

Article

Product Formation from the Chlorine-Initiated Oxidation of Amyl Acetate Under Atmospheric Conditions

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Abstract

The degradation formed during the gas-phase reaction of amyl acetate, $\text{CH}_3\text{COO}(\text{CH}_2)_4\text{CH}_3$, initiated by chlorine atoms ($\bullet\text{Cl}$), was investigated under atmospheric conditions using gas chromatography–mass spectrometry. The main products identified were acetic acid, formaldehyde, acetaldehyde, butyraldehyde, and propionaldehyde. Calibration curves were established for each identified product at different concentrations to enable their quantification by gas chromatography coupled with flame ionization detection. Product yields were subsequently determined from the calibration data, allowing a quantitative evaluation of the formation of the major oxidation products. The results obtained contribute to a better understanding of the atmospheric degradation pathways of amyl acetate and related ester compounds, providing useful information for assessing the atmospheric processing of ester-containing emissions, including those associated with biofuel applications.

Keywords: esters; chlorine atoms; product yields; atmospheric degradation; mechanisms

1. Introduction

The atmosphere contains volatile organic compounds (VOCs) emitted from both anthropogenic and natural sources. Many of these VOCs participate in photochemical reactions that lead to the formation of ozone and other secondary pollutants through interactions with sunlight and atmospheric oxidants [1–6]. In the troposphere, hydroxyl radicals ($\bullet\text{OH}$) are the dominant oxidizing species responsible for the degradation of VOCs. Although chlorine atoms ($\bullet\text{Cl}$) occur at much lower concentrations, they can also contribute significantly to VOC oxidation in coastal, marine, and some industrial or urban environments because of their high reactivity toward many organic compounds [7]. Rate coefficients for reactions of VOCs with $\bullet\text{Cl}$ atoms are frequently one to two orders of magnitude larger than those for reactions with $\bullet\text{OH}$ radicals, making chlorine chemistry relevant despite the much lower atmospheric abundance of $\bullet\text{Cl}$.

Acetates, an important class of VOCs, are widely used in industrial applications, mainly as solvents and in the manufacture of fragrances and flavoring agents [8]. They are also naturally emitted by vegetation [9]. Industrial sources of acetate emissions include adhesives, sealants, paints, coatings, and cleaning products [10–12]. In addition, esters have attracted increasing attention in atmospheric chemistry due to the growing use of biodiesel fuels, which consist primarily of fatty acid alkyl esters. The atmospheric oxidation of these compounds can lead to the formation of oxygenated products and secondary



Academic Editor: Kei Sato

Received: 24 July 2026

Revised: 12 August 2026

Accepted: 13 August 2026

Published: 19 August 2026

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pollutants that may influence air quality. Although short-chain acetates are structurally simpler than biodiesel constituents, studies on their oxidation mechanisms provide valuable insight into the atmospheric processing of ester-containing organic compounds. Due to their widespread use and emission into the atmosphere, the atmospheric degradation of short-chain esters has been the subject of numerous experimental and theoretical investigations [13–27].

Atmospheric degradation of acetates is a complex process driven by photochemical oxidation, resulting in the formation of several oxygenated products with potential environmental implications [28]. Amyl acetate is commonly used in cosmetic products such as nail polishes, enamels, and lacquers, and also as a solvent in inks, adhesives, thinners, and cleaning formulations [2,29,30]. Its atmospheric oxidation occurs predominantly via reaction with $\bullet\text{OH}$ radicals under typical tropospheric conditions. However, reactions with $\bullet\text{Cl}$ atoms may also represent an important degradation pathway in environments where chlorine atom concentrations are enhanced, owing to the much higher reactivity of $\bullet\text{Cl}$ toward many VOCs. The oxidation of amyl acetate may contribute to the formation of secondary pollutants involved in photochemical smog and ozone formation, thereby affecting urban air quality.

Several quantitative product studies have previously been reported for the atmospheric degradation of short-chain acetates. In the reaction of methyl acetate with $\bullet\text{Cl}$ atoms, the main quantified products were $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H}$ ($35 \pm 5\%$) and $\text{CH}_3\text{C}(\text{O})\text{OH}$ ($65 \pm 14\%$) [31]. Picquet-Varrault et al. (2001) [32] reported that the $\bullet\text{OH}$ -initiated oxidation of ethyl acetate produces mainly acetic acid (0.75 ± 0.13), acetoxyacetaldehyde (0.15 ± 0.05), acetic anhydride (0.02 ± 0.01), formic acetic anhydride (0.02 ± 0.01), and peroxyacetyl nitrate (PAN). For the oxidation of n-propyl acetate, the major products identified were acetoxyacetaldehyde (0.22 ± 0.06), formic acetic anhydride (0.28 ± 0.03), acetic acid (0.15 ± 0.02), acetaldehyde (0.35 ± 0.10), peroxypropionyl nitrate (PPN), and probably acetoxypropionaldehyde (0.30 ± 0.10) [32].

To date, no experimental studies reporting the identification and quantification of products from the reaction of amyl acetate with $\bullet\text{Cl}$ atoms have been published. Only one theoretical investigation concerning the oxidation of isoamyl acetate has been reported [33]. That study proposed several H-abstraction pathways initiated by $\bullet\text{OH}$ radicals and $\bullet\text{Cl}$ atoms. According to the calculated relative energies, the most favorable pathway involves H-abstraction from the carbon adjacent to the ester oxygen atom, leading to the formation of products such as acetic formic anhydride, isobutyraldehyde, formaldehyde, acetaldehyde, acetone, chloromethane, methanol, acetic 3-methylbutanoic anhydride, and 3-methylbutanal. A second possible pathway involves H-abstraction from the tertiary carbon atom, producing compounds such as acetone, 2-oxoethyl acetate, formaldehyde, acetic formic anhydride, methanol, chloromethane, and 3-oxobutyl acetate [33].

In this work, quantitative studies of the reaction products and their corresponding yields from the gas-phase reaction of amyl acetate with $\bullet\text{Cl}$ atoms (Reaction (1)) are presented for the first time. Such studies contribute to the broader understanding of the atmospheric oxidation of ester-containing compounds, including those relevant to renewable biofuel emissions. In addition, the observed products are compared with those reported for structurally related esters in the literature. For this purpose, mixtures of oxidant/amyl acetate/air were irradiated under atmospheric conditions using fluorescent lamps. Reaction products were identified by gas chromatography coupled with mass spectrometry (GC–MS), while product quantification was performed using gas chromatography coupled with flame ionization detection (GC–FID).



2. Experimental Section

The experiments were carried out in a 405 L Pyrex glass atmospheric simulation chamber at (298 ± 2) K and atmospheric pressure. The chamber consists of a cylindrical borosilicate glass reactor sealed at both ends with aluminum flanges. The entire structure is surrounded by reflective stainless-steel sheets and equipped with an air-cooling system to maintain stable experimental temperatures during irradiation. The reactor is 1.5 m long with an internal diameter of 60 cm and is surrounded by fluorescent lamps emitting UV–Vis radiation with maximum emissions at 360 nm (Philips TL 0.5 W) and/or 254 nm (Philips TUV 40 W), used for radical generation. The chamber evacuation system consists of a turbomolecular pump backed by a two-stage rotary pump, allowing pressures down to 10^{-3} Torr to be achieved. An internal stainless-steel fan mounted on the front flange ensured homogeneous mixing of the gaseous mixtures inside the reactor.

Prior to each experiment, the chamber was repeatedly filled with synthetic air up to 1000 mbar and evacuated to vacuum until no residual peaks corresponding to reactants or products were detected in the chromatograms. The chamber was equipped with both high- and low-pressure gauges for accurate pressure monitoring during all experiments.

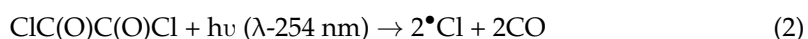
The reactor was coupled to a Shimadzu GC-2014B gas chromatograph (Shimadzu GC-2014B Shimadzu Corporation, Kyoto, Japan) equipped with a flame ionization detector (GC–FID) (Rtx-5 Restek Corporation, Bellefonte, PA, USA) and an Rtx-5 fused silica capillary column (30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m film thickness) (DVB/CAR/PDMS Supelco Inc., Bellefonte, PA, USA). Gas samples were collected offline using solid-phase microextraction (SPME) with a DVB/CAR/PDMS (divinylbenzene/carboxene/polydimethylsiloxane) fiber. The SPME fiber was exposed directly to the reaction mixture for 10 min to preconcentrate the analytes and was then immediately transferred to the GC injector, where thermal desorption was carried out for 2 min at 180 °C. The column temperatures were set at 40–65 °C.

For product identification experiments, mixtures of amyl acetate, oxalyl chloride, and synthetic air were irradiated inside the chamber. Reaction products were analyzed using a VARIAN Saturn 2200 gas chromatograph coupled with a mass spectrometer (GC–MS) equipped with an HP-5MS capillary column (Agilent, Santa Clara, CA, USA, Part 19091S-433; 30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m film thickness). Gas samples were collected offline using the same DVB/CAR/PDMS SPME fiber. Prior to analysis, the fiber was exposed to the reaction mixture for 10 min to preconcentrate the products and subsequently thermally desorbed in the GC injector for 2 min at 180 °C. The injector temperature was maintained at 200 °C, and the column oven was operated at 55 °C.

The SPME extraction time (10 min) was selected based on preliminary saturation experiments performed to determine an appropriate extraction time that provided reproducible sampling within the linear response range of the SPME fiber.

Dark-control experiments and product stability tests were performed to evaluate possible wall losses and photolysis of the reactant and the identified products. Under the experimental conditions employed, the combined losses were always lower than 5% over the duration of the experiments. Therefore, no correction for photolysis or wall losses was applied to the reported product yields.

•Cl atoms were generated by UV photolysis of oxalyl chloride (ClC(O)C(O)Cl) according to Reaction (2):



Before quantification of the identified products by GC–FID, calibration curves were constructed for both the reactant and the detected oxidation products. Known concentra-

tions of each compound, ranging from 0.10 to 10 ppm, were introduced into the reactor, which was subsequently filled with synthetic air to atmospheric pressure. Samples were collected using the SPME fiber and analyzed by GC–FID under the same experimental conditions used in the reaction studies. Calibration curves were obtained from plots of chromatographic peak area versus concentration.

Special care was taken in the calibration of acetic acid because of its tendency to interact with surfaces. Calibration mixtures were prepared directly in the atmospheric simulation chamber and analyzed using the same reactor, SPME extraction time, fiber, and GC–FID conditions employed in the reaction experiments. Thus, reproducible losses or adsorption effects occurring during sampling and analysis were incorporated into the calibration response. The calibration was linear over the 0.60–10.50 ppm concentration range ($R^2 = 0.995$), and each point was measured in triplicate.

Product yields were determined from concentration–time profiles by simultaneously monitoring the decrease in amyl acetate concentration and the increase in product concentration during irradiation. Reaction yields were obtained from the slopes derived by least-squares analysis of product concentration versus reacted amyl acetate.

Materials

The chemicals used in the experiments were used without further purification. The reported purities provided by the manufacturers were as follows: amyl acetate (Sigma-Aldrich, $\geq 99\%$, Buenos Aires, Argentina), oxalyl chloride (Sigma-Aldrich, 99%, Buenos Aires, Argentina), formaldehyde (Sigma-Aldrich, 37%, Buenos Aires, Argentina), acetaldehyde (Sigma-Aldrich, 99.5%, Buenos Aires, Argentina), butyraldehyde (Sigma-Aldrich, 95%, Buenos Aires, Argentina), and synthetic air (99.999% Córdoba, Argentina).

3. Results and Discussion

Mixtures of amyl acetate and oxalyl chloride in synthetic air were irradiated in the atmospheric simulation chamber in order to investigate the oxidation products formed during the Cl-initiated reaction. The experiments were performed under conditions corresponding to approximately 60% consumption of the initial amyl acetate concentration.

The identification of reaction products requires prior knowledge of the possible degradation pathways. Therefore, information available in the literature for structurally related esters and analogous oxidation systems was considered to assist in the interpretation of the experimental results. Different chromatograms were obtained depending on the irradiation time and the extent of reaction progress during photolysis.

Under the experimental conditions employed, formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, and acetic acid were identified as major products of the reaction between amyl acetate and $\bullet\text{Cl}$ atoms by GC–MS analysis. The identification was based on retention time analysis and a comparison of the obtained mass spectra with reference spectra from the NIST library. Details concerning the experimental setup and chromatographic conditions have been previously described in our earlier work [34]. Propionaldehyde was identified as a reaction product by GC–MS but was not quantified due to the lack of an authentic calibration standard.

Once the reaction products had been identified by GC–MS, quantitative analyses were performed using GC–FID. Acetic acid exhibited the highest chromatographic response under the experimental conditions employed. Therefore, calibration curves were constructed prior to product quantification in order to establish the relationship between compound concentration and detector response within the expected concentration ranges. Because the products were formed in different amounts during the oxidation of amyl acetate by Cl atoms, individual calibration curves were prepared using concentration ranges selected

according to the intensity of the corresponding chromatographic signals. The concentration intervals employed for each compound are summarized in Table 1.

Table 1. Concentration ranges employed for the construction of the calibration curves used in the quantification of amyl acetate oxidation products.

VOCs	Concentration Ranges [ppm]
$\text{CH}_3\text{C}(\text{O})\text{OH}$	0.60 to 10.50
CH_3CHO	0.15 to 2.20
HCHO	0.10 to 9.80
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	0.08 to 2.70
$\text{CH}_3\text{COO}(\text{CH}_2)_4\text{CH}_3$	0.47 to 8.20

Figure 1 presents the calibration curves obtained for (a) formaldehyde, (b) acetaldehyde, (c) butyraldehyde, (d) acetic acid, and (e) amyl acetate. The concentration ranges selected for each compound were suitable for the quantitative determination of the reaction products under the experimental conditions employed. Correlation coefficients (R^2) close to 0.99 were obtained for all calibration curves, indicating excellent linearity between compound concentration and chromatographic response. For each calibration point, the concentration of the calibration compound was calculated by considering the dilution produced after partial evacuation of the reactor and subsequent refilling to atmospheric pressure with synthetic air.

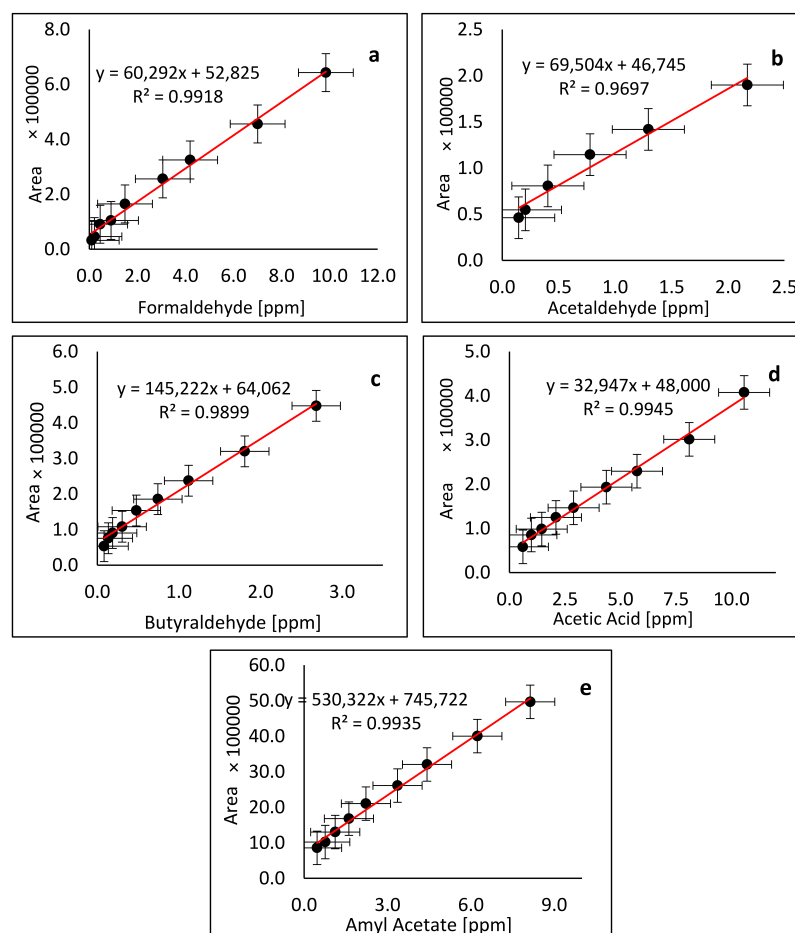


Figure 1. Calibration curves at different concentrations of the identified products and the ester studied: (a) formaldehyde, (b) acetaldehyde, (c) butyraldehyde, (d) acetic acid, and (e) amyl acetate.

The analytical sensitivity varied among the compounds according to their physicochemical properties and their interaction with the chromatographic system, resulting in different detector responses. Nevertheless, all calibration curves showed satisfactory reproducibility and repeatability. Each calibration point was measured in triplicate to evaluate the reliability and consistency of the analytical procedure.

To evaluate the temporal evolution of the reaction system, concentration–time profiles were constructed for both amyl acetate consumption and product formation. Product yields were determined by plotting the increase in product concentration against the decrease in amyl acetate concentration as the reaction proceeded. The corresponding yields were obtained from the slopes derived by least-squares analysis of these plots. The calculated yields were then corrected for secondary chemical consumption of the products using the procedure described by Tuazon et al. [35]. Under the experimental conditions employed, these corrections were small, being lower than 5% for all quantified products.

The concentration–time profiles for the reaction of amyl acetate with $\bullet\text{Cl}$ atoms, together with the identified oxidation products, are presented in Figure 2. The corresponding plots of product formation versus amyl acetate consumption are shown in Figure 3. In all cases, satisfactory linear relationships were obtained from the least-squares analysis.

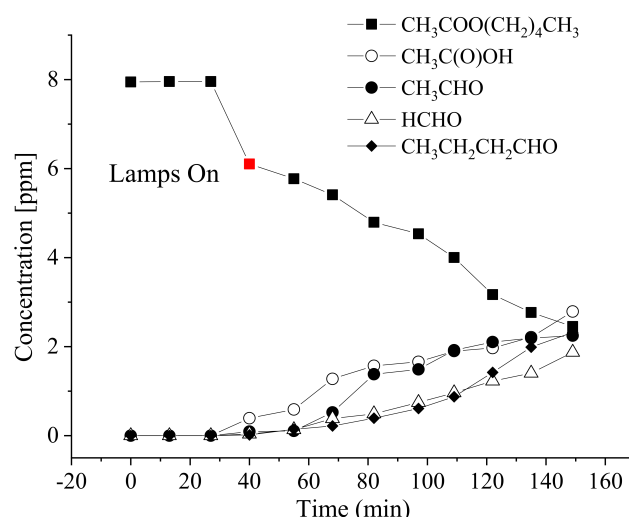


Figure 2. Concentration–time profiles for the reaction of amyl acetate with $\bullet\text{Cl}$ atoms. The UV lamps were switched on 40 min after the beginning of the experiment, marking the initiation of the reaction (indicated by the red symbol).

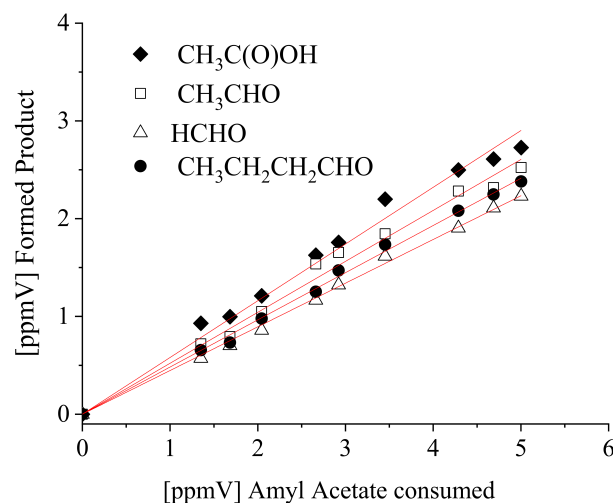


Figure 3. Plot of the product concentrations as a function of reacted amyl acetate with $\bullet\text{Cl}$ atoms.

To quantify the concentrations of the products formed during the reaction, the slopes obtained from the plots shown in Figure 3 were corrected using the corresponding chromatographic response factors determined from the calibration curves presented in Figure 1a–e. This procedure allowed the quantitative determination of the reaction product yields.

Table 2 summarizes the formation yields obtained for the identified oxidation products. Yields of (54 ± 3) , (65 ± 1) , (53 ± 2) , and (61 ± 5) % were determined for acetic acid $\text{CH}_3\text{C}(\text{O})\text{OH}$, acetaldehyde CH_3CHO , formaldehyde HCHO , and butyraldehyde $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$, respectively. The reported uncertainties correspond to the combination of the 2σ statistical error derived from the regression analysis together with the uncertainties associated with the subtraction procedure. The yield values presented represent the average of three independent experiments performed for each quantified product.

Table 2. Identified oxidation products from the reaction of amyl acetate with $\bullet\text{Cl}$ atoms and their corresponding formation yields.

Reaction	Products	Yields (%)
$\text{CH}_3\text{COO}(\text{CH}_2)_4\text{CH}_3$ + $\bullet\text{Cl}$	$\text{CH}_3\text{C}(\text{O})\text{OH}$	54 ± 3
	CH_3CHO	65 ± 1
	HCHO	53 ± 2
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	61 ± 5

A partial carbon balance was estimated based on the quantified products by Equation (3):

$$\text{Carbon Balance}(\%) = \frac{\sum Y_i \times n_{\text{Ci}}}{n_{\text{CAA}}} \quad (3)$$

where Y_i = the molar yield of product i , expressed as a fraction (e.g., 54% = 0.54); n_{Ci} = the number of carbon atoms in product i ; n_{CAA} = the number of carbon atoms in amyl acetate (7). The calculation was performed considering the carbon contribution of each product relative to the seven carbon atoms present in amyl acetate. The identified products (acetic acid, acetaldehyde, formaldehyde, and butanal) accounted for approximately 76% of the carbon from the reacted amyl acetate. The remaining carbon fraction may be attributed to non-quantified products, mainly CO and CO_2 , as well as minor oxygenated compounds.

A detailed degradation mechanism for the reaction of amyl acetate with $\bullet\text{Cl}$ atoms was previously proposed in our earlier work [34]. In the present work, this mechanism is briefly revisited only to provide the basis for the quantitative analysis of the reaction products and the discussion of their formation yields. The atmospheric oxidation is expected to proceed mainly through H-atom abstraction from the alkyl chain, with the relative abstraction probabilities estimated by Structure–Activity Relationship (SAR) calculations [36,37] as follows: 0.7% at $-\text{CH}_3\text{C}(\text{O})\text{O}-$; 30% at $-\text{C}(\text{O})\text{OCH}_2-$ (C1); 23% at $-\text{CH}_2-$ (C2); 23% at $-\text{CH}_2-$ (C3); 19% at $-\text{CH}_2-$ (C4); and 3% at $-\text{CH}_3$ (C5).

The initially formed alkyl radicals rapidly react with O_2 to generate peroxy radicals, which subsequently react with other peroxy radicals to form alkoxy radicals [38–40]. These alkoxy intermediates may undergo different reaction pathways, including decomposition and α -ester rearrangement reactions. Figures 4 and 5 illustrate the proposed mechanism for the Cl -initiated oxidation of amyl acetate.

According to the proposed mechanism, channel A from Figure 4 leads mainly to the formation of butyraldehyde $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$, acetic acid $\text{CH}_3\text{C}(\text{O})\text{OH}$, and formaldehyde HCHO . In channel B, the decomposition of the corresponding alkoxy radicals produces butyraldehyde $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$, propionaldehyde, $\text{CH}_3\text{CH}_2\text{CHO}$, and formaldehyde HCHO . Channels C and D, from Figure 5, are mainly associated with the formation of short-chain aldehydes, such as formaldehyde, acetaldehyde, and propionaldehyde.

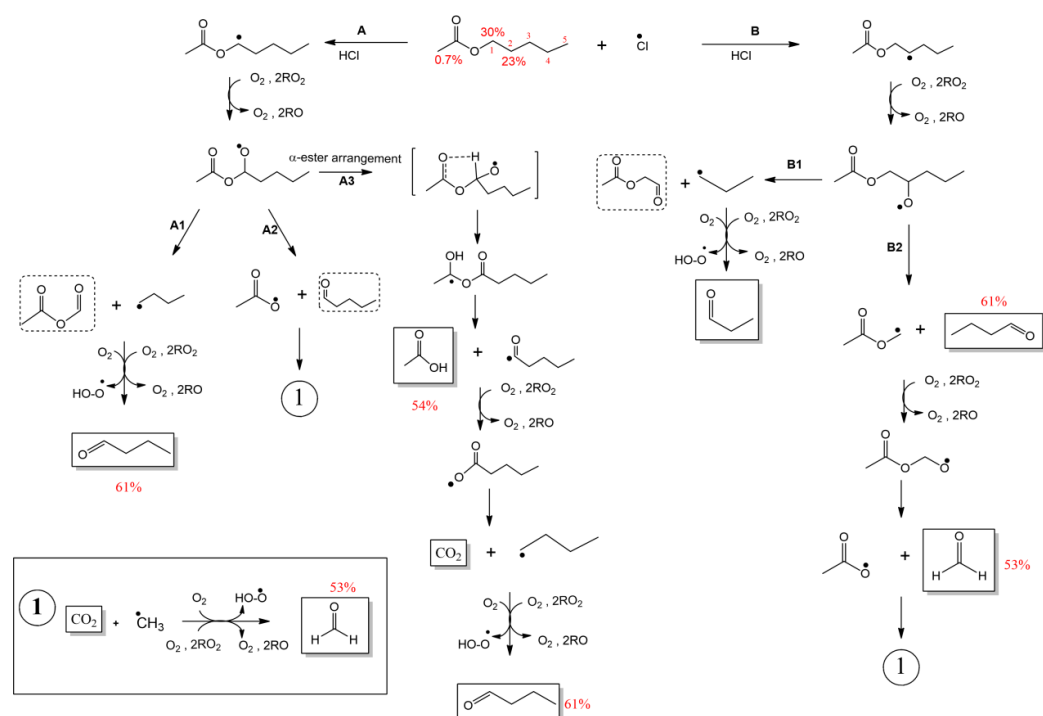


Figure 4. Oxidation mechanism of amyl acetate with $\bullet\text{Cl}$ atoms via H-abstraction involving channels A and B. A1–A3 and B1–B2 denote the subsequent reaction pathways associated with channels A and B, respectively. Dashed boxes indicate the species involved in the proposed reaction pathways, whereas solid boxes indicate the identified products. The numbers in red indicate the corresponding product yields. Products were identified in full agreement with the experimentally determined yields.

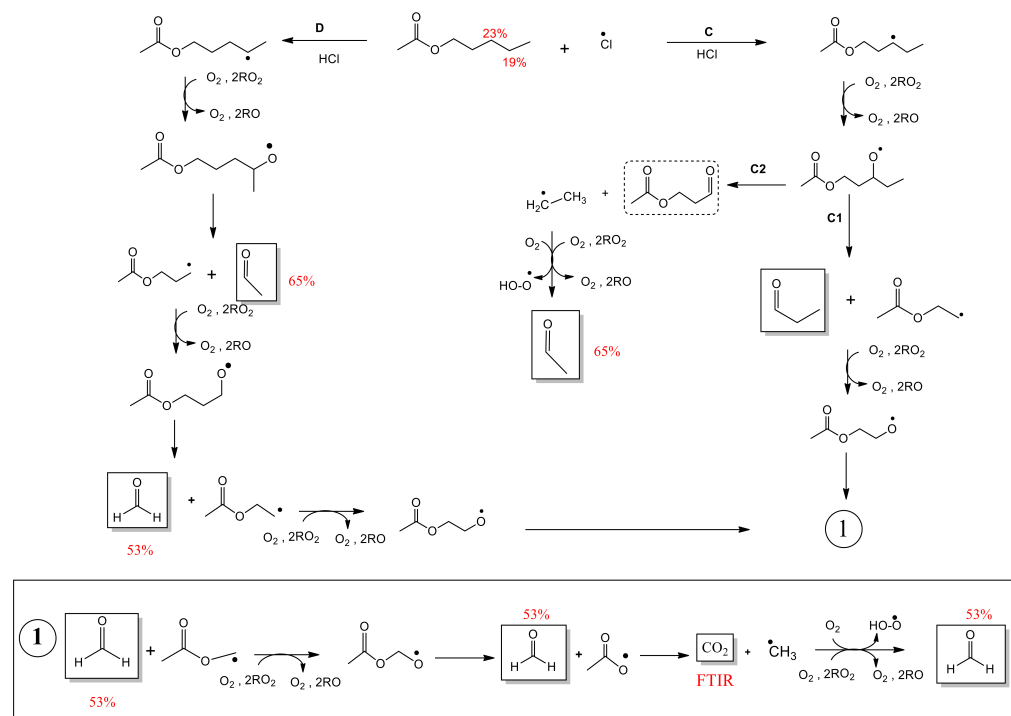


Figure 5. Oxidation mechanism of amyl acetate with $\bullet\text{Cl}$ atoms via H-abstraction involving channels C and D. C1–C2 denote the subsequent reaction pathways associated with channels C, respectively. Dashed boxes indicate the species involved in the proposed reaction pathways, whereas solid boxes indicate the identified products. The numbers in red indicate the corresponding product yields. Products were identified in full agreement with the experimentally determined yields.

Although propionaldehyde was identified by GC–MS, its yield could not be determined because no authentic standard was available. Consequently, the relative importance of pathways B1 and C1 cannot be quantitatively assessed.

The product yields obtained in this study are consistent with this distribution, since the major products associated with these channels were quantified in significant amounts. However, a direct relationship between the SAR branching ratios and individual product yields is not expected because overlapping formation pathways contribute to several products.

Previous investigations have reported product yields for the oxidation of methyl acetate, ethyl acetate, and propyl acetate initiated by $\bullet\text{Cl}$ atoms and $\bullet\text{OH}$ radicals [26,27]. These three compounds possess structural similarities to amyl acetate, albeit with shorter carbon chains. According to the results of Christensen et al. 2000 [31] for methyl acetate, $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$, degradation, and the fate of $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{O}\bullet$ will lead to the formation of acetic formic anhydride, $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H}$ ($35 \pm 5\%$), acetic acid, $\text{CH}_3\text{C}(\text{O})\text{OH}$ ($65 \pm 14\%$), and carbon monoxide, CO. These observations are consistent with the reaction sequence proposed for channel A in Figure 4.

In addition, Tuazon et al. 1998 [41] proposed that $\text{RC}(\text{O})\text{OCHO}\bullet\text{R}'$ alkoxy radicals may undergo α -ester rearrangement reactions to produce the corresponding carboxylic acid, $\text{RC}(\text{O})\text{OH}$, together with an acyl radical, $\text{R}'\text{C}(\text{O})\bullet$. This mechanism corresponds to pathway A3, shown in Figure 4. According to Cavalli et al. 2000 [42], the formation of anhydrides is favored under low- NO_x conditions, whereas in the presence of NO_x , the α -ester rearrangement pathway becomes more important, promoting the formation of carboxylic acids.

In the present work, acetic acid was identified and quantified as a major oxidation product. Although the corresponding anhydride could potentially be formed, its identification was not possible because an authentic standard was not available in our laboratory under the experimental conditions employed.

On the other hand, Picquet-Varrault et al. [32] reported that the major products from the OH-initiated oxidation of ethyl acetate at (298 ± 5) K and atmospheric pressure were acetic acid (75 ± 13) % and peroxyacetyl nitrate (PAN) (75 ± 20) %. These results support the importance of the α -ester rearrangement pathway discussed above.

For the oxidation of n-propyl acetate, the main products identified were formic acetic anhydride (28 ± 3) %, acetoxyacetaldehyde (22 ± 6) %, acetaldehyde (35 ± 10) %, acetic acid (15 ± 2) %, acetoxypropionaldehyde (30 ± 10) %, and peroxypropionyl nitrate (PPN) [32]. The authors indicated that proposing a complete degradation mechanism was difficult because several of the observed products could be formed through multiple competing reaction pathways. Similar behavior may also occur in the oxidation of amyl acetate, given the complexity of the possible alkoxy radical decomposition and rearrangement processes involved [32].

Recently, Hutama et al. 2024 [33] reported a theoretical investigation on the degradation of isoamyl acetate, initiated by $\bullet\text{OH}$ radicals and $\bullet\text{Cl}$ atoms. Their study indicated that H-atom abstraction at the C2 (R2) and C4 (R4) positions represents the most favorable reaction pathways. The radicals formed through these channels were predicted to evolve toward thermodynamically stable products. In addition, the authors proposed that the reactions of isoamyl acetate with $\bullet\text{Cl}$ atoms at the R2 and R4 sites proceed through essentially barrierless mechanisms.

The theoretical results reported by Hutama et al. [33] are consistent with the experimental observations obtained in the present work and with our previous study concerning product identification [34]. In particular, the products identified and quantified in this work are in agreement with the reaction channels associated with the most favorable H-atom abstraction sites predicted by the theoretical calculations.

4. Atmospheric Implications and Conclusions

The atmospheric degradation of amyl acetate occurs mainly through reactions with hydroxyl radicals ($[\text{OH}]$ is 2.0×10^6 radicals. cm^{-3} for about 12 h [43]) and chlorine atoms ($[\text{Cl}]$ is $(3.3 \pm 1.1) \times 10^4$ atoms. cm^{-3} for 24 h [44]), with estimated atmospheric lifetimes of approximately 22 h and 62 h, respectively, as previously reported by Straccia et al. [34]. These values indicate that amyl acetate is efficiently removed from the atmosphere near its emission sources, suggesting that its impact is expected to be more important at local and regional scales rather than on global atmospheric transport.

Although hydroxyl radicals represent the dominant atmospheric oxidant for most VOCs, chlorine atoms can play an important role in specific environments where their concentrations are enhanced. In the marine boundary layer, $\bullet\text{Cl}$ atom concentrations have been reported [45] in the range of 1×10^4 atoms/ cm^3 , with peak values reaching approximately 1×10^5 atoms/ cm^3 in coastal and highly industrialized regions. Under these conditions, the higher reactivity of $\bullet\text{Cl}$ atoms toward organic compounds may lead to significant local oxidation of VOCs, making Cl-initiated degradation pathways relevant for assessing the atmospheric fate of amyl acetate and the formation of secondary oxidation products.

The oxidation of amyl acetate leads to the formation of several oxygenated volatile organic compounds (OVOCs), including formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, and acetic acid. Many of these products are highly reactive in the troposphere and may participate in subsequent photochemical oxidation cycles, contributing to the formation of secondary pollutants such as ozone and peroxyacyl nitrates (PANs) [46,47]. The ozone formation potential associated with amyl acetate oxidation was previously estimated by our group using the empirical approach proposed by Dash et al. [48] with Equation (4), which relates the $\bullet\text{OH}$ rate coefficient and the molecular structure of the VOC to its maximum ozone production. Based on this approach, the average ozone production for amyl acetate was estimated to be approximately 2.15 ppm [34]. This value suggests that the atmospheric degradation of amyl acetate may contribute to photochemical smog formation in polluted urban atmospheres.

$$\text{O}_3 = \frac{n'[k_a(\text{OH})]^2}{4.6[2.7 \times 10^{-5} - k(\text{OH})]} \times \left(\frac{1}{k_a(\text{OH})} - \frac{1 - e^{-1.24 \times 10^{-4}/k_a(\text{OH})}}{2.7 \times 10^{-5}} \right) \quad (4)$$

Some of the identified degradation products are also environmentally relevant from a health perspective. Formaldehyde, for example, is recognized as a hazardous air pollutant and has been classified as a human carcinogen [49–51]. Similarly, acetaldehyde and other short-chain carbonyl compounds are known to participate in atmospheric radical propagation cycles and in the formation of secondary pollutants. Therefore, the oxidation of amyl acetate may indirectly influence both atmospheric chemistry and air quality through the production of secondary reactive species.

The environmental fate of the oxidation products also depends strongly on their physicochemical properties [52]. Acetic acid, one of the major products identified in this work, is highly soluble in water and may be efficiently removed from the atmosphere by wet deposition processes. Consequently, meteorological conditions such as humidity, temperature, and precipitation may significantly influence the atmospheric persistence and transport of these oxidation products [53].

The product distribution obtained in this study is generally consistent with previously reported oxidation mechanisms for structurally related esters [20,23,54] and with recent theoretical investigations concerning H-atom abstraction pathways in amyl acetate oxidation. The experimental results support the importance of alkoxy radical decomposition and α -ester rearrangement reactions during the atmospheric degradation process.

Overall, although amyl acetate emissions at low concentrations may not represent a major atmospheric concern, large emissions could contribute to the deterioration of air quality through the formation of ozone and secondary oxidation products. In addition, some degradation products may participate in aerosol formation, NO_x transport processes, and PAN chemistry. These results highlight the importance of continuing investigations on the atmospheric degradation mechanisms of esters and their role in tropospheric oxidation and halogen chemistry. Furthermore, mechanistic studies of relatively simple esters provide valuable insights into the atmospheric behavior of more complex ester-containing compounds, including fatty acid alkyl esters that constitute biodiesel fuels.

Author Contributions: Data Curation, V.G.S.C. and E.B.; Investigation, V.G.S.C. and E.B.; Writing—original draft V.G.S.C.; Writing—review & editing, V.G.S.C., E.B., M.B.B. and M.A.T.; Methodology, M.B.B. and M.A.T.; Project administration, M.B.B. and M.A.T.; Supervision, Writing—review & editing, M.B.B. and M.A.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: https://fcq.biblio.unc.edu.ar/cgi-bin/koha/opac-detail.pl?biblionumber=9539&query_desc=vianni (accessed on 12 August 2026).

Acknowledgments: FONCyT, CONICET, and SECyT UNC, Argentina. V.G.S.C and E.B wish to acknowledge CONICET for their doctoral fellowship and support.

Conflicts of Interest: The authors declare no conflict of interest.

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