Atmospheric Reactivity of Vinyl Acetate: Kinetic and Mechanistic Study of Its Gas-Phase Oxidation by OH, O-3, and NO3

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Atmospheric Reactivity of Vinyl Acetate: Kinetic and Mechanistic Study of Its Gas-Phase Oxidation by OH, O₃, and NO₃

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Vinyl acetate is widely used in industry. It has been classified as a high-production volume (HPV) chemical in the United States. To evaluate its impact on the environment and air quality, its atmospheric reactivity toward the three main tropospheric oxidants (OH, NO₃, and O₃) has been investigated. Kinetic and mechanistic experiments have been conducted at room temperature and atmospheric pressure using an indoor Pyrex simulation chamber coupled to Fourier transform infrared (FTIR) and UV−visible spectrometers. Rate constants for the reactions of vinyl acetate with OH, NO₃, and O₃ were equal to $(2.3 \pm 0.3) \times 10^{-11}$, $(7.3 \pm 1.8) \times 10^{-15}$, and $(3.0 \pm 0.4) \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹, respectively. From these data, tropospheric lifetimes of vinyl acetate have been estimated as follows: $\tau_{OH} = 6$ h, $\tau_{NO_3} = 6$ days, and $\tau_{O_3} = 5$ days. This demonstrates that reaction with OH radicals is the main tropospheric loss process of this compound. From the mechanistic experiments, main oxidation products have been identified and quantified and oxidation schemes have been proposed for each studied reaction.

1. Introduction

Vinyl acetate (VA) is widely used in industry. It is listed in the OECD (Organisation for Economic Co-operation and Development) integrated high-production volume (HPV) database, with annual production and/or importation volumes of >1 million pounds in the United States (*1*). The major use of vinyl acetate monomer is the production of polyvinyl acetate and vinyl acetate copolymers which are used in water-based paints, adhesives, and paper coatings. Vinyl acetate is also emitted by carpets containing PVC (*2*) and is used in safety glass interlayer and in hair sprays (*3*). Because of its numerous applications and its high volatility (vapor pressure of 89 mmHg at 293 K), VA can contribute to indoor air pollution and to photochemical smog events.

Once emitted into the troposphere, vinyl acetate is expected to be oxidized by ozone and OH and NO₃ radicals, but only a few studies that aimed to determine its atmospheric reactivity have been performed. With regard to the OH-initiated oxidation process, only one experimental rate study has recently been published by Blanco (*4*). In this study, the
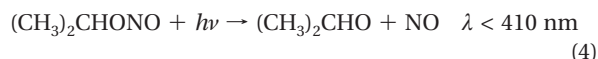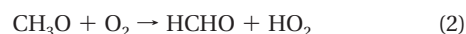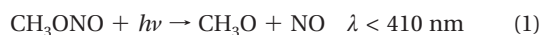
rate constant was investigated as a function of temperature (in the range of 287−313 K) using the relative rate technique. Moreover, no mechanistic study has ever been performed for the OH oxidation of vinyl acetate. With regard to the ozonolysis of VA, one experimental rate study has been performed by Grosjean (*5*), who measured the pseudo-first-order decay of ozone. Moreover, in the studies published by Grosjean (*6, 7*), some ozonolysis products were detected but the carbon balance remained incomplete. For NO₃-initiated oxidation of VA, no experimental rate study has ever been performed and the oxidation products remain unknown.

In conclusion, despite a large release of vinyl acetate into the atmosphere, its tropospheric fate is still incompletely known. To improve our understanding of the environmental impact of industrial chemicals, we report here a room-temperature kinetic and mechanistic study on the O₃-, OH-, and NO₃-initiated oxidation of vinyl acetate.

2. Experimental Section

All experiments were performed in an evacuable environmental chamber comprising a Pyrex reactor of 977 L surrounded by two sets of 40 fluorescent tubes (Philips TL05 and TL03) and 16 arc lamps. The reactor contains two multiple-reflection optical systems interfaced with a Fourier transform infrared (FTIR) spectrometer and an UV−visible grating spectrometer. The FTIR spectrometer is a BOMEM DA8-ME device with a glowbar as the mid-infrared source. Infrared spectra were recorded with a resolution of 0.5 cm⁻¹ and a path length of 156 m. For absolute rate determination of the NO₃ oxidation of vinyl acetate, the nitrate radical was monitored by its absorption at 662 nm using the UV−visible spectrometer. This spectrometer consists of a source (a high-pressure xenon arc lamp, Osram XBO, 450 W), a multipass optical system inside the reactor (optimum path length of 72 m), a monochromator (HR 320 Jobin-Yvon), and a CCD camera made of 1024 × 58 pixels (CCD 3000, Jobin-Yvon) as a detector. In this configuration, the CCD covers a spectral range of ca. 60 nm, and the instrument has a maximum resolution of 0.15 nm. Details of this environmental chamber and its spectroscopic devices have been described previously (*8, 9*).

OH and NO₃ Radical Generation. Hydroxyl radicals were generated by the photolysis of methyl or isopropyl nitrites which were prepared via addition of a dilute solution of H₂SO₄ to a mixture of NaNO₂ and the corresponding alcohol (*10*).

$$\mathrm{CH_3ONO} + h\nu \rightarrow \mathrm{CH_3O} + \mathrm{NO} \quad \lambda < 410 \text{ nm} \quad (1)$$

$$\mathrm{CH_3O} + \mathrm{O_2} \rightarrow \mathrm{HCHO} + \mathrm{HO_2} \quad (2)$$

$$\mathrm{HO_2} + \mathrm{NO} \rightarrow \mathrm{OH} + \mathrm{NO_2} \quad (3)$$

$$(\mathrm{CH_3})_2\mathrm{CHONO} + h\nu \rightarrow (\mathrm{CH_3})_2\mathrm{CHO} + \mathrm{NO} \quad \lambda < 410 \text{ nm} \quad (4)$$

$$(\mathrm{CH_3})_2\mathrm{CHO} + \mathrm{O_2} \rightarrow \mathrm{CH_3COCH_3} + \mathrm{HO_2} \quad (5)$$

$$\mathrm{HO_2} + \mathrm{NO} \rightarrow \mathrm{OH} + \mathrm{NO_2} \quad (6)$$

From reactions 2 and 5, one can see that the photolysis of methyl nitrite produces formaldehyde, whereas the photolysis of isopropyl nitrite produces mainly acetone. As a consequence, depending on the studied chemical system, isopropyl or methyl nitrites can be used preferentially to prevent any interference in the quantification of oxidation products.

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The nitrate radicals were generated from the thermal decomposition of dinitrogen pentoxide ($N_2O_5 \leftrightharpoons NO_2 + NO_3$) which was synthesized in a vacuum line following a method adapted from Schott (*11*) and Atkinson (*12*). N_2O_5 was produced through these reactions:

$$NO_2(g) + O_3(g) \rightarrow NO_3 + O_2(g) \qquad (7)$$

$$NO_3(g) + NO_2(g) \leftrightharpoons N_2O_5(g) \qquad (8)$$
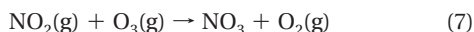
Details of the synthesis have been described previously (*15*).

Rate Constant Determination. The rate constant of the OH-induced oxidation was determined by the relative rate technique using propene as a reference compound. The rate constant k(propene+OH) has been taken to be equal to $(2.9 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (*13*).

Considering the OH oxidation of the studied and reference compounds and provided that the decrease in the concentrations of both compounds is due to only the reaction with OH radicals and that neither VA nor propene is re-formed in any process, the following relation holds:

$$\ln \frac{[VA]_0}{[VA]_t} = \frac{k_{VA}}{k_{propene}} \times \ln \frac{[propene]_0}{[propene]_t} \qquad (I)$$

where subscripts 0 and t indicate the concentration at the beginning of the experiment and at time t, respectively. Equation 1 yields a straight line with a slope of $k_{VA}/k_{propene}$ and an intercept of zero.

The rate constant for the ozonolysis of vinyl acetate was determined by the absolute rate technique. Vinyl acetate and ozone were monitored using FTIR spectrometry. Assuming that VA is consumed only by the reaction with ozone, the decrease in the VA concentration is equal to the speed of the ozonolysis reaction

$$-\frac{d[VA]}{dt} = k_{VA+O_3}[VA][O_3] \qquad (II)$$

Then, for each point, we approximated this relationship with small intervals of [VA] and time. Hence, by plotting $-\Delta$[VA] versus [VA][O$_3$]Δt, we obtained a straight line with a slope corresponding to k_{VA+O_3}.

The NO$_3$ oxidation rate constant was determined by both relative and absolute rate techniques during the same experiment. Indeed, during an experiment, NO$_3$ was monitored by UV–visible spectrometry while vinyl acetate and the reference compound, here propene, were monitored by FTIR. The rate constant of the NO$_3$ oxidation of propene was taken to be equal to $(6.4 \pm 1.1) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. This value was re-evaluated in 2009 after a new absolute rate determination in which both propene and NO$_3$ were monitored for the first time (*14*) and a careful re-examination of the previously published data. This comparison with previous data has shown that the obtained rate constant is in good agreement with three published determinations but disagrees with three others that are 50% higher than that in this work. Actually, the value recommended by IUPAC (9.5×10^{-15} cm^3 molecule^{-1} s^{-1}) is based on these last three studies which are in disagreement with the new absolute rate determination. Consequently, the value recommended by IUPAC was not considered here.

Experimental Procedure. All experiments were conducted at atmospheric pressure and 293 ± 3 K. The initial concentrations of the reactants [vinyl acetate, propene, and O$_3$ (or N$_2O_5$ or alkyl nitrite)] were in the parts per million range in a synthetic mixture of 80% N$_2$ and 20% O$_2$. For OH oxidation, NO was added to the mixture to minimize the formation of nitrate radicals and ozone. For ozonolysis experiments, CO was added as an OH scavenger at a
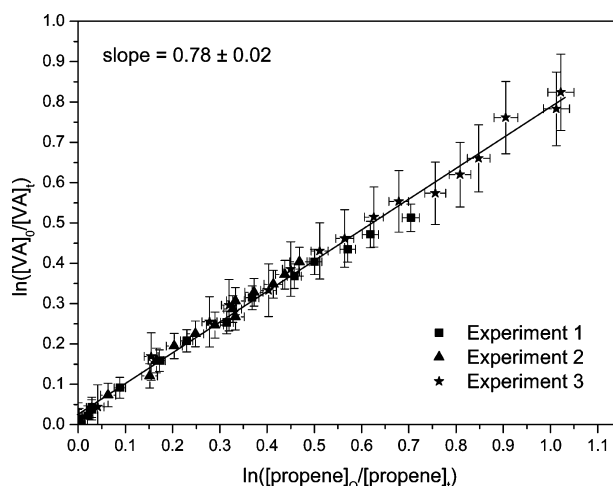

FIGURE 1. Relative kinetic plot for OH oxidation of vinyl acetate with propene as a reference compound.

concentration of $\sim$2000 ppm (2 mbar). With such a high concentration of CO, more than 90% of the OH radicals are scavenged, and we verified whether the oxidation of vinyl acetate by OH radicals becomes negligible compared to its ozonolysis. Experimental conditions for all experiments are listed in Table S1 of the Supporting Information. During the experiments, compounds were monitored via acquisition of infrared spectra every $\sim$5 min (corresponding to 100 co-added interferograms). 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 band intensities of the main infrared and UV–visible absorption bands of reactants and products are listed in Table S2 of the Supporting Information.

Chemicals. Dry synthetic air was generated using N$_2$ (from liquid nitrogen evaporation, >99.995% pure, <5 ppm H$_2$O, Linde Gas) and O$_2$ (quality N45, >99.995% pure, <5 ppm H$_2$O, Air Liquide). Vinyl acetate was from Aldrich (99%).

3. Results and Discussion

3.1. OH-Initiated Oxidation. *3.1.1. Kinetic Study.* A plot of the relative rate measurements for the reaction of vinyl acetate with OH radical using propene as a reference compound is given in Figure 1. Three experiments were performed and are in very good agreement. The value of the final rate constant is given in Table 1. We calculated its uncertainty by adding the relative uncertainties corresponding to the statistical error and to the error in the reference rate constant (here 10%). The statistical error was calculated as 2σ, where σ is the standard deviation on the linear regression (for confidence limits equal to 95%). This linear regression analysis was performed using the method developed by Brauers and Finlayson-Pitts (*15*) which takes into account the uncertainties on both abscissa and ordinate scales.

In Table 1, the rate constant for the OH-initiated oxidation of vinyl acetate obtained in this study is compared to the data already published. Our value is in good agreement with the experimental determination published by Blanco (*4*) but is approximately half of the value estimated by Grosjean (*16*) using a structure–activity relationship (SAR). As a consequence, this new experimental determination confirms the previous experimental value and shows that the rate constant proposed by Grosjean (*16*) is overestimated by a factor of 2.

3.1.2. Mechanistic Study. From infrared spectra, the main products for the OH-induced oxidation of vinyl acetate have been identified and quantified; after subtraction of the absorption bands of the remaining reactants (isopropyl nitrite, vinyl acetate, and NO) and products arising from

TABLE 1. Rate Constants for the Oxidation of Vinyl Acetate by OH, NO₃, and O₃ Compared to Published Values

reaction	method	k_{VA}/k_{ref}	k^a	ref
VA + OH	relative rate	0.78 ± 0.02	$(2.3 \pm 0.3) \times 10^{-11}$	this work
	relative rate	−	$(2.48 \pm 0.61) \times 10^{-11}$	4
	SAR	−	4.9×10^{-11}	16
VA + NO₃	relative rate	1.17 ± 0.07	$(7.5 \pm 1.7) \times 10^{-15}$	this work
	absolute rate	−	$(7.1 \pm 1.9) \times 10^{-15}$	this work
	SAR	−	141×10^{-15}	16
VA + O₃	absolute rate	−	$(3.0 \pm 0.4) \times 10^{-18}$	this work
	absolute rate	−	$(3.2 \pm 0.5) \times 10^{-18}$	5

^{a} Uncertainties in absolute rate constants were calculated as 2σ on the linear regression, whereas uncertainties in relative rate constants include the statistical error in the linear regression (2σ) and the error in the reference rate constant.
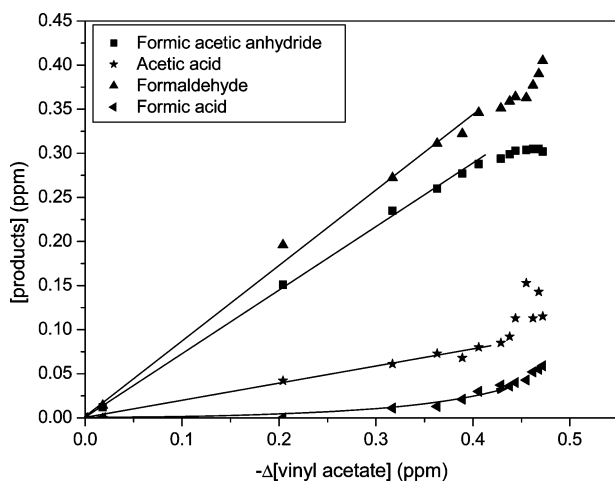
FIGURE 2. Formation yields of products by OH-induced oxidation of vinyl acetate for experiment 4.

isopropyl nitrite photolysis [mainly HNO₃, NO₂, acetone, and isopropyl nitrate (17)], remaining bands were attributed to reaction products of vinyl acetate, i.e., formaldehyde, formic acetic anhydride, and formic and acetic acids. Traces of PAN as a secondary product were also detected and attributed to the photolysis and/or OH oxidation of acetaldehyde which is a very minor product of isopropyl nitrite photolysis [less than 2% according to Meunier et al. (17) and Devolder (18)]. Moreover, for the same reason, the formation of formaldehyde arising from isopropyl nitrite photolysis is considered to be negligible. Typical concentration−time profiles of reactants and products are given as an example in Figure S1 of the Supporting Information.

By plotting the formation of products versus the disappearance of vinyl acetate (see Figure 2), we find that formaldehyde, formic acetic anhydride, and acetic acid, whose plots have initial slopes different from zero, are primary products. On the other hand, formic acid appears to be a secondary product. The increase in the fractional yield of acetic acid during the course of the experiment suggests that this product is also a secondary product. Moreover, one can notice that its secondary formation is very similar to that of formic acid and can be explained by the hydrolysis of small amounts of formic acetic anhydride.

Formation yields of primary oxidation products were determined from the initial slope of the plots of [product] versus −Δ[vinyl acetate] (see Table 2). Indicated errors of yields take into account the estimated uncertainties in reactant and product IR absorption band calibrations (see Table S2 of the Supporting Information) and the uncertainty in the calculation of yields. This last one is two standard deviations (for confidence limits equal to 95%) of the initial slope of the curve of [product] versus −Δ[vinyl acetate]. Errors due to the integration of absorption bands in infrared spectra

have been disregarded because they are not significant compared to errors in integrated band intensities and statistical errors.

From the oxidation product analysis, a mechanism based on a hypothetical OH oxidation scheme has been proposed (see Scheme 1). Formic acetic anhydride which is a major oxidation product can be formed conjointly with formaldehyde by the decomposition of CH₃C(O)OCH(OH)CH₂O• and/or CH₃C(O)OCH(O•)CH₂OH radicals (Scheme 1, channels 1 and 3′). Primary formation of acetic acid can be explained by a rearrangement of CH₃C(O)OCH(O•)CH₂OH proceeding by an H-atom transfer through a five-membered ring transition state called α-ester rearrangement (Scheme 1, channel 4′). This rearrangement which is characteristic of ester oxidation processes has been observed for other acetates and propionates (19−22). The OH-CH₂C(O)• radical coproduced by this channel can react with O₂ to form OH-CH₂C(O)OO•. This latter can react with NO to produce formaldehyde and CO₂ and/or with NO₂ to produce hydroxy-PAN [OH-CH₂C(O)OONO₂]. However, hydroxy-PAN which exhibits characteristic IR bands of -OONO₂ (at 1747, 1300, and 791 cm⁻¹), -C=O (at 1831 cm⁻¹), and -OH (at 3600 cm⁻¹) (23) was not detected here. This can be explained by the instability of this compound at room temperature. Indeed, Niki (23), who has studied the Cl- and OH-induced oxidations of glycolaldehyde in the presence of NO₂, has observed the fast disappearance of hydroxy-PAN (in <15 min) with the concomitant formation of formaldehyde and CO₂. This explains why HCHO is produced by channels 3, 4′, and 7′ and has a formation yield close to unity. From these observations, the branching ratios of channels 1 and 3′ and channel 4′ were estimated to be 0.75 ± 0.07 and 0.20 ± 0.03, respectively. This suggests that decomposition is the major reaction pathway of the CH₃C(O)OCH(OH)CH₂O• radical, whereas the CH₃C(O)OCH(O•)CH₂OH radical can decompose and undergo an α-ester rearrangement. Moreover, no product arising from the reaction of these hydroxyalkoxy radicals with O₂ has been observed. These results are in good agreement with previous mechanistic studies of OH oxidation of oxygenated and unsaturated VOCs. In particular, it was shown that unimolecular dissociation is the main atmospheric fate of most β-hydroxyalkoxy species (24, 25) and that alkoxy radicals of the type RC(O)OCH(O•)R can undergo an α-ester rearrangement (19−22). This work provides the first mechanism for OH-induced oxidation of vinyl acetate.

3.2. NO₃-Initiated Oxidation. *3.2.1. Kinetic Study.* Both absolute and relative rate determinations were performed for NO₃ oxidation of vinyl acetate during the same experiments. Plots of relative and absolute rate measurements are given in Figures S2 and S3, respectively, of the Supporting Information. For relative rate determination, three experiments that are in very good agreement were performed. For absolute determination, only two experiments were used because technical problems occurred during the third experiment, affecting the detection of NO₃. As previously

reaction	product	yield (%)	ref
VA + OH	formic acetic anhydride	75 ± 7	this work
	formaldehyde	96 ± 12	this work
	acetic acid	20 ± 3	this work
	formic acid	secondary	this work
	carbon budget	**90 ± 18**	**this work**
VA + NO₃[a]	formic acetic anhydride	44 ± 6	this work
	formaldehyde	46 ± 8	this work
	organic nitrates	not quantified	this work
	carbon budget	**44 ± 6**	**this work**
VA + O₃	formic acetic anhydride	97 ± 8	this work
		not measured	7
	formaldehyde	20 ± 6	this work
		44.8 ± 0.5	7
	formic acid	12	7
	carbon budget	**78 ± 7**	**this work**
		14.2 ± 0.1	**7**

[a] Yields for the VA + NO₃ reaction are final yields, i.e., yields obtained once peroxynitrates have decomposed.

SCHEME 1. Oxidation of Vinyl Acetate by OH Radicals
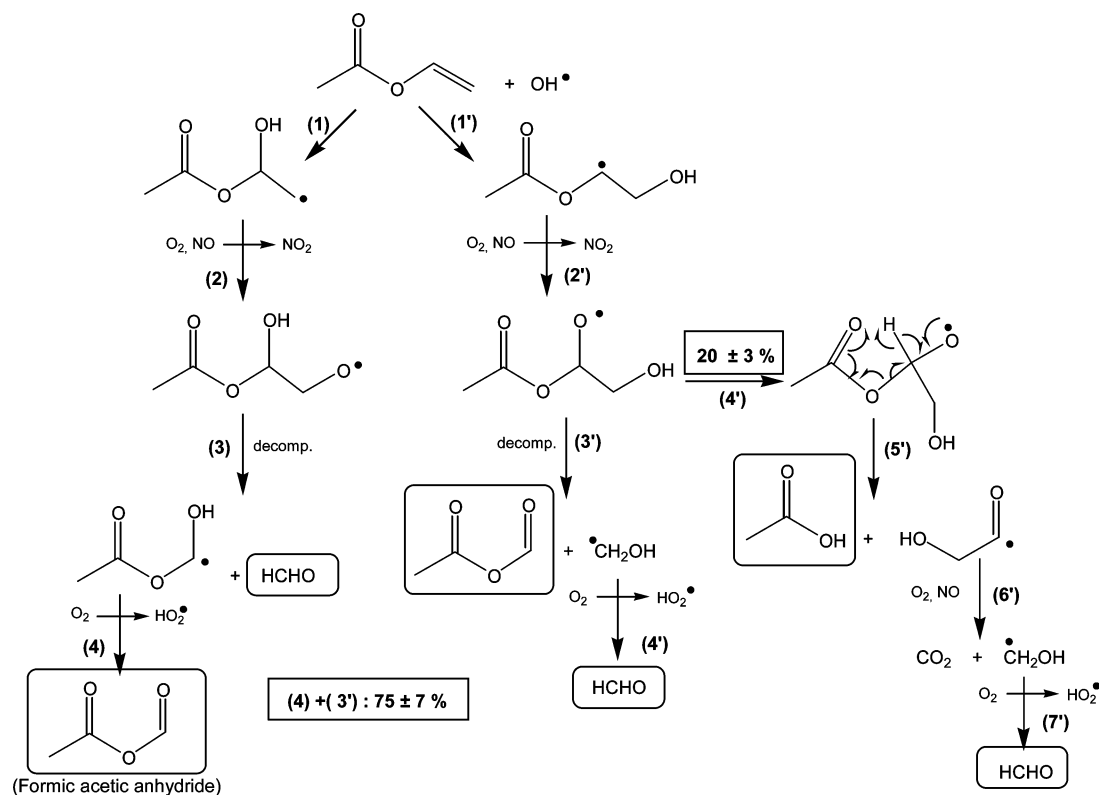
described, the uncertainty in the relative rate constant was calculated via addition of the relative uncertainties corresponding to the statistical error and to the error in the reference rate constant (here 17%). The uncertainty in the absolute rate constant was calculated as 2σ on the linear regression using the method developed by Brauers and Finlayson-Pitts (15).

Rate constants obtained by both techniques are compared to the only value previously published in Table 1. Grosjean (16) used an estimation based on a SAR which correlates rate constants and ionization potentials of molecules. First, it can be observed that there is good agreement between the values obtained by our two techniques. Then, from our experimental data, one can conclude that the SAR proposed by Grosjean (16) strongly overestimates (by a factor of 20) the rate constant for the reaction of NO₃ with vinyl acetate.

3.2.2. Mechanistic Study. NO₃ oxidation products of vinyl acetate have been identified and quantified from the residual IR spectra obtained after subtraction of the absorption bands of the remaining reactants (vinyl acetate and N₂O₅) and products arising from N₂O₅ decomposition and hydrolysis (NO₂ and HNO₃). The main oxidation products are formaldehyde and formic acetic anhydride. Residual bands at 815−865 and 775−810 cm⁻¹ were attributed to a mixture of organic nitrates and peroxynitrates (26). As no standard spectra of nitrates and peroxynitrates are available, it was not possible to identify them individually. It has been observed that formation yields of formaldehyde and formic acetic anhydride increase over the course of the reaction. This is explained by the fact that peroxy radicals produced by NO₃ oxidation of vinyl acetate can either react with NO₂ to form a thermally unstable peroxynitrate in equilibrium

SCHEME 2. Oxidation of Vinyl Acetate by NO₃ Radicals
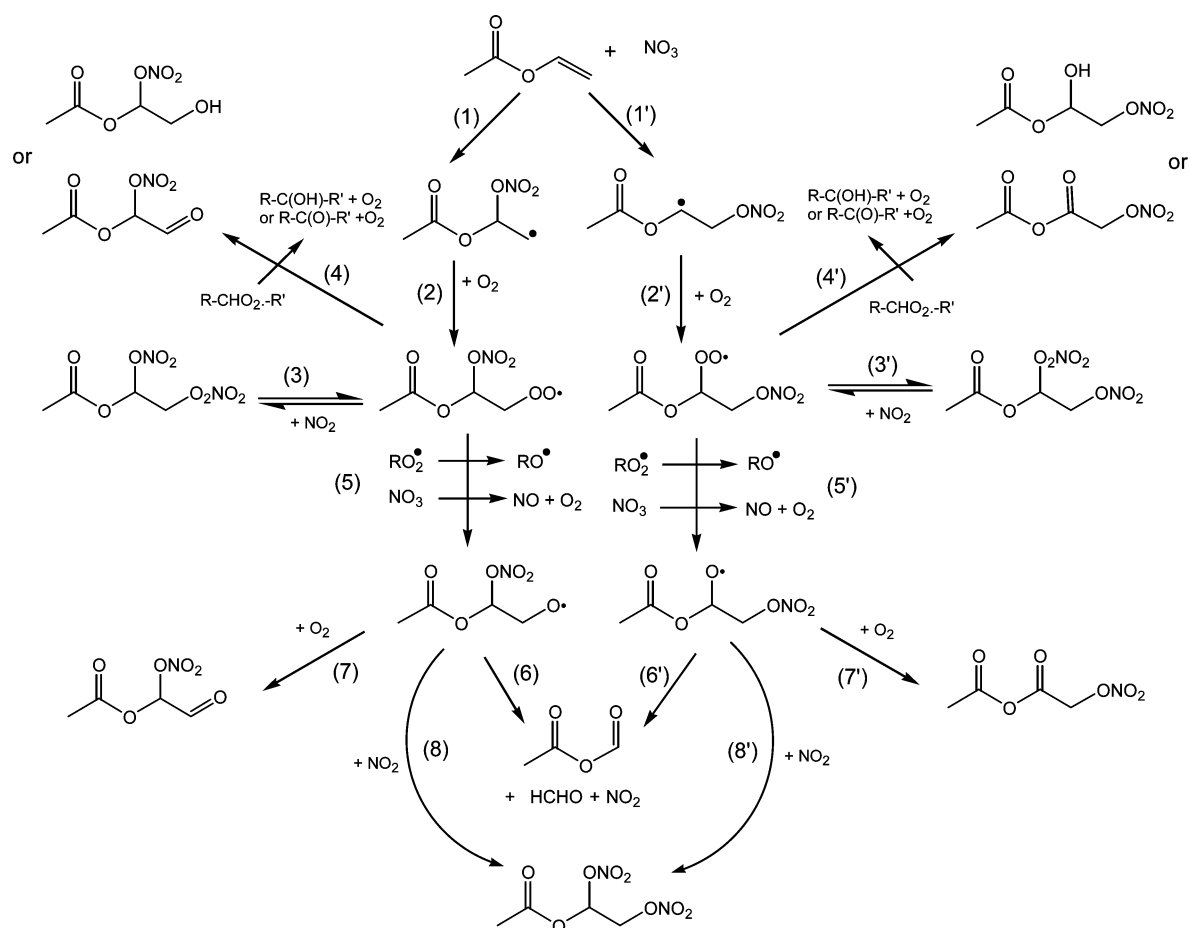
with the peroxy radical or give an alkoxy radical (by self-reaction or by reaction with NO_3) or even give an alcohol and a carbonyl compound (see Scheme 2).

In other words, peroxynitrates are involved in equilibria that affect their lifetimes and may delay the formation of the various products. Hence, they play the role of a reservoir of peroxy radicals. In our experiments, NO_2 concentrations are close to several parts per million, while they do not exceed a few tens of parts per billion in the troposphere. As a consequence, the yields of peroxynitrates measured in these experiments might be higher than what would be obtained under real tropospheric conditions, and obtained yields of formaldehyde and formic acetic anhydride may be smaller. Therefore, to obtain representative yields, we added a few parts per million of NO at the end of the experiment to decompose peroxynitrates, and "final yields" were calculated from the [product]/($-\Delta$[vinyl acetate]) ratios obtained once all peroxynitrates had decomposed (see Table 2).

Both formaldehyde and formic acetic anhydride have yields close to 0.45, suggesting that they are coproducts. As no other absorption bands except those of organic nitrates have been observed in the residual spectra, we can assume that the missing carbon is organic nitrates.

From these data, a mechanism based on an assumed NO_3 oxidation scheme has been proposed (see Scheme 2). The NO_3 electrophilic addition on one of the two double-bonded carbons was considered to be more favorable than an H-abstraction which was neglected (27, 28). This is followed by an addition of O_2 that produces an alkylperoxy radical. This peroxy radical can lead to either a peroxynitrate by reaction with NO_2 (channels 3 and 3′), a carbonyl and an alcohol (channels 4 and 4′), or an alkoxy radical (channels

5 and 5′). This alkoxy radical can then either undergo an H-abstraction by O_2 at the α-position (channels 7 and 7′), a decomposition leading to formaldehyde and formic acetic anhydride (channels 6 and 6′), or a reaction with NO_2 leading to the formation of a dinitrate (channels 8 and 8′). From obtained formation yields of formaldehyde and formic acetic anhydride, we can deduce that the sum of the branching ratio of channels 6 and 6′ is 0.45. However, NO_3 electrophilic addition at either position in the C=C bond cannot be distinguished since each organic nitrate was not identified or quantified individually. For the same reason, it was not possible to determine branching ratios of any other channels.

3.3. O₃-Initiated Oxidation. *3.3.1. Kinetic Study.* The absolute kinetic plot for the ozonolysis of vinyl acetate is given in Figure S4 of the Supporting Information, with data corresponding to the sum of two experiments. The obtained rate constant and its corresponding uncertainty are given in Table 1. Uncertainties were calculated using the method developed by Brauers and Finlayson-Pitts (15). The obtained rate constant is compared to the only value published so far (5) in Table 1. One can observe that both determinations are in good agreement within the uncertainties.

3.3.2. Mechanistic Study. The ozonolysis of vinyl acetate was investigated under dry conditions and using CO as an OH scavenger. From infrared spectra, two primary products have been identified: formic acetic anhydride and formaldehyde. Formation yields of these two primary products were determined from the initial slope of the plots of [product] versus $-\Delta$[vinyl acetate] (see Figure S5 of the Supporting Information) and compared to those obtained by the only study published in the literature (7) in Table 2. Indicated errors of yields take into account the estimated uncertainties

SCHEME 3. Ozonolysis of Vinyl Acetate
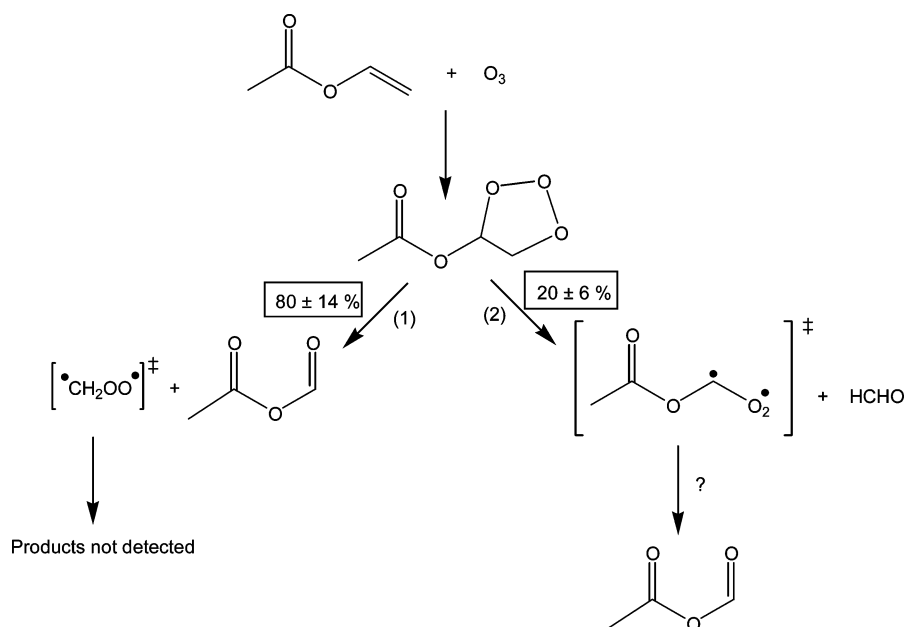
in reactant and product IR absorption band calibrations and the uncertainty in the calculation of yields.

In this study, formic acetic anhydride was detected with a yield close to unity whereas the yield of formaldehyde was found to be 0.20 ± 0.06. As a consequence, the carbon balance is incomplete, and some organic matter remains unidentified. Previous studies on the ozonolysis of VOCs of the type R-CH=CH$_2$ have shown that the Criegee radical, [$^\bullet$CH$_2$OO$^\bullet$]*, that can stabilize and decompose to form CO and CO$_2$ is formed. Under dry conditions, stabilized Criegee is believed to undergo a variety of reactions which can lead to the formation of formic acid, formic acid anhydride [HC(O)-O-C(O)H], and hydroperoxymethyl formate (HOO-CH$_2$-O-CHO) (6, 29−31). However, no formic acid or formic acid anhydride was detected in infrared spectra. Moreover, formation of carbon monoxide cannot be detected in our experiments as it was introduced at the beginning of the experiment at a very high concentration to scavenge the OH radicals. We therefore suspect that this missing carbon can be CO, CO$_2$, or hydroperoxymethyl formate (for which the infrared spectrum was not available in our laboratory).

In the study on the ozonolysis of vinyl acetate published by Grosjean (7), experiments were conducted under humid conditions (HR = $55 \pm 10\%$). Formaldehyde and formic acid were detected as oxidation products. Formic acetic anhydride was not observed, but this compound may rapidly undergo hydrolysis under humid conditions. These differences in the experimental conditions of both studies limit strongly the relevance of any comparison of product yields.

From these data, a mechanism based on the assumed ozonolysis scheme has been proposed (see Scheme 3). The reaction of vinyl acetate with O$_3$ produces an ozonide that decomposes to form a carbonyl compound and a Criegee biradical via channels 1 and 2: channel 1 yields the formation of formic acetic anhydride and the biradical [$^\bullet$CH$_2$OO$^\bullet$]*, whereas channel 2 yields the formation of a "large" Criegee intermediate and formaldehyde. If we assume that formaldehyde is not formed by reactions involving the [$^\bullet$CH$_2$OO$^\bullet$]* radical, the branching ratio of channel 2 can be estimated from the yield of formaldehyde to be 0.20 ± 0.06. The yield of formic acetic anhydride which is close to unity reveals that this product is formed by both channels 1 and 2. However, no mechanism can be proposed to explain the

formation of this compound from the biradical CH$_3$C(O)OC$^\bullet$HOO$^\bullet$ under dry conditions.

4. Atmospheric Implications

Tropospheric lifetimes of vinyl acetate toward OH and NO$_3$ radicals and ozone are estimated assuming typical tropospheric concentrations of the three oxidants [[OH] = 2×10^6 molecules/cm^3; [NO$_3$] = 2.5×10^8 molecules/cm^3 (10 ppt); [O$_3$] = 7.4×10^{11} molecules/cm^3 (30 ppb)] (32). They are as follows: τ_{OH} = 6 h, τ_{NO_3} = 6 days, and τ_{O_3} = 5 days. Thus, it appears that the reaction with OH radicals is the main tropospheric loss process of vinyl acetate and that the chemistry induced by NO$_3$ and O$_3$ does not really affect the fate of this compound. When it reacts with OH radicals, it may contribute to the formation of photooxidants close to the emission sources.

From the mechanistic study, the main products of OH, NO$_3$, and O$_3$ oxidation of vinyl acetate were detected. However since OH oxidation is the main tropospheric fate of vinyl acetate, we can consider that NO$_3$ and O$_3$ oxidation products have a small probability to be formed in the atmosphere. Therefore, only OH oxidation products are considered for the atmospheric implications which are formic acetic anhydride, acetic acid, and formaldehyde. Acids and anhydrides are not very reactive toward OH and other atmospheric oxidants but are highly soluble in water. Hence, they may be incorporated in rain droplets before reacting in the gas phase and can therefore have a significant impact in the aqueous phase, in particular on the acidity of rains. In addition, these acids can impact the chemical composition of organic aerosols. Formaldehyde is reactive in the gas phase since it can photolyze and react with OH radicals to produce HOx radicals. Hence, it plays a key role in the tropospheric OH budget.

free access to DOASIS software and Dr. T. Brauers and Pr. B. J. Finlayson-Pitts for free access to the routine developed for linear regression analysis.

Supporting Information Available

Initial conditions of the experiments (Table S1), integrated band intensities of the main absorption band of reactants and oxidation products (in base e) (Table S2), concentration−time profiles of reactants and products corresponding to the photolysis of a vinyl acetate/isopropyl nitrite/NO mixture (experiment 4) (Figure S1), relative kinetic plot for NO_3 oxidation of vinyl acetate with propene as a reference compound (Figure S2), absolute kinetic plot for NO_3 oxidation of vinyl acetate (Figure S3), absolute kinetic plot for O_3 oxidation of vinyl acetate (Figure S4), and formation yields of products by ozonolysis of vinyl acetate for experiment 6 (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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