constant was calculated by taking into account the uncertainties on each single experiment and by modeling the distribution of values by a Gaussian curve. Here,  $1\sigma$  of this distribution was retained as statistical error.

The SAR value obtained by Grosjean et al.<sup>11</sup> for reaction of methyl vinyl ether with  $\text{NO}_3$  is about twice as small as the one

obtained here. Our values for ethyl, propyl, and butyl vinyl ethers are in agreement with those of Pfrang et al.<sup>9</sup> and Zhou et al.<sup>12</sup> within the uncertainties. One can notice that the uncertainties associated with the present study are much smaller than the one of Pfrang et al.<sup>9</sup> on ethyl vinyl ether, but they are on the same order as those obtained by Zhou et al.<sup>12</sup>

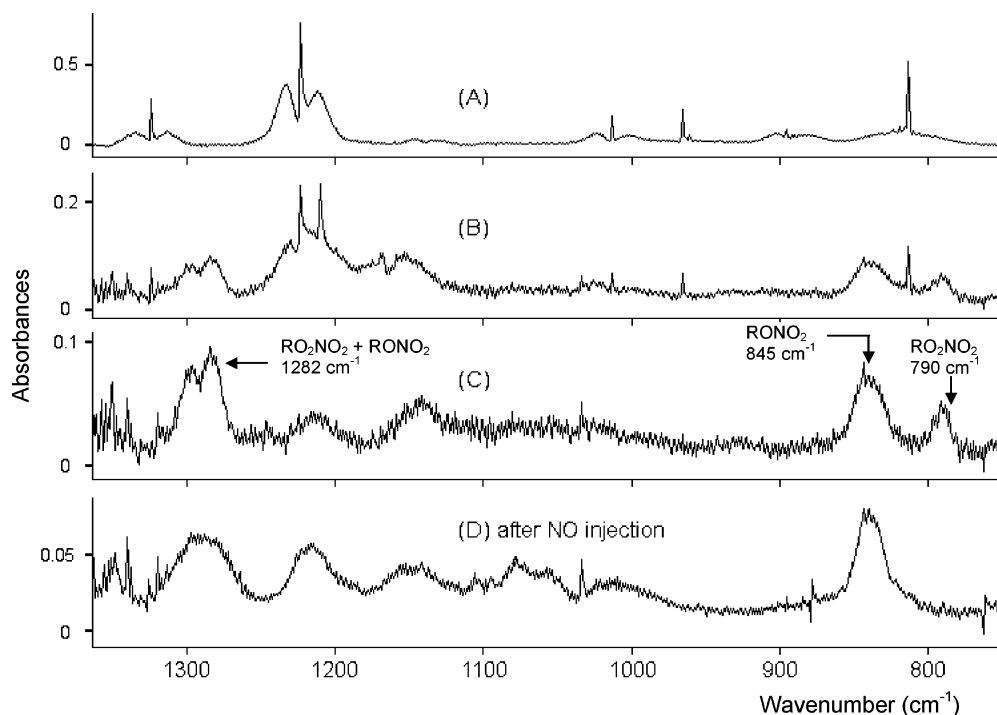
To evaluate the influence of the oxygenated function on the oxidation rate, measured rate constants for vinyl ethers ( $\text{ROCH}=\text{CH}_2$ ) were compared to those published for terminal alkenes ( $\text{RCH}=\text{CH}_2$ ). These rate constants are presented in Table 3. It appears clearly that when the oxygenated function is added, the reactivity is strongly enhanced. For example, reactivity of methyl vinyl ether toward  $\text{NO}_3$  is about 75 times higher than the one of 1-propene. Similarly, the butyl vinyl ether rate constant is about 100 times higher than the one of 1-hexene. Hence, it can be concluded that the activating effect of the ether function on the reactivity toward  $\text{NO}_3$  is very strong. This effect could be attributed to the mesomeric donor effect of the oxygen atom which could stabilize the nitro alkyl radical in the case of an  $\text{NO}_3$  addition on the external carbon.

Moreover, one can also observe that the rate constants tend to go increasingly with the R alkyl chain length since rate constants for methyl vinyl ether and butyl vinyl ether are respectively  $7.2 \times 10^{-13}$  and  $17.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . However, taking into account the uncertainties on these rate constants, one cannot conclude whether a plateau is reached or whether rate constants increase regularly with the alkyl chain length. For ethyl vinyl ether, for example, assuming that the contribution of the H-abstraction on the  $\text{CH}_3\text{-CH}_2\text{-O}$  group is equal to half the rate constant of diethyl ether ( $\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$ ) (i.e.,  $k_{\text{diethyl ether}+\text{NO}_3} = (3.1 \pm 0.1) \times 10^{-15}$ ),<sup>26</sup> one can consider that H-abstraction corresponds to less than 1% of the total rate constant and  $\text{NO}_3$  adds mainly on the double bond. So the increase of the rate constant with the alkyl chain cannot be explained by the H-abstraction on the additional carbons. Hence, the increase of the rate constants could be explained by an inductive donor effect of alkyl groups and a plateau may be reached.

**Mechanistic Study.** The main detected products were formaldehyde and alkyl formate ( $\text{R-OC(=O)H}$ ), with the alkyl group being identical to that of the studied vinyl ether ( $\text{R-O-CH=CH}_2$ ). In addition to these oxidation products, nitric acid was largely produced during the experiments by heterogeneous reaction on the walls:

**TABLE 2: Reaction Rate Constants for the Reaction of Studied Vinyl Ethers with the Nitrate Radical at Atmospheric Pressure and at 298 K, for Each Experiment, and the Subsequent Global Results for Each Compounds**

compound	type of experiment	$k$ ( $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ )	other works
methyl vinyl ether	with $\text{NO}_2$ excess	$(7.6 \pm 0.4) \times 10^{-13}$	$4.68 \times 10^{-13}$ (Grosjean et al. <sup>11</sup> )
	with $\text{NO}_2$ excess	$(6.1 \pm 1.1) \times 10^{-13}$	
	with $\text{NO}_2$ excess	$(6.3 \pm 0.5) \times 10^{-13}$	
	final $k$	$(7.2 \pm 1.5) \times 10^{-13}$	
ethyl vinyl ether	with $\text{NO}_2$ excess	$(13.0 \pm 1.5) \times 10^{-13}$	$(17 \pm 13) \times 10^{-13}$ (Pfrang et al. <sup>9</sup> ) $(14.0 \pm 3.5) \times 10^{-13}$ (Zhou et al. <sup>12</sup> )
	with $\text{NO}_2$ excess	$(13.2 \pm 0.6) \times 10^{-13}$	
	$\text{N}_2\text{O}_5$ continuous flow	$(14.9 \pm 3.4) \times 10^{-13}$	
	final $k$	$(13.1 \pm 2.7) \times 10^{-13}$	
propyl vinyl ether	stepwise injections of $\text{N}_2\text{O}_5$	$(13.0 \pm 4.1) \times 10^{-13}$	$(18.5 \pm 5.3) \times 10^{-13}$ (Zhou et al. <sup>12</sup> )
	stepwise injections of $\text{N}_2\text{O}_5$	$(12.9 \pm 4.5) \times 10^{-13}$	
	with $\text{NO}_2$ excess	$(12.5 \pm 3.2) \times 10^{-13}$	
	with $\text{NO}_2$ excess	$(15.2 \pm 2.8) \times 10^{-13}$	
final $k$	$(13.3 \pm 3.0) \times 10^{-13}$		
butyl vinyl ether	with $\text{NO}_2$ excess	$(15.9 \pm 1.8) \times 10^{-13}$	$(21.0 \pm 5.4) \times 10^{-13}$ (Zhou et al. <sup>12</sup> )
	with $\text{NO}_2$ excess	$(18.9 \pm 1.6) \times 10^{-13}$	
	with $\text{NO}_2$ excess	$(16.6 \pm 1.3) \times 10^{-13}$	
	final $k$	$(17.0 \pm 3.7) \times 10^{-13}$	



**Figure 2.** Some IR spectra from 700 to 1400 cm<sup>-1</sup>, obtained during a NO<sub>3</sub> oxidation experiment of methyl vinyl ether. Spectrum A is a standard spectrum of methyl vinyl ether, spectrum B was obtained a few minutes after the beginning of the experiment (HNO<sub>3</sub> bands have been subtracted for clarity), spectrum C is the residual spectrum of spectrum B (methyl vinyl ether, methyl formate, formaldehyde and HNO<sub>3</sub> have been subtracted), and spectrum D is the residual spectrum obtained after NO injection (the same compounds have been subtracted as for spectrum C).

**TABLE 3: Comparison of Rate Constants at Room Temperature and Atmospheric Pressure of Reaction of Vinyl Ethers and Relevant Alkenes with Nitrate Radicals (in molecules cm<sup>-3</sup> s<sup>-1</sup>)**

R-	alkene R-CH=CH <sub>2</sub>	vinyl ether R-O-CH=CH <sub>2</sub>
CH <sub>3</sub> -	$(9.5 \pm 0.8) \times 10^{-15a}$	$(7.2 \pm 1.5) \times 10^{-13b}$
C <sub>2</sub> H <sub>5</sub> -	$(13.5 \pm 4.1) \times 10^{-15c}$	$(13.1 \pm 2.7) \times 10^{-13b}$
C <sub>3</sub> H <sub>7</sub> -	$(15 \pm 5) \times 10^{-15d}$	$(13.3 \pm 3.0) \times 10^{-13b}$
C <sub>4</sub> H <sub>9</sub> -	$(18 \pm 7) \times 10^{-15d}$	$(17.0 \pm 3.7) \times 10^{-13b}$

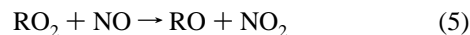
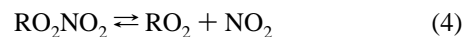
<sup>a</sup> See Morris et al.,<sup>47</sup> Japar et al.,<sup>48</sup> Atkinson et al.,<sup>49</sup> Atkinson et al.,<sup>50</sup> Canosa-Mas et al.,<sup>51</sup> and IUPAC evaluated kinetic data.<sup>24</sup> <sup>b</sup> This work. <sup>c</sup> See Atkinson.<sup>52</sup> <sup>d</sup> See Canosa-Mas et al.<sup>53</sup>



Once having subtracted the standard spectra of formaldehyde, alkyl formate, and nitric acid to acquired infrared spectra, residual bands remained at 790, 845, 1033, 1208, 1282, 1680, and 1730 cm<sup>-1</sup>. The band at 1033 cm<sup>-1</sup> features methanol and was observed during experiments relative to methyl vinyl ether but its formation could not be explained. No aliphatic alcohol formation was observed during NO<sub>3</sub>-oxidation of the other vinyl ethers. Other bands at 790, 845, and 1282 cm<sup>-1</sup> featured a mixture of oxygenated nitrates and peroxy nitrates<sup>27</sup> (see Figure 2a-c). As no standard spectra of oxygenated nitrates and peroxy nitrates were available, it was not possible to identify or quantify each single compound. Moreover, as the two main IR bands of alkyl formate overlap residual bands at 1208 and 1730 cm<sup>-1</sup>, the quantification of this compound was not easy and its measurement had to be associated with large uncertainties.

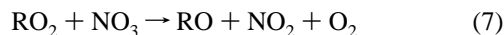
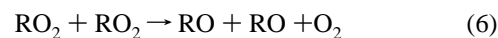
Nevertheless it has been possible to separate oxygenated nitrate spectra from peroxy nitrate spectra, as a few ppm of oxide nitrogen (NO) were added into the chamber at the end of some experiments in order to decompose peroxy nitrates. Indeed, NO converts quickly the peroxy radicals into alkoxy radicals (reaction 5), and so shifts the equilibrium (eq 4) to favor the

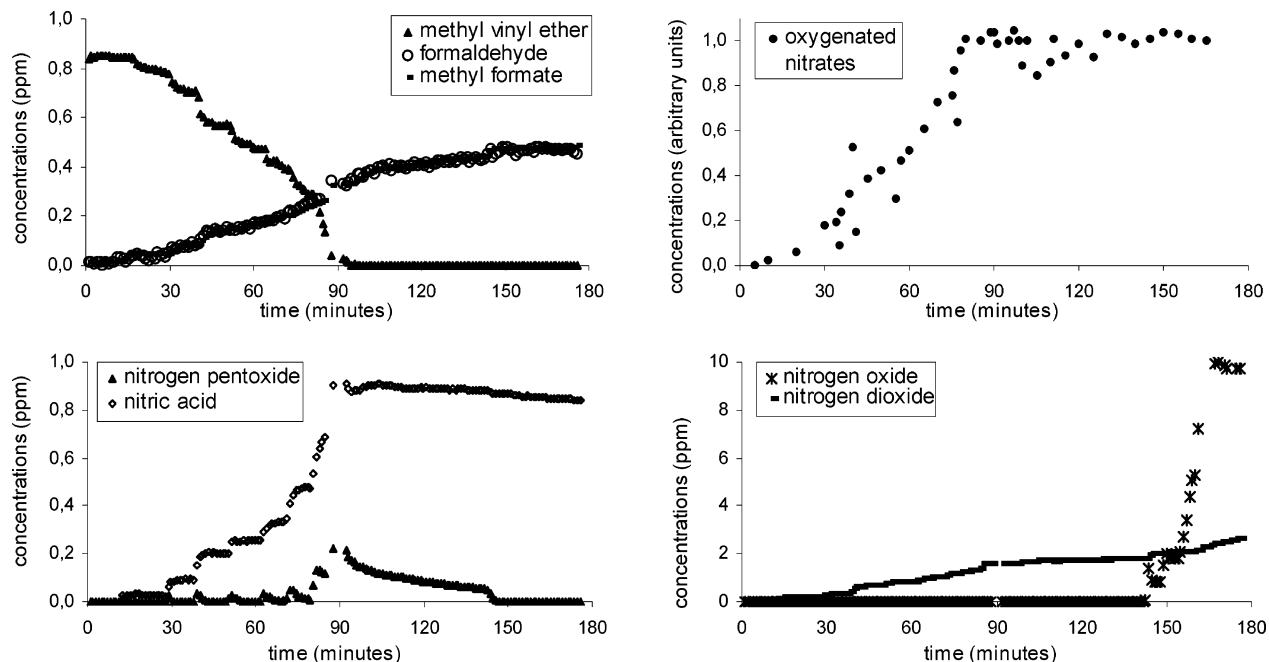
decomposition of peroxy nitrate. For each experiment on which this procedure was applied, it was noticed that the bands at 792 and 1729 cm<sup>-1</sup> vanished and only oxygenated nitrates remained in the mixture.



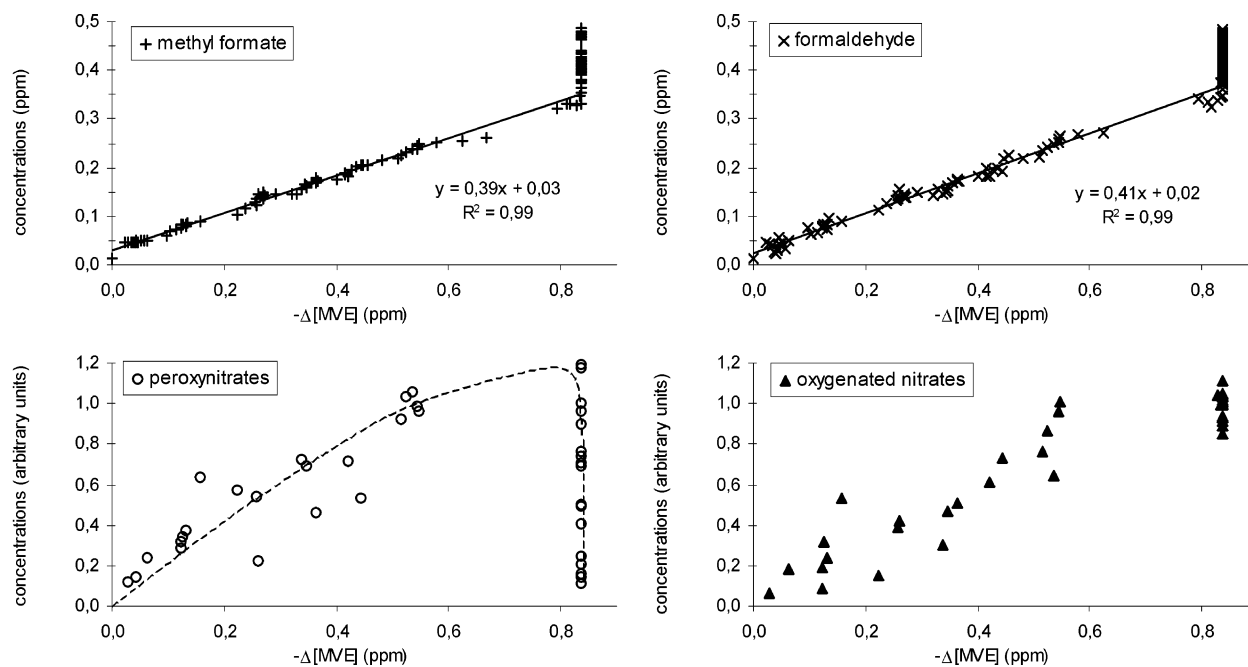
Then, using the IR residual spectrum that corresponds to oxygenated nitrates (RO-C(O)-CH<sub>2</sub>(ONO<sub>2</sub>) + CHO-CH(OR)ONO<sub>2</sub>, see Figure 5 and Figure 2d), it was possible to deduce a qualitative spectrum corresponding to the sum of peroxy nitrates by subtracting the oxygenated nitrates spectrum to a residual spectrum acquired before NO injection.

Typical time-resolved concentration profiles of reactants and products are shown on Figure 3 and formation yields of formaldehyde and alkyl formate were obtained by calculating the initial slopes of the plots [formaldehyde] and [alkyl formate] vs -Δ[vinyl ether] (see Figure 4). The same curves have been plotted for nitrates and peroxy nitrates. However, since reference spectra were not calibrated, plots of nitrates and peroxy nitrates are given in arbitrary units by measuring the intensities of their absorption bands. Typical curves extracted from the same experiment are also presented in Figure 4. A secondary production of formaldehyde and alkyl formate is noticeable on this curve as its end inflects strongly, which is explained by the peroxy nitrates decomposition (see oxidation scheme in Figure 5). Indeed VOCs oxidation generally yields to a peroxy radical (RO<sub>2</sub>)<sup>28</sup> which can either react with NO<sub>2</sub> to produce a thermally unstable peroxy nitrate in equilibrium with the peroxy radical (see equilibrium 4), or give an alkoxy radical:



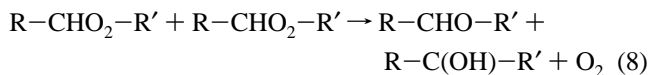


**Figure 3.** Evolution through time of the chamber mixture during a  $\text{NO}_3$  oxidation experiment of methyl vinyl ether. Dinitrogen pentoxide was added by stepwise injections.



**Figure 4.** Formation yields of different products during a  $\text{NO}_3$  oxidation experiment of methyl vinyl ether. The bold line indicates the tendency of the evolution of the oxygenated nitrates, while the tear line indicates that of alkyl peroxy nitrates.

or even give alcohol and a carbonyl compound through an instable state:



In other words the peroxy nitrates play the role of reservoir of peroxy radicals, which delays the release of the peroxy radicals and explains the secondary production of the different products. Since the production yields of formaldehyde and alkyl formate are equal for the four studied vinyl ethers, within uncertainties, the coproduction of the two compounds may be assumed. These results are in good agreement with those of

Klotz et al.<sup>8</sup> for methyl vinyl ether, who observed the formation of formaldehyde and methyl formate with equal yields of about 50%.

It should be noticed that yields obtained here are not necessary representative of the tropospheric conditions as experiments were carried out with high  $\text{NO}_2$  levels (several ppm), whereas tropospheric concentrations do not exceed a few tens of ppb. The consequence is that yields of peroxy nitrates are much higher than those that should be obtained under real tropospheric conditions, and consequently, obtained yields of formaldehyde and alkyl formate were smaller. Yields under real atmospheric conditions can be approximated by calculating the ratios  $[\text{formaldehyde}] / (-\Delta[\text{vinyl ether}])$  and  $[\text{alkyl formate}] / (-\Delta[\text{vinyl ether}])$  once all peroxy nitrates have decomposed, meaning after

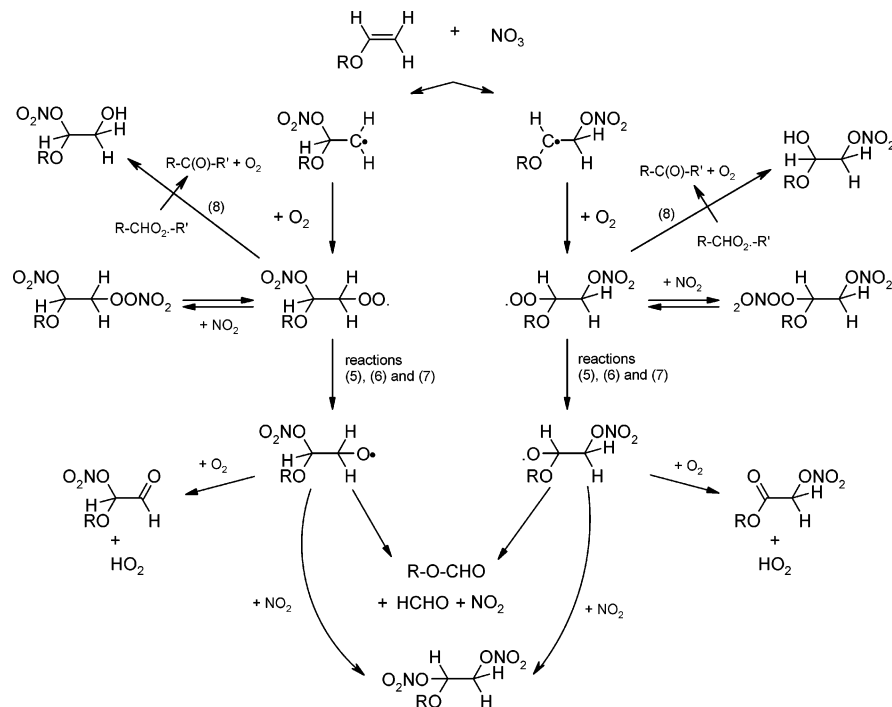


Figure 5. Proposed mechanistic pathways after NO<sub>3</sub> oxidation of aliphatic vinyl ethers.

TABLE 4: Formaldehyde and Alkyl Formate Primary-Like and Global Yields Obtained from All Performed Mechanistic Experiments

vinyl ether	experiment no.	primary yield (%)		final yield (%)	
		formaldehyde	alkyl formate	formaldehyde	alkyl formate
methyl	1	47 ± 6	47 ± 4	53 ± 9	54 ± 6
	2	41 ± 17	39 ± 11	59 ± 20	60 ± 14
ethyl	3	60 ± 5	48 ± 2		
	4	47 ± 12	37 ± 6		
	5	52 ± 8	46 ± 4	68 ± 13	60 ± 7
propyl	6	48 ± 12	37 ± 6	50 ± 12	50 ± 3
	7	57 ± 22	60 ± 16	54 ± 22	54 ± 12
butyl	8	46 ± 8	44 ± 5		
	9	44 ± 10	43 ± 8		
	10	47 ± 7	52 ± 5		
	11	40 ± 4	44 ± 2	49 ± 8	52 ± 4

NO injection (see Table 4). To calculate these “final” yields, it was checked that loss processes of products, i.e., mainly reaction with NO<sub>3</sub>, were negligible for the duration of the experiments:  $k(\text{HCHO} + \text{NO}_3) = 5.6 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$ <sup>29,30</sup> and  $k(\text{alkyl formate} + \text{NO}_3) < 10^{-16}$ <sup>31</sup> (at  $T = 300 \text{ K}$  and atmospheric pressure) leading to lifetimes higher than respectively 4 and 20 h under the conditions of this work.

From these observations, a mechanism based on the assumed NO<sub>3</sub> oxidation scheme is now discussed (see Figure 5). It is considered that NO<sub>3</sub> electrophilic addition on one of the two double bonded carbon occurs rather than an H-abstraction.<sup>2,32</sup> This addition is followed by an O<sub>2</sub> addition which produces a peroxy radical. Then this radical can yield a peroxy radical (see equilibrium 4). It can also yield carbonyl + alcohol. Finally, it can lead to an alkoxy radical by reactions 5–7. Three possible pathways are assumed for the subsequent reaction of alkoxy radical:

- H-abstraction by O<sub>2</sub> on the α-position of the alkoxy radical results in oxygenated nitrates and HO<sub>2</sub> release. Two different oxygenated nitrates can be formed depending on the nitrate attack position.

- Scissions of the C–C bond on the α-position and of the C–ONO<sub>2</sub> bond on the β-position of the alkoxy lead to formaldehyde, alkyl formate, and NO<sub>2</sub>. The produced com-

pounds are the same whatever the double bonded carbon on which NO<sub>3</sub> adds. The coproduction of formate and formaldehyde is confirmed by their equal formation yields.

- NO<sub>2</sub> addition on the alkoxy radical leads to a dinitrate which is identical for the two oxidation pathways. However, as formaldehyde and alkyl formate yields remain equal whatever the NO<sub>2</sub> concentration is, the production of this dinitrate may be a minor process.

All these observations largely agree with those made by Klotz et al.<sup>8</sup> about methyl vinyl ether. This work has extended the knowledge of reactivity of ethyl vinyl ether, propyl vinyl ether and butyl vinyl ether which react similarly to methyl vinyl ether with NO<sub>3</sub> since main products are formaldehyde and alkyl formate. Identically to Klotz et al.,<sup>8</sup> expected products of H-abstraction by NO<sub>3</sub> (the same as those produced of H-abstraction by OH) were not detected, i.e., formic anhydride and vinyl formate, which confirms that H-abstraction is a minor process. Moreover, no traces of epoxide were either detected.

#### 4. Environmental Impact

Tropospheric lifetimes of methyl, ethyl, *n*-propyl, and *n*-butyl vinyl ethers were estimated with respect to NO<sub>3</sub> oxidation (using rate constants measured in this work) and through OH and O<sub>3</sub>

**TABLE 5: Calculated Lifetimes of the Four Studied Vinyl Ethers with Respect to NO<sub>3</sub>, OH, and O<sub>3</sub>, Considered at Their Usual Concentrations Where MVE, EVE, PVE, and BVE Refer to Methyl Vinyl Ether, Ethyl Vinyl Ether, Propyl Vinyl Ether, and Butyl Vinyl Ether**

oxidant	rate constants (in cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	oxidant concentration	studied vinyl ether lifetimes
NO <sub>3</sub>	$k_{MVE} = (7.2 \pm 1.5) \times 10^{-13}$ (this work),	2 ppt (remote atmosphere)	3–8 h
	$k_{EVE} = (13.1 \pm 2.7) \times 10^{-13}$ (this work), $k_{PVE} = (13.3 \pm 3.0) \times 10^{-13}$ (this work), $k_{BVE} = (17.0 \pm 3.7) \times 10^{-13}$ (this work)	50 ppt (polluted atmosphere)	8–20 min
OH	$k_{MVE} = (4.53 \pm 0.70) \times 10^{-11,6}$	$2 \times 10^6$ molecule cm <sup>-3</sup>	1–3 h
	$k_{EVE} = (7.24 \pm 0.81) \times 10^{-11,6,7}$		
	$k_{PVE} = (10.5 \pm 1.4) \times 10^{-11,6}$		
	$k_{BVE} = (11.1 \pm 1.4) \times 10^{-11,6}$		
O <sub>3</sub>	$k_{EVE} = (1.95 \pm 0.14) \times 10^{-16,6,7}$	50 ppb	1 h
	$k_{PVE} = (2.35 \pm 0.38) \times 10^{-16,6}$		
	$k_{BVE} = (2.85 \pm 0.15) \times 10^{-16,6}$		

oxidation (using rate constants measured by Thiault et al.<sup>6,7</sup>). Calculated values are reported in Table 5.

It is concluded that nighttime chemistry does really affect the tropospheric fate of vinyl ethers, since their lifetimes with respect to NO<sub>3</sub> attack range from 0.1 times to 3 times their lifetimes with respect to OH or to O<sub>3</sub>. Hence a significant part of vinyl ethers can be oxidized by NO<sub>3</sub> during the night for typical NO<sub>3</sub> concentrations in remote and polluted atmospheres. Lifetimes of vinyl ethers in the troposphere are short, but those of their products are much greater (formaldehyde,  $\tau_{OH} = 16$  h;<sup>24</sup> alkyl formate,  $\tau_{OH} = 3–30$  days<sup>33,34</sup>), so that they can travel on a rather long distance toward the troposphere and impact on a regional scale. For example, formaldehyde (as aldehydes in general) is known to play a role in the tropospheric OH budget.<sup>35</sup> Moreover, oxidation of oxygenated nitrates and formates can play a role in multiphase chemistry, as these functionalities have been identified in the condensed phase during chamber experiments.<sup>36,37</sup> Finally nitrates play the role of reservoir of NO<sub>2</sub>, released by peroxy nitrates decomposition (as explained in the mechanistic discussion), or by oxygenated nitrate photolysis.<sup>32</sup>

Since formaldehyde is carcinogenic<sup>38–41</sup> and nitrates are likely to be toxic and to be an irritant<sup>2–4</sup> they might impact on human health. This impact may be particularly important in indoor atmospheres, as vinyl ethers are used as solvents in paints, adhesives, or ink additives and as photolysis rate of NO<sub>3</sub> may be quite small and its precursors are present at significant level.

## 5. Conclusion

This work reports kinetic and mechanistic data on NO<sub>3</sub>-oxidation of a series of four aliphatic vinyl ethers: methyl, ethyl, *n*-propyl, and *n*-butyl vinyl ethers. It led to experimentally determined rate constants which are likely to enhance kinetic databases in order to give rise to SARs and to allow better prediction of rate constants for unstudied compounds for the purpose of being integrated in modeling programs.

Nevertheless, although the obtained uncertainties are quite reasonable, it would be suitable to carry out experimental determinations of these rate constants with an absolute kinetic method in order to reduce uncertainties.

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