

# Atmospheric Oxidation of Vinyl and Allyl Acetate: Product Distribution and Mechanisms of the OH-Initiated Degradation in the Presence and Absence of NO<sub>x</sub>

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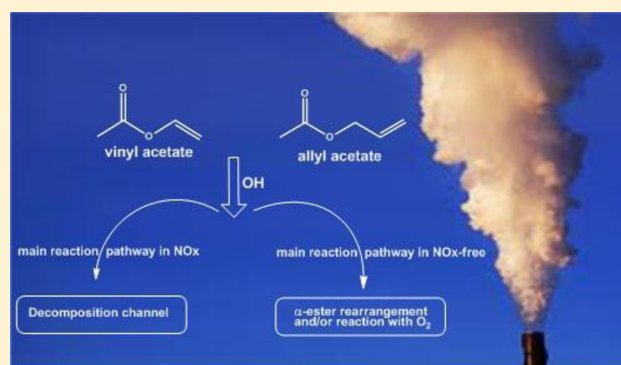
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## Supporting Information

**ABSTRACT:** The products formed from the reactions of OH radicals with vinyl acetate and allyl acetate have been studied in a 1080 L quartz-glass chamber in the presence and absence of NO<sub>x</sub> using in situ FTIR spectroscopy to monitor the reactant decay and product formation. The yields of the primary products formed in the reaction of OH with vinyl acetate were: formic acetic anhydride (84 ± 11)%; acetic acid (18 ± 3)% and formaldehyde (99 ± 15)% in the presence of NO<sub>x</sub> and formic acetic anhydride (28 ± 5)%; acetic acid (87 ± 12)% and formaldehyde (52 ± 8)% in the absence of NO<sub>x</sub>. For the reaction of OH with allyl acetate the yields of the identified products were: acetoxyacetaldehyde (96 ± 15)% and formaldehyde (90 ± 12)% in the presence of NO<sub>x</sub> and acetoxyacetaldehyde (26 ± 4)% and formaldehyde (12 ± 3)% in the absence of NO<sub>x</sub>. The present results indicate that in the absence of NO<sub>x</sub> the main fate of the 1,2-hydroxyalkoxy radicals formed after addition of OH to the double bond in the compounds is, in the case of vinyl acetate, an α-ester rearrangement to produce acetic acid and CH<sub>2</sub>(OH)CO• radicals and in the case of allyl acetate reaction of the radical with O<sub>2</sub> to form acetic acid 3-hydroxy-2-oxo-propyl ester (CH<sub>3</sub>C(O)OCH<sub>2</sub>C(O)-CH<sub>2</sub>OH). In contrast, in the presence of NO<sub>x</sub> the main reaction pathway for the 1,2-hydroxyalkoxy radicals is decomposition. The results are compared with the available literature data and implications for the atmospheric chemistry of vinyl and allyl acetate are assessed.



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## INTRODUCTION

Volatile organic compounds (VOCs) are removed in the troposphere either by physical processes (wet and dry deposition), and/or are transformed by chemical processes such as photolysis, reaction with hydroxyl (OH) radicals, reaction with nitrate (NO<sub>3</sub>) radicals and reaction with O<sub>3</sub>.<sup>1–3</sup>

The photochemical interactions of VOCs with nitrogen oxides (NO<sub>x</sub>) in the troposphere lead to the formation of secondary pollutants such as ozone, which is a serious problem in many urban areas.

The atmospheric chemistry of various classes of VOCs has been extensively discussed<sup>3</sup> and reviews and evaluations of various kinetic and mechanistic aspects of VOC tropospheric chemistry have been published intermittently over the last 15 years.<sup>4–12</sup>

Acetate esters are used on a large scale in industry and many are classified as high-production volume (HPV) chemicals. The widespread use of acetates in industrial activities inevitably results in emissions of these compounds into the atmosphere. Unsaturated acetates, in particular, have many industrial

applications. Vinyl acetate (CH<sub>3</sub>C(O)OCH=CH<sub>2</sub>) is used primarily to produce polymers like polyvinyl acetate, polyvinyl alcohol (via trans-esterification of polyvinyl acetate), and a variety of copolymers.<sup>13</sup> The main uses of polyvinyl acetate and vinyl acetate copolymers are applications in polymer dispersions. Homopolymer and copolymer dispersions are important binders for indoor and outdoor paints, special coatings, and textile finishing agents. Vinyl acetate monomer polymers are cost-effective raw materials used in the manufacture of a wide range of adhesive products.<sup>13</sup>

Allyl acetate (CH<sub>3</sub>C(O)OCH<sub>2</sub>CH=CH<sub>2</sub>) is used in many industries and is an important synthetic flavouring agent in foods and beverages.<sup>14</sup> It is used in the synthesis of several chemicals, for example, in the preparation of copolymers with maleic anhydride, acrylonitrile, vinyl chloride-vinyl laurate,

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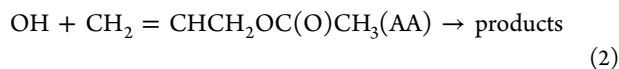
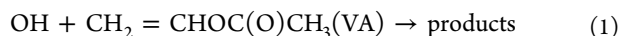
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vinylidene chloride, ethylene, methyl cyanoacrylate, and other monomers and in the production of fire resistant rigid polyurethane foams.<sup>15</sup> It is an important intermediate in the synthesis of 1,4-butanediol, which in turn is used principally in the synthesis of linear polyester resins.<sup>16</sup> Other applications of allyl acetate include use as a building block for detergent compositions (replacing sodium tripolyphosphate), in hair conditioning formulations, and in the manufacture of ester-containing siloxanes for brake fluids.<sup>15</sup>

The OH radical is the principal atmospheric oxidant, reacting with almost all organic compounds, and plays a pivotal role in the day-time degradation of these compounds in the troposphere.<sup>1</sup> Rate coefficients have been measured at 298 K and atmospheric pressure for the reactions of OH radicals with a number of saturated and unsaturated esters.<sup>17–23</sup> This kinetic information, when taken in conjunction with typical tropospheric OH radical levels, shows that for unsaturated esters, such as vinyl acetate and allyl acetate, reaction with OH radicals constitutes the main atmospheric sink for these compounds and results in lifetimes of only a few hours. Although it has been established that reaction with OH radicals is the main tropospheric sink for the unsaturated esters the mechanisms and products of their OH-radical initiated photooxidation have not been studied extensively. In order to assess the impact of these species on air quality through, for example, photooxidant and SOA formation, apart from kinetic data, mechanistic and product information on their tropospheric degradation is required. To this end, room temperature product investigations on the gas-phase reactions of OH radicals with vinyl acetate (VA) and allyl acetate (AA) in the presence and absence of NO<sub>x</sub> have been performed.



The reactions of the OH radical with VA and AA proceed almost entirely by addition of the OH radical to the double bond in the compounds. There has only been one previous product study for both the reaction of OH with vinyl acetate<sup>24</sup> and allyl acetate<sup>25</sup> and both studies were performed at atmospheric pressure and room temperature in the presence of NO<sub>x</sub> using FTIR for the product analysis. Picquet-Varrault et al.<sup>24</sup> reported formaldehyde (HCHO), formic acetic anhydride (CH<sub>3</sub>C(O)OC(O)H) and acetic acid (CH<sub>3</sub>C(O)OH) as the main products in the reaction of OH with vinyl acetate and Picquet-Varrault et al.<sup>25</sup> reported acetoxyacetaldehyde (CH<sub>3</sub>C(O)OCH<sub>2</sub>CHO) and formaldehyde as the main products from the reaction of OH with allyl acetate.

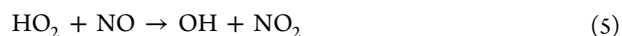
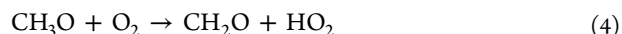
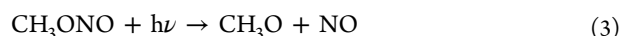
To our knowledge this work is the first product investigation of the OH-radical initiated photooxidation of vinyl acetate and allyl acetate performed in the absence of NO<sub>x</sub>. The studies serve to validate the previous product studies of Picquet-Varrault et al.<sup>24,25</sup> performed in the presence of NO<sub>x</sub> and also provide valuable information on product and mechanistic changes that may occur when the photooxidation of the compounds takes place in NO<sub>x</sub>-poor environments.

Based on the product studies chemical mechanisms for the gas-phase atmospheric reactions of VA and AA with OH radicals have been elucidated which can be used in the various types of models that are employed to determinate the impacts of VOCs on the environment.

## EXPERIMENTAL SECTION

All the experiments were performed in a 1080 L quartz-glass reaction chamber at (298 ± 2) K and a total pressure of (760 ± 10) Torr of synthetic air (760 Torr = 101.325 kPa). A detailed description of the reactor can be found elsewhere<sup>26</sup> and only a brief description is given here. A pumping system consisting of a turbo-molecular pump backed by a double stage rotary fore pump was used to evacuate the reactor to 10<sup>-3</sup> Torr. Three magnetically coupled Teflon mixing fans are mounted inside the chamber to ensure homogeneous mixing of the reactants. The photolysis system consists of 32 superactinic fluorescent lamps (Philips TL05 40W: 320 – 480 nm, λ<sub>max</sub> = 360 nm) and 32 low-pressure mercury vapor lamps (Philips TUV 40W; λ<sub>max</sub> = 254 nm), which are spaced evenly around the reaction vessel. The lamps are wired in parallel and can be switched individually, which allows variation of the light intensity, and thus also the photolysis frequency/radical production rate, within the chamber. The chamber is equipped with a White type multiple-reflection mirror system with a base length of (5.91 ± 0.01) m for sensitive in situ long path infrared absorption monitoring of reactants and products in the spectral range 4000–700 cm<sup>-1</sup>. The White system was operated at 82 traverses, giving a total optical path length of (484.7 ± 0.8) m. Infrared spectra were recorded with a spectral resolution of 1 cm<sup>-1</sup> using a Nicolet Nexus FT-IR spectrometer equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector.

Hydroxyl radicals were generated by the photolysis of CH<sub>3</sub>ONO/NO/air mixtures using the fluorescent lamps:



The photolysis of CH<sub>3</sub>ONO apart from producing OH radicals also forms HCHO, therefore, in order to quantify the formation yield of formaldehyde, that is a product in both of the reactions studied, the photolysis of H<sub>2</sub>O<sub>2</sub> with the mercury lamps was also used as source of OH radicals:

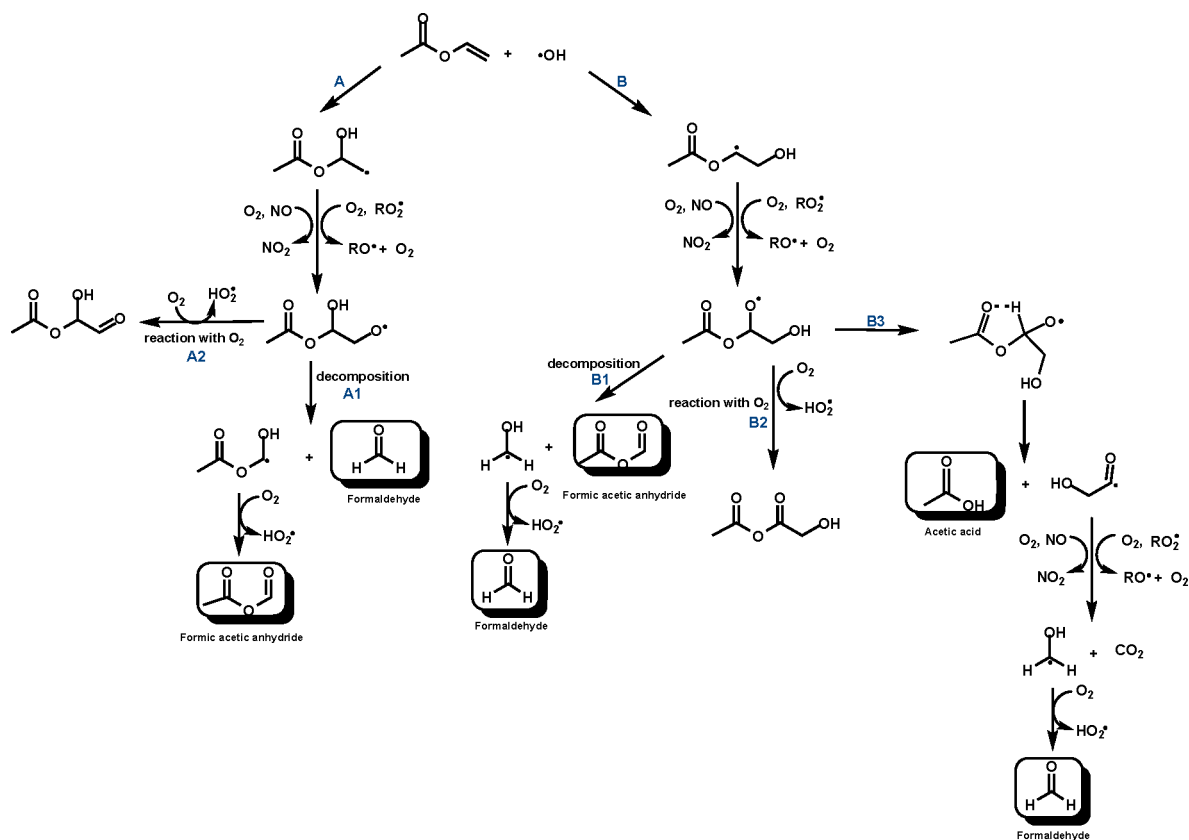


The quantification of reactants and products was performed by comparison with calibrated reference spectra contained in the IR spectral databases of the laboratories in Wuppertal and Laboratoire Interuniversitaire des Systemes Atmosphériques (LISA), Paris, France.<sup>27</sup>

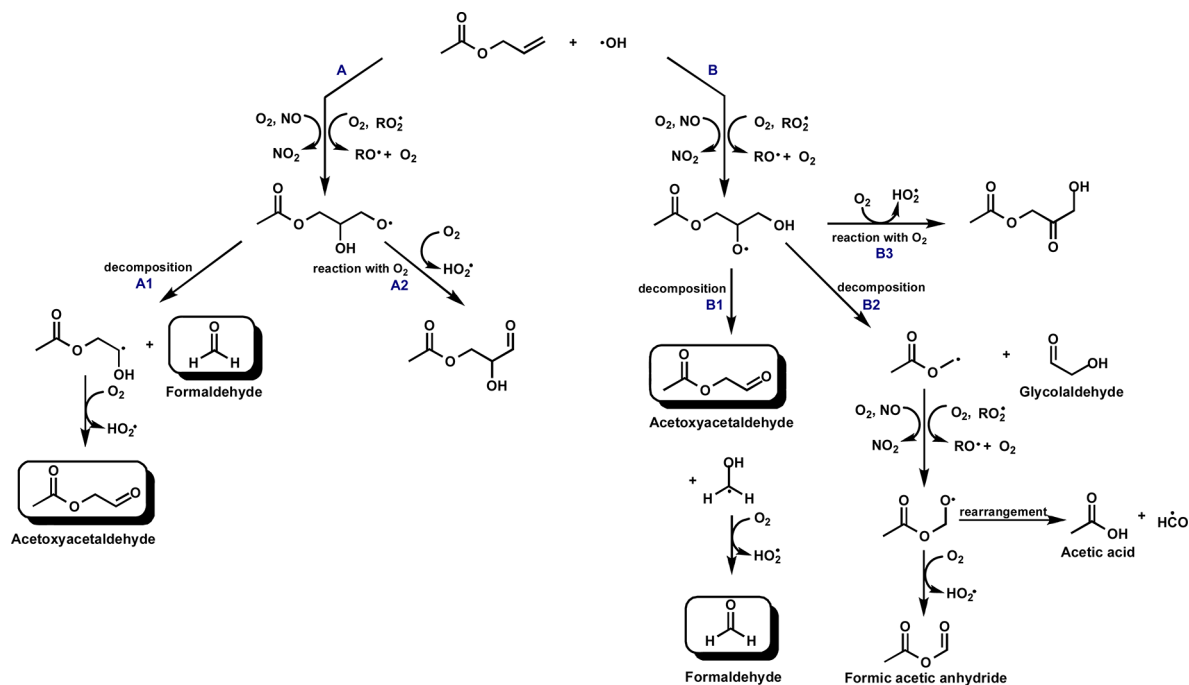
The initial concentrations used in the experiments in ppmV (1 ppmV = 2.46 × 10<sup>13</sup> molecules cm<sup>-3</sup> at 298 K and 760 Torr of total pressure) were 0.49–0.74 for VA and 0.42 – 0.63 for AA. The concentrations of CH<sub>3</sub>ONO and H<sub>2</sub>O<sub>2</sub> were typically around 6 and 14 ppm, respectively. The concentration of NO was typically around 4 ppm.

The following infrared absorption frequencies (in cm<sup>-1</sup>) were used to monitor the reactants: vinyl acetate at 1148.6 and allyl acetate at 3098.4. Products were monitored at the following absorption frequencies (in cm<sup>-1</sup>): formaldehyde at 2766; formic acetic anhydride at 1041.4; acetic acid at 1184 and acetoxyacetaldehyde at 2707.

The chemicals used in the experiments had the following purities as given by the manufacturer and were used as supplied: synthetic air (Air Liquide, 99.999%), vinyl acetate (Aldrich, 99%), allyl acetate (Aldrich, 99%), H<sub>2</sub>O<sub>2</sub> (Interox,



**Figure 1.** Simplified mechanism for the OH-radical initiated oxidation of vinyl acetate ( $\text{CH}_2=\text{CHOC}(\text{O})\text{CH}_3$ ) via addition of OH to the terminal carbon of the double bond.



**Figure 2.** Simplified mechanism for the OH-atom initiated oxidation of allyl acetate ( $\text{CH}_2=\text{CHCH}_2\text{OC}(\text{O})\text{CH}_3$ ) via addition of OH to the terminal carbon of the double bond.

85%) and nitrogen monoxide (Messer Griesheim, 99%). Methyl nitrite was synthesized by the dropwise addition of 50%  $\text{H}_2\text{SO}_4$  to a saturated solution of sodium nitrite in methanol.

## RESULTS AND DISCUSSION

To investigate the mechanisms of the OH-radical initiated oxidation of vinyl acetate and allyl acetate, mixtures of  $\text{CH}_3\text{ONO}/\text{NO}/\text{acetate}/\text{air}$  or  $\text{H}_2\text{O}_2/\text{acetate}/\text{air}$  were irradiated

for periods of 15–20 min during the course of which infrared spectra were recorded with the FTIR spectrometer.

Product quantification for reactions 1 and 2 was obtained using  $\text{CH}_3\text{ONO}/\text{NO}/\text{acetate}/\text{air}$  mixtures except for  $\text{HCOH}$  where  $\text{H}_2\text{O}_2/\text{acetate}/\text{air}$  mixtures were used to avoid interference from  $\text{HCOH}$  formation that occurs when using  $\text{CH}_3\text{ONO}$  as the OH radical source. Typically 64 interferograms were coadded per spectrum over a period of approximately 1 min and 15–20 such spectra were collected.

In order to have a basis for the discussion of the experimental results the possible reaction pathways that can occur in the reactions of OH radicals with the unsaturated acetates will first be outlined.

Reactions of OH radicals with vinyl and allyl acetate proceed mainly by initial addition of OH to the  $>\text{C}=\text{C}<$  bonds in the molecules forming  $\beta$ -hydroxyalkyl radicals, which in turn rapidly react with oxygen forming  $\beta$ -hydroxyalkyl peroxy radicals. Addition of OH is mainly to the terminal C atom in the double bond, that is, to the least substituted carbon.

In the presence of  $\text{NO}_x$  the peroxy radicals react with NO to give mainly 1,2-hydroxyalkoxy radicals.<sup>24,25</sup> In the absence of  $\text{NO}_x$  the peroxy radicals will undergo self- and cross-peroxy reactions which will also result, to a large extent, in the formation of 1,2-hydroxyalkoxy radicals, however, molecular channels are also possible which will result in the formation of multifunctional products containing hydroxy, carbonyl and ester functionalities.<sup>28</sup>

For the VA + OH reaction the possible hydroxyalkoxy radicals are  $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{OH})\text{CH}_2\text{O}^\bullet$  and  $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{O}^\bullet)\text{CH}_2\text{OH}$ , whereby the latter is expected to dominate, and for the AA + OH reaction they are  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}^\bullet$  and  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{O}^\bullet)\text{CH}_2\text{OH}$  and again the latter is expected to dominate. In the case of the OH + allyl acetate reaction, H-atom abstraction from the  $-\text{CH}_2-$  group can occur, but based on structure reactivity relationships (SAR), this is expected to contribute no more than 6% to the overall reaction.<sup>29</sup>

Under atmospheric conditions, these hydroxyalkoxy radicals can (a) react with  $\text{O}_2$  forming  $\text{HO}_2$  and the corresponding carbonyl compound; (b) undergo  $\beta$ -scission forming a carbonyl compound and another radical; and (c) undergo a hydrogen shift isomerization forming dihydroxy substituted radicals.<sup>4,3,30</sup> Additionally, Tuazon et al.<sup>31</sup> have shown that alkoxy radicals with the structure  $\text{RC}(\text{O})\text{OCH}(\text{O}^\bullet)\text{R}'$  can undergo a fast rearrangement involving hydrogen transfer to the carbonyl group and further decomposition to produce the corresponding carboxylic acid  $\text{RC}(\text{O})\text{OH}$  and a  $\text{R}'\text{C}(\text{O}^\bullet)=\text{O}$  radical, that is, an  $\alpha$ -ester rearrangement reaction.

Simplified exemplary reaction mechanisms for the addition reactions of OH radicals with vinyl acetate and allyl acetate in the presence and in the absence of  $\text{NO}_x$  are shown in Figures 1 and 2, respectively.

For the VA + OH reaction, the hydroxyalkoxy radicals formed in the OH radical addition step can

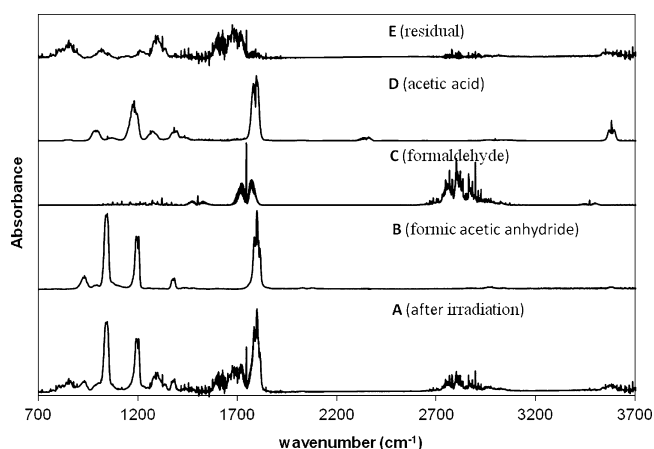
- decompose to give formic acetic anhydride ( $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H}$ ) with formaldehyde as a coproduct (Figure 1, routes A1 and B1),
- react with  $\text{O}_2$  to form hydroxycarbonyl ester compounds, that is, acetic acid 1-hydroxy-2-oxoethyl acetate ( $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{OH})\text{C}(\text{O})\text{H}$ ) and acetic 2-hydroxyacetic anhydride ( $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{CH}_2\text{OH}$ ) (Figure 1, routes A2 and B2, respectively), and

- for the hydroxyalkoxy radical adjacent to the ester entity, isomerize through an  $\alpha$ -ester rearrangement followed by decomposition to give acetic acid and the  $\bullet\text{C}(\text{O})\text{CH}_2\text{OH}$  radical (Figure 1, route B3) which will react with  $\text{O}_2$  to form  $\text{CO}_2$  and the  $\bullet\text{CH}_2\text{OH}$  radical. Further reaction of the  $\bullet\text{CH}_2\text{OH}$  radical with  $\text{O}_2$  will form formaldehyde.

For the AA + OH reaction, the hydroxyalkoxy radicals formed in the OH radical addition can

- decompose to give the corresponding acetoxyacetaldehyde ( $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{H}$ ) and formaldehyde (Figure 2, routes A1 and B1),
- react with  $\text{O}_2$  to form hydroxycarbonyl ester compounds, that is,  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{OH})\text{C}(\text{O})\text{H}$  and  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$  (Figure 2, routes A2 and B3, respectively) and
- for the hydroxyalkoxy radical adjacent to the ester entity, decompose to give glycolaldehyde ( $\text{HC}(\text{O})\text{CH}_2\text{OH}$ ) and  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2^\bullet$  radicals which will react further to form formic acetic anhydride, acetic acid and CO (Figure 2, route B2).

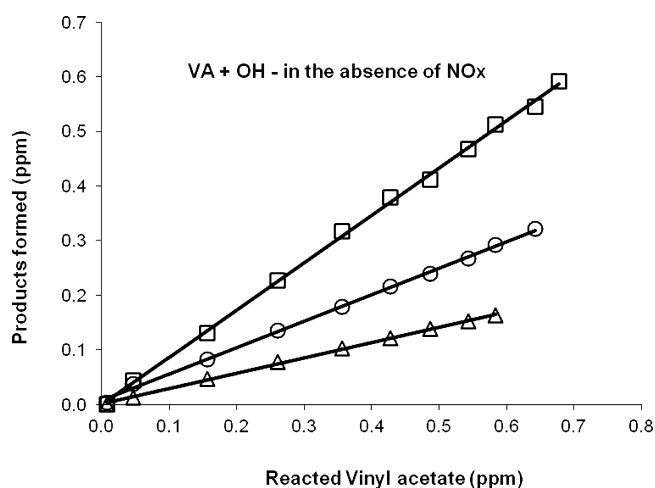
**Vinyl Acetate with OH.** Figure 3, panel A, shows an IR spectrum acquired after UV irradiation of a vinyl acetate/



**Figure 3.** Infrared spectral data: panel A shows the infrared spectrum of a  $\text{CH}_2=\text{CHOC}(\text{O})\text{CH}_3/\text{H}_2\text{O}_2/\text{NO}/\text{air}$  reaction mixture after irradiation and residual vinyl acetate. Panel B shows a reference spectrum of formic acetic anhydride ( $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H}$ ), panel C a reference spectrum of formaldehyde and panel D a reference spectrum of acetic acid. Panel E shows the residual product spectrum obtained after subtraction of features due to  $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H}$ ,  $\text{HC}(\text{O})\text{H}$  and  $\text{CH}_3\text{C}(\text{O})\text{OH}$  from the spectrum in panel A.

$\text{H}_2\text{O}_2/\text{NO}/\text{air}$  mixture where residual absorptions due to VA have been subtracted. Figure 3, panels B, C, and D, show reference spectra of formic acetic anhydride ( $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H}$ ), formaldehyde, and acetic acid, respectively, and panel E shows the residual spectrum that is obtained after subtraction of known products from the spectrum in panel A. Formation of formaldehyde, acetic acid and formic acetic anhydride was observed in experiments performed in both the presence and absence of  $\text{NO}_x$ . No evidence could be found in the IR product spectra for the formation of hydroxycarbonyl ester compounds such as  $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{OH})\text{C}(\text{O})\text{H}$  supporting that the channel involving reaction of the hydroxyalkoxy radicals with  $\text{O}_2$  is negligible (Figure 1, channels B2 and A2, respectively).

Concentration–time profiles of VA and the identified products, formaldehyde, acetic acid and formic acetic anhydride in the presence and absence of  $\text{NO}_x$  are shown in Supporting Information (SI) Figures S1 and S2, respectively. The concentration–time contours support that formic acetic anhydride, formaldehyde and acetic acid are all primary products in both the presence and absence of  $\text{NO}_x$ . The reaction of OH with formaldehyde has a recommended rate coefficient of  $8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K,<sup>32</sup> which is only a factor of 3 slower than that for OH with vinyl acetate of  $2.48 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>18</sup> Formaldehyde will, therefore, be subject to considerable secondary consumption in the reaction system. The yield for  $\text{HC(O)H}$  has, therefore, been corrected for secondary consumption by OH using the method outlined in Tuazon et al.<sup>33</sup> Plots of the concentrations of formaldehyde, acetic acid and formic acetic anhydride, as a function of consumed vinyl acetate show reasonable linearity under all experimental conditions. Such plots are shown in Figure 4 for the products formed in the VA



**Figure 4.** Plots of the concentrations of the reaction products formic acetic anhydride ( $\Delta$ ), formaldehyde ( $\circ$ ), and acetic acid ( $\square$ ) as a function of reacted vinyl acetate (VA) obtained from experiments performed on the OH + VA reaction in the absence of  $\text{NO}_x$ . The formaldehyde concentrations have been corrected for secondary consumption by reactions with OH radicals.

+ OH reaction in the absence of  $\text{NO}_x$ . A corresponding yield plot for experiments performed in the presence of  $\text{NO}_x$  is shown in Figure S3 in the SI.

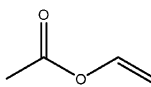
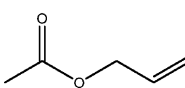
*In the Presence of  $\text{NO}_x$ .* Assuming that wall loss of formic acetic anhydride in the reactor is negligible, analysis of the slope in SI Figure S3 gives a product yield of  $(84 \pm 11) \%$  for the formation of formic acetic anhydride from the reaction of OH with vinyl acetate (See Table 1). Using the correction procedure gives a yield of  $(99 \pm 15) \%$  for formaldehyde formation. Analysis of the slope in SI Figure S3 gives a product yield of  $(18 \pm 3) \%$  for the formation of acetic acid from the reaction of OH with vinyl acetate. Since the reaction of acetic acid with OH is very slow<sup>32</sup> no correction has been applied for secondary consumption by OH.

The yields obtained in this work for formic acetic anhydride ( $84 \pm 11) \%$ , formaldehyde ( $99 \pm 15) \%$  and acetic acid of  $(18 \pm 3) \%$  are in excellent agreement with the yields of  $(75 \pm 7) \%$ ,  $(96 \pm 12) \%$ , and  $(20 \pm 3) \%$ , respectively, reported by Picquet-Varrault et al.<sup>24</sup> from a study on the reaction of OH radicals with VA performed in the presence of  $\text{NO}_x$  in a 977 L pyrex reactor using the photolysis of either methyl or isopropyl nitrite as source of OH radicals and FTIR for the analysis of reactants and products. The sum of the formic acid anhydride and acetic acid yields is  $102 \pm 12 \%$ , in excellent agreement with the formaldehyde yield of  $99 \pm 15 \%$  and showing that within 10–15% all of the reaction products (or pathways) are accounted for.

The reaction products observed in this work and reported previously by Picquet-Varrault et al.<sup>24</sup> show that in the presence of  $\text{NO}_x$ , formic acetic anhydride and HCHO are the major oxidation products of the OH + VA reaction (Table 1). This supports that the main fate of the intermediate  $\text{CH}_3\text{C(O)-OCH(OH)CH}_2\text{O}^\bullet$  and/or  $\text{CH}_3\text{C(O)OCH(O}^\bullet\text{)CH}_2\text{OH}$  radicals is decomposition, via cleavage of the C–C bond between the alkoxy radical and  $-\text{CH}_x\text{OH}$  entities ( $x = 1$  or 2) to form formic acetic anhydride with HCHO as coproduct (Figure 1, channels A1 and B1). The formation of acetic acid can be explained by an  $\alpha$ -ester rearrangement of  $\text{CH}_3\text{C(O)OCH(O}^\bullet\text{)CH}_2\text{OH}$  radicals (Figure 1, channel B3). The coproduced  $\text{HOCH}_2\text{C(O)}^\bullet$  radicals in this reaction channel are expected to react further to form  $\text{HC(O)H}$ .

No evidence could be found for the formation of hydroxydicarbonyl compounds which could be produced via reaction of the  $\text{CH}_3\text{C(O)OCH(OH)CH}_2\text{O}^\bullet$  and  $\text{CH}_3\text{C(O)-OCH(O}^\bullet\text{)CH}_2\text{OH}$  radicals with  $\text{O}_2$  (Figure 1, channels A2 and

**Table 1.** Formation Yields of the Oxidation Products Identified from the OH Radical Oxidation of Vinyl and Allyl Acetate Studied in the Presence and the Absence of  $\text{NO}_x$ <sup>a</sup>

UNSATURATED ESTER	PRODUCT	YIELD (%) (with $\text{NO}_x$ )	YIELD (%) ( $\text{NO}_x$ -free)
	Formic acetic anhydride	$84 \pm 11$	$28 \pm 5$
	Formaldehyde	$99 \pm 15$	$52 \pm 8$
	Acetic acid	$18 \pm 3$	$87 \pm 12$
	Acetoxyacetaldehyde	$96 \pm 15$	$26 \pm 4$
	Formaldehyde	$90 \pm 12$	$12 \pm 3$

<sup>a</sup>The errors quoted are  $2\sigma$  statistical errors from the linear regression analysis.

B2, respectively). The results obtained in the experiments in the presence of  $\text{NO}_x$  support that decomposition is the main pathway for the 1,2-hydroxyalkoxy radicals formed in the VA + OH reaction.

**In the Absence of  $\text{NO}_x$ .** Analysis of the slopes of the plots of product concentrations against reacted vinyl acetate shown in Figure 4 give a product yield of  $(28 \pm 5) \%$  for the formation of formic acetic anhydride,  $(52 \pm 8) \%$  for formaldehyde and  $(87 \pm 12) \%$  for acetic acid from the reaction of OH with vinyl acetate in the absence of  $\text{NO}_x$  (Table 1). Although a large suite of peroxy–peroxy self- and cross reactions can take place in the reaction system in the absence of  $\text{NO}_x$  the combined measured yields of acetic acid and formic acetic anhydride support that the majority of all the possible  $\beta$ -hydroxyperoxy +  $\text{RO}_2$  reactions occurring in the system must result in the formation of  $\beta$ -hydroxyperoxy radicals irrespective of the nature of the  $\text{RO}_2$  radicals. We are not aware of any  $\text{RO}_2 + \text{RO}_2/\text{HO}_2$  reactions which can lead to formation of acetic acid and formic acetic anhydride, therefore, the results strongly support that in the absence of  $\text{NO}_x$ , formation of acetic acid through an  $\alpha$ -ester rearrangement of the  $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{O}^\bullet)\text{CH}_2\text{OH}$  is by far the dominant reaction channel (Figure 1, channel B3). This is in complete contrast to the case in the presence of  $\text{NO}_x$  where, as discussed above, the channel forming formic acetic anhydride dominates (channels A1 and/or B1 in the Figure 1) but only accounts for around 28% of the reaction in the absence of  $\text{NO}_x$ .

A yield of only  $(52 \pm 8) \%$  has been obtained for HCHO, however, according to the reaction mechanism shown in Figure 1, formaldehyde should be formed with a yield of near 100%, irrespective of whether acetic acid or formic acetic anhydride is the dominant product. Since the formation yield of HCHO has been corrected for secondary reaction with OH radicals this cannot be the reason for the yield shortfall.

High concentrations of  $\text{HO}_2$  radicals and other peroxy radicals will be produced in the reaction system and, apart from reaction with OH radicals, reaction of HCHO with  $\text{HO}_2$  or other peroxy radicals will also contribute to its secondary removal. For example, the reaction of  $\text{HO}_2$  radicals with HCHO at room temperature is known to be fairly fast ( $7.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )<sup>32</sup> and is known to produce the metastable hydroperoxide  $\text{CH}_2(\text{OH})\text{OOH}$  and formic acid.<sup>31,34,35</sup> Secondary formation of formic acid is very prevalent in the  $\text{NO}_x$ -free system supporting that secondary consumption of HCHO by reaction with  $\text{HO}_2$  or other peroxy radicals is mainly responsible for the shortfall in the HCHO yield. The combined concentrations of uncorrected HCHO (0.17 ppm), CO (0.36 ppm), and HCOOH (0.1 ppm) are close (about 94%) to the amount of reacted vinyl acetate reacted (0.67 ppm) which further supports secondary consumption of HCHO by OH and, in particular, peroxy radicals.

This is the first product study of the reaction of VA with OH under  $\text{NO}_x$ -free conditions. As stated above measured product distribution under  $\text{NO}_x$ -free conditions contrasts very starkly with that obtained in the presence of  $\text{NO}_x$  and highlights the need for product studies under a wide range of atmospherically relevant  $\text{NO}_x$  conditions.

**Allyl Acetate with OH.** In the reaction of OH radicals with allyl acetate, acetoxyacetaldehyde and formaldehyde have been identified as products both in the presence and absence of  $\text{NO}_x$ . SI Figure S4, panel A, shows an IR spectra acquired after UV irradiation of a mixture of allyl acetate and  $\text{H}_2\text{O}_2$  in air ( $\text{NO}_x$ -free) where residual absorptions due AA have been subtracted. SI Figure S4, panel B, shows a reference spectra of

acetoxyacetaldehyde ( $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{H}$ ), panel C a reference spectra of formaldehyde and panel D the residual spectrum that is obtained after subtraction of known products from the spectrum in panel A.

Concentration–time profiles of AA and the identified products acetoxyacetaldehyde and formaldehyde in the presence and in the absence of  $\text{NO}_x$  are shown in SI Figures S5 and S6, respectively. The concentration–time contours support that acetoxyacetaldehyde and formaldehyde are primary products. Plots of the concentrations of acetoxyacetaldehyde and formaldehyde as a function of consumed allyl acetate in the presence and absence of  $\text{NO}_x$  are linear and examples are shown in SI Figures S7 and S8 for the  $\text{NO}_x$ -containing and  $\text{NO}_x$ -free conditions, respectively.

**In the Presence of  $\text{NO}_x$ .** Analysis of the slopes of the plots shown in SI Figure S7 give a product yield of  $(96 \pm 15) \%$  for acetoxyacetaldehyde and  $(90 \pm 12) \%$  for formaldehyde in the reaction of OH with allyl acetate in the presence of  $\text{NO}_x$  (see Table 1). The yield of  $(96 \pm 15) \%$  obtained for acetoxyacetaldehyde can be compared to yields of  $(97 \pm 25) \%$ ,  $(100 \pm 25) \%$ , and  $(90 \pm 24) \%$  reported by Picquet-Varrault et al.<sup>25</sup> from a study on the reaction of OH radicals with allyl acetate in the presence of  $\text{NO}_x$  performed in two different environmental chambers (i) an indoor Pyrex photoreactor (LISA, Créteil) of 977 L which contains a multiple reflection optical system interfaced to a FTIR spectrometer (BOMEM DA8-ME) and; (ii) the outdoor half-spherical 200  $\text{m}^3$  Teflon-film bag EUPHORE chamber in Valencia, Spain where an FTIR spectrometer (Nicolet Magna 550) was used for the analysis.

The yield obtained in this study for acetoxyacetaldehyde is in excellent agreement with the values reported by Picquet-Varrault et al.<sup>25</sup> For formaldehyde our yield value of  $(90 \pm 12) \%$  is in very good agreement with the yield values of  $(90 \pm 15) \%$  and  $(97 \pm 12) \%$  reported by Picquet-Varrault et al.<sup>25</sup> using the experimental system (i) described above; but it is in disagreement with their yield value of  $(37 \pm 8) \%$  for formaldehyde determined using the experimental system (ii). They attribute the low formaldehyde yield obtained in the EUPHORE chamber to the lower levels of  $\text{NO}_x$  present in this chamber during the experiments compared to the higher  $\text{NO}_x$  levels used in the indoor photoreactor experiments (systems i and ii). As will be discussed below, the yield of HCHO obtained in this work under  $\text{NO}_x$ -free conditions was low which would support the explanation given by Picquet-Varrault et al.<sup>25</sup> for the low HCHO yield in the experiments performed in the EUPHORE chamber.

As shown in Figure 2 acetoxyacetaldehyde and formaldehyde can be formed by the decomposition of  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}^\bullet$  and/or  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{O}^\bullet)\text{CH}_2\text{OH}$  radicals (channels A1 and B1) which are formed by consecutive addition of OH and  $\text{O}_2$  to the double bond followed by reaction of the peroxy radicals thus formed with NO. Formation of acetic acid and formic acetic anhydride was also observed in the reaction system (see SI, Figure S5), however, the formation was secondary in nature indicating that they are being formed from secondary oxidation of acetoxyacetaldehyde and not directly through the decomposition channel B2 shown in Figure 2. At the end of the experiments the calculated yields of acetic acid and formic acetic anhydride were typically less than 4 and 1% respectively.

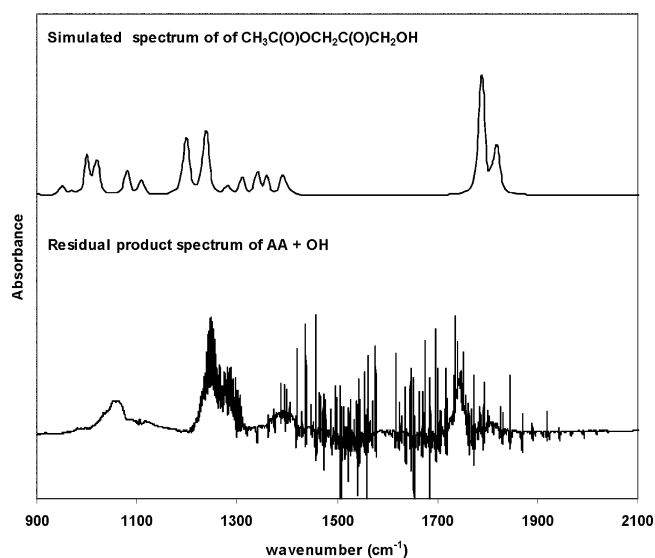
The results show that in the reaction of OH with AA the overwhelming fate of the 1,2-hydroxyalkoxy radicals formed will

be, in the presence of  $\text{NO}_x$ , decomposition via cleavage of the C–C bond binding the alkoxy radical and hydroxy-containing entities and that other possible reaction pathways are negligible.

**In the Absence of  $\text{NO}_x$ .** Analysis of the slopes of the plots shown in SI Figure S8 give a product yield of  $(26 \pm 4)$  % for acetoxyacetaldehyde and  $(12 \pm 3)$  % for formaldehyde in the reaction of OH with allyl acetate in the absence of  $\text{NO}_x$  (see Table 1). These compounds can be formed from decomposition of  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}^\bullet$  and/or  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{O}^\bullet)\text{CH}_2\text{OH}$  radicals (Figure 2, channels A1 and B1), formed by consecutive addition of OH and  $\text{O}_2$  to the double bond with followed by further reactions of the peroxy radicals thus formed with other peroxy radicals in the system. The yields of acetoxyacetaldehyde and formaldehyde are much lower than were observed in the system with  $\text{NO}_x$  indicating a dramatic change in the chemistry of the alkoxy radicals under  $\text{NO}_x$ -free conditions. The mechanism shown in Figure 2 predicts equal yields of acetoxyacetaldehyde and formaldehyde, however, as explained above for the study on OH with vinyl acetate, in the absence of  $\text{NO}_x$ , the disparity in yields can probably be attributed to secondary consumption of HCHO by  $\text{HO}_2$  or other peroxy radicals. Secondary formation of HCOOH was observed which lends further support to this explanation.

No evidence could be found for the formation of glycolaldehyde ( $\text{HC}(\text{O})\text{CH}_2\text{OH}$ ),  $\text{CH}_3\text{C}(\text{O})\text{OH}$  and formic acetic anhydride ( $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H}$ ), which could be formed from the decomposition of  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{O}^\bullet)\text{CH}_2\text{OH}$  radicals (Figure 2, channel B2). The residual IR product spectrum from the reaction of OH with AA in the absence of  $\text{NO}_x$  shows a carbonyl absorption centered around  $1746\text{ cm}^{-1}$  and several absorptions in the fingerprint region centered around 1381, 1246, 1106, and  $1058\text{ cm}^{-1}$ . Since glycolaldehyde and formic acetic anhydride are apparently not being formed in the reaction system, from a process of simple elimination it is concluded that the main fate of any  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{O}^\bullet)\text{CH}_2\text{OH}$  radicals formed in the absence of  $\text{NO}_x$  must be reaction with  $\text{O}_2$  (Figure 2, channel B3) to form  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$  and  $\text{HO}_2$  radicals. The compound could also be formed in the self-reaction of  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{O}_2^\bullet)\text{CH}_2\text{OH}$  radicals or their reaction with other peroxy radicals. Such reactions could also lead to the formation of  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ , however, weak absorptions in the OH stretching region of the IR product spectra suggest that such a route is probably not very important. In any case, in most  $\text{RO}_2 + \text{RO}_2$  reactions the channel leading to RO often dominates.<sup>28</sup>

Unfortunately, the polyfunctional compound  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$  is not commercially available for comparative and quantification purposes. However, an infrared spectrum has been simulated for  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$  using the Gaussian 03 ab initio quantum chemistry package. The spectrum was calculated using the B3LYP/6-31+G level of theory.<sup>36–38</sup> The simulated infrared spectrum is compared in Figure 5 with the residual product spectrum from the allyl acetate with OH reaction in the absence of  $\text{NO}_x$ . The residual product spectrum shown in Figure 5 is unfortunately not very well resolved due to successive spectral stripping of identified products. The salient features of the residual spectrum, although somewhat wavenumber shifted have some resemblance to the computed IR spectrum suggesting that the residual product spectrum may possibly be due to formation of



**Figure 5.** Comparison of the residual product IR spectrum obtained from experiments performed on the reaction of OH with allyl acetate in the absence of  $\text{NO}_x$  with a computed IR spectrum for the expected major product  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$ .

$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$ , however, this needs to be validated using an authentic sample of the compound.

The differences in the mechanisms observed with and without  $\text{NO}_x$  can be explained by the differences in the exothermicities of the reactions producing the alkoxy radicals. Peroxy radical self-reactions are generally thermoneutral, while the reactions of peroxy radicals with NO are very exothermic. Thus, the alkoxy radicals ( $\text{RO}^\bullet$ ) formed by the reaction between  $\text{RO}_2^\bullet$  and NO will have considerable internal excitation energy and rapid decomposition of these activated alkoxy radicals through C–C bond rupture can compete effectively with collisional thermalization of the radicals. On the contrary, the alkoxy radicals formed in the self-reaction of peroxy radicals ( $\text{RO}_2^\bullet$ ) will have little or no excitation energy, and reactions of the radical with  $\text{O}_2$  or other possible pathways, such as the  $\alpha$ -ester rearrangement in the case of vinyl acetate, become effective. Chemical activation effects in the atmospheric chemistry of different alkoxy radicals have been reported previously.<sup>39–41</sup>

**Atmospheric Implications.** The main tropospheric chemical removal of unsaturated compounds is reaction with OH radicals and kinetic studies have shown that tropospheric lifetimes of vinyl acetate and allyl acetate with respect to degradation through reaction with OH radicals are approximately 3 and 5 h, respectively.<sup>18,19</sup>

The product studies reported here have shown that the fate of the alkoxy radicals formed in the OH-initiated oxidation of vinyl acetate and allyl acetate is very dependent on the manner of their formation. For example, in regions of the troposphere, where NO levels are such that the main fate of the peroxy radicals ( $\text{RO}_2^\bullet$ ) is reaction with NO, then prompt decomposition of the excited alkoxy radicals ( $\text{RO}^\bullet$ ) via cleavage of the C–C bonds between the alkoxy radical and OH group-containing entities dominates forming HCHO and formic acetic anhydride in the case of the VA + OH reaction and acetoxyaldehyde and HCHO in the case of the AA + OH reaction.

In the cleaner regions of the free troposphere, where  $\text{NO}_x$  levels are such the peroxy radicals will mainly undergo reactions

with other peroxy radicals, that is,  $\text{CH}_3\text{OO}$  and  $\text{HO}_2$ , the major fate of the alkoxy radicals formed in the reactions of OH with VA and AA starkly contrasts with that which observed in the presence of  $\text{NO}_x$ . For example, the dominant fate of the  $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{O}^\bullet)\text{CH}_2\text{OH}$  radical formed in the OH-initiated oxidation of vinyl acetate under atmospheric conditions where peroxy–peroxy reactions are important will be an  $\alpha$ -ester rearrangement producing acetic acid and HCHO whereas for the  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{O}^\bullet)\text{CH}_2\text{OH}$  radical formed in the AA+OH reaction the main fate appears to be reaction with  $\text{O}_2$  to form the multifunctional compound  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$ .

To the best of our knowledge, this is the first product study performed on the OH-initiated degradation of vinyl and allyl acetate in the absence of  $\text{NO}_x$ . The work has highlighted that the change in product distributions for the reactions of some alkoxy radicals under different  $\text{NO}_x$  environments can be quite extreme and that product studies under a range of  $\text{NO}_x$  condition relevant for the atmosphere are necessary for the construction VOC degradation mechanisms that can be more universally applied for diverse atmospheric conditions. The chemistry present in most atmospheric models is usually tailored for the description of pollution in urban areas and thus the models do not perform well for low  $\text{NO}_x$  environments. The present study provides mechanistic data that can be used in future computer model studies of air chemistry to assess the environmental impact of emissions vinyl acetate and allyl acetate under both high and low  $\text{NO}_x$  conditions.

## ■ ASSOCIATED CONTENT

### Supporting Information

Concentration–time profiles in the presence and absence of  $\text{NO}_x$  for the reaction of vinyl acetate with OH radicals (Figure S1 and Figure S2, respectively); and for the reaction of allyl acetate with OH radicals (Figure S5 and Figure S6, respectively). Yield plots for the reaction of OH radicals with vinyl acetate in the presence of  $\text{NO}_x$  (Figure S3) and yield plots for the reaction of OH radicals with allyl acetate in the presence and absence of  $\text{NO}_x$  (Figure S7 and Figure S8, respectively); and IR spectra plots for the identification of products for the reaction of OH radicals with allyl acetate in the absence of  $\text{NO}_x$  (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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