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FTIR Spectroscopic Study of the OH-Induced Oxidation of Isopropyl, Isobutyl, and *tert*-Butyl Acetates

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OH-induced oxidation mechanisms of isopropyl, isobutyl, and *tert*-butyl acetates have been investigated at room temperature (298 ± 5 K) and atmospheric pressure by photolyzing CH_3ONO /acetate/ NO mixtures with FTIR spectrometry as analytical device. All main oxidation products of isopropyl and isobutyl acetates were detected and their formation yields were determined: from isopropyl acetate, acetic anhydride (0.72 ± 0.07), acetone (0.26 ± 0.03), acetic acid (0.06 ± 0.03), and peroxyacetyl nitrate; from isobutyl acetate, acetone (0.78 ± 0.12), formic acetic anhydride (0.52 ± 0.06), acetoxyacetaldehyde (0.18 ± 0.06), acetic acid (0.08 ± 0.02), and peroxyisobutyryl nitrate. For *tert*-butyl acetate, preliminary results have been obtained and two oxidation products were detected: acetic anhydride (0.49 ± 0.04) and acetone (0.24 ± 0.04). From these data, oxidation schemes of these acetates were elucidated. This study shows that the presence of the ester function promotes the H-atom abstraction on the carbon in the α -position of the oxygenated function. Concerning the reactivity of alkoxy radicals, this study confirms the α -ester rearrangement proposed recently by Tuazon et al. (*J. Phys. Chem. A*, **1998**, 102, 2316). Moreover, it has been shown that nonlinear alkoxy radicals formed by the oxidation of acetates predominantly decompose instead of reacting with O_2 and isomerizing.

1. Introduction

Oxygenated volatile organic compounds have been widely released into the atmosphere by evaporation during their use in industrial activities for decades. Therefore, they play an increasing role on the atmospheric production of ozone and other photooxidants. Among these compounds, esters are currently used in industry as solvents in paints and adhesives and as automobile fuel substitutes.¹ They are also emitted from natural sources (vegetation and biomass combustion²) and are formed in the atmosphere as oxidation products of some ethers used as automobile fuel additives.^{3–5} In particular, isopropyl and *tert*-butyl acetates are emitted during the combustion of esterified rapeseed oil used recently as substitution fuel.⁶ *tert*-Butyl acetate is also produced by the atmospheric oxidation of ethyl *tert*-butyl ether (ETBE).⁴ To evaluate the impact of these emissions on the formation of photooxidants and therefore on health and environment, a good understanding of the atmospheric oxidation of acetates by OH radicals is needed as this process is their main daytime fate. The present study is focused on the oxidation mechanisms of three nonlinear acetates: isopropyl, isobutyl, and *tert*-butyl acetates and follows up previous works on kinetics of the OH-induced oxidation of linear and branched acetates⁷ and on mechanisms of the oxidation of linear acetates.⁸

Some previous mechanistic studies have already been carried out for isopropyl and *tert*-butyl acetates,^{9–11} but they are sparse and sometimes incomplete. The most complete study, performed by Tuazon et al.,¹⁰ led to the detection of acetic anhydride, acetone, acetic acid, and peroxyacetyl nitrate as the main oxidation products of isopropyl acetate. Kerr and Stocker⁹ have detected the formation of acetone and peroxyacetyl nitrate during

the oxidation of isopropyl acetate. Le Calvé¹¹ has identified acetic acid, acetic anhydride, and acetone as products but they were not precisely quantified. In both of these last studies the carbon balance was not achieved. Tuazon et al.¹⁰ carried out the only previous study of the atmospheric oxidation of *tert*-butyl acetate. Unfortunately, they were not able to detect all oxidation products, and 31% of the carbon balance was missing. Concerning isobutyl acetate, no mechanistic study has been published yet.

To complete these previous data and to improve our understanding of the reactivity of acetates, we report here the results of a mechanistic study of the OH-induced oxidation of isopropyl, isobutyl, and *tert*-butyl acetates.

2. Experimental Section

Experiments were performed in an evacuable environmental chamber comprising a Pyrex reactor of 977 liters surrounded by two set of 40 fluorescent tubes (Philips TL05 and TL03). The emissions of these “black lamps” are respectively centered on 360 and 420 nm. Moreover, 16 arc lamps provide an irradiation with a broad spectral range from 300 to 600 nm. The reactor contains a multiple reflection optical system interfaced to a FTIR spectrometer (BOMEM DA8-ME). Details of this environmental chamber have been described previously by Doussin et al.¹²

Hydroxyl radicals were generated by photolyzing methyl nitrite. Methyl nitrite was prepared by adding a dilute solution of H_2SO_4 to a mixture of NaNO_2 and methanol.¹³ The initial concentrations of the reactants (acetate, methyl nitrite, and NO) were in the ppm range in a synthetic mixture of 80% N_2 and 20% O_2 (NO was added to limit formation of nitrate radicals and ozone). All experiments were conducted at 298 ± 5 K with

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TABLE 1: Integrated Band Intensities of the Main Infrared Absorption Band of Acetates and Their Oxidation Products

compound	main absorption band (cm ⁻¹)	IBI (cm/molecule) ^a	ref
isopropyl acetate	1306–1202	$(5.01 \pm 0.09) \times 10^{-17}$	this work
isobutyl acetate	1320–1150	$(5.69 \pm 0.18) \times 10^{-17}$	this work
<i>tert</i> -butyl acetate	1305–1215	$(3.89 \pm 0.05) \times 10^{-17}$	this work
acetoxyacetone	1313–1137	$(3.30 \pm 0.11) \times 10^{-17}$	this work
acetone	1260–1150	$(1.02 \pm 0.02) \times 10^{-17}$	this work
peroxyacetyl nitrate	1330–1255	2.08×10^{-17}	29

^a Calculated using natural logarithm.

continuous irradiation during one or 2 h. Compounds were monitored by acquiring infrared spectra every about 5 min (corresponding to 100 coadded interferograms) with a resolution of 0.7 cm⁻¹ and a path length between 96 and 186 m.

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 absorption band of acetates and their oxidation products are presented in Table 1. Concerning acetic acid, acetoxyacetaldehyde, acetic anhydride, and formic acetic anhydride, these data have already been published by Picquet-Varrault et al.⁸

Chemicals. Methyl nitrate, formic acetic anhydride (CH₃C(O)OCHO), propionic acetic anhydride (CH₃C(O)OC(O)C₂H₅), acetoxyacetaldehyde (CH₃C(O)OCH₂CHO), and acetoxyacetone (CH₃C(O)OCH₂C(O)CH₃), which were supposed to be oxidation products of isopropyl, isobutyl, and *tert*-butyl acetates, were synthesized.⁸ Other organic reagents were obtained from commercial sources: isopropyl and isobutyl acetates were from Fluka ($\geq 99\%$), *tert*-butyl acetate was from Aldrich ($\geq 99\%$), acetone and acetic acid were from Prolabo ($\geq 99\%$). Synthetic air was generated using O₂ (quality N45, $\geq 99.995\%$, H₂O ≤ 5 ppm, Air Liquide) and N₂ (from liquid nitrogen evaporation, $\geq 99.995\%$, H₂O ≤ 5 ppm, Linde).

3. Results and Discussion

Isobutyl Acetate. To investigate the mechanism of the OH-induced oxidation of isobutyl acetate, two experiments were performed by photolyzing CH₃ONO/isobutyl acetate/NO mixtures. Concentration ranges were 1–7 ppm for methyl nitrite, 2–3 ppm for isobutyl acetate, 0.5–2 ppm for NO. Reactants and products were analyzed by FTIR spectrometry. Figure 1 shows a residual spectrum acquired after ~ 3000 s obtained by subtraction of remaining reactants (isobutyl acetate, NO, CH₃ONO) and products arising from CH₃ONO photolysis (HNO₃, NO₂, CH₃ONO₂, CO, HCHO, HCOOH, HONO, CO₂). These last compounds were identified and quantified by photolyzing methyl nitrite alone. Remaining products, which are attributed to oxidation of isobutyl acetate, are acetone, formic acetic anhydride, acetic acid, and acetoxyacetaldehyde. In a lesser extent, some organic nitrates which are peroxyacetyl, peroxyisobutyryl (PiBN), and isopropyl nitrates were also detected. Formaldehyde, formic acid, and methyl nitrate may also be oxidation products of isobutyl acetate, but their formation due to this reaction was not confirmed since these compounds are also largely produced by the photolysis of CH₃ONO.

It can be seen, on the plot of products vs. loss of isobutyl acetate (Figure 2), that all oxygenated oxidation products (acetone, formic acetic anhydride, acetoxyacetaldehyde, and acetic acid) whose plots have initial slope different from zero are primary products. PAN and PiBN were indistinguishable

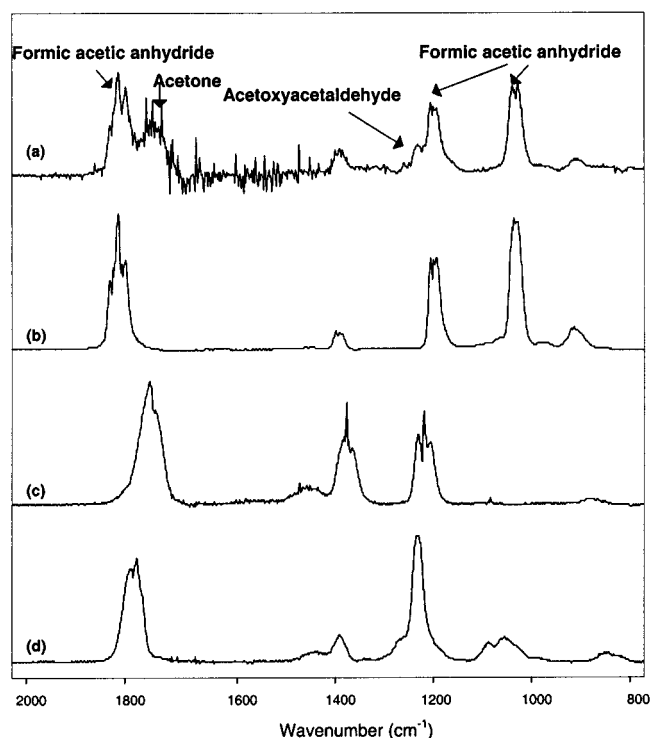


Figure 1. (a) Residual infrared spectrum after the photolysis of CH₃ONO/isobutyl acetate/NO mixture obtained by subtraction of remaining reactants and products arising from CH₃ONO photolysis, compared with reference spectra of (b) formic acetic anhydride, (c) acetone, and (d) acetoxyacetaldehyde.

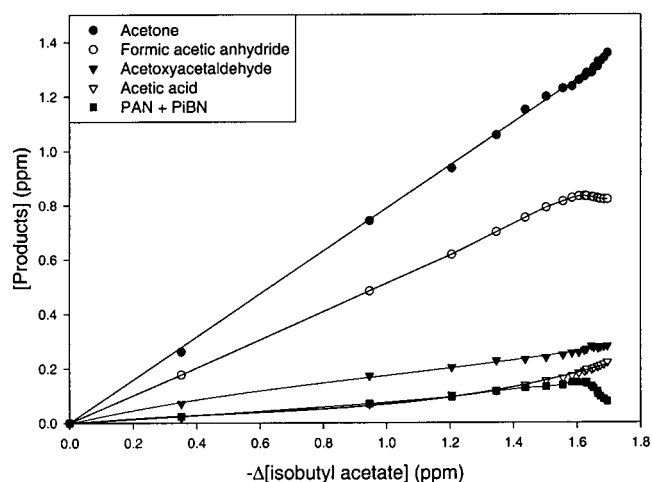


Figure 2. Experimental plots of the formation of oxidation products vs. loss of isobutyl acetate.

due to near detection limit concentrations and similar absorption spectra. Hence we were unable to obtain precise kinetic profiles. Therefore, it was difficult to determine if these compounds are primary and/or secondary products.

Acetone, which is the main oxidation product, is formed conjointly to acetic acid or formic acetic anhydride by the decomposition of CH₃C(O)OCH(O[•])CH(CH₃)₂ (Scheme 1A, channel 5) and CH₃C(O)OCH₂C(O[•])(CH₃)₂ radicals (Scheme 1B, channel 6). Another possible formation channel of acetone is the α -ester rearrangement^{8,10,14,15} of the CH₃C(O)OCH(O[•])CH(CH₃)₂ radical (Scheme 1A, channel 2). This rearrangement proceeds by an H-atom transfer through a five-membered ring transition state as shown in Scheme 2. It leads to the formation of acetic acid and CH(CH₃)₂C(O)OO[•], which can react with NO₂ to form PiBN and/or with NO to form acetone. However,

A

$$\begin{array}{c} \text{OH} \\ | \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$

$\xrightarrow{\text{O}_2, \text{NO}} \text{NO}_2$

$$\begin{array}{c} \text{O} \quad \text{CH}_3 \\ || \quad | \\ \text{CH}-\text{CH}-\text{CH}_3 \\ \text{(isobutyraldehyde)} \end{array} + \text{CH}_3 + \text{CO}_2 \xrightarrow{\text{decomp. (1)}} \begin{array}{c} \text{O} \quad \text{CH}_3 \\ || \quad | \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{CH}-\text{CH}-\text{CH}_3 \end{array}$$

$\xrightarrow{\text{rearrang. (2)}} \begin{array}{c} \text{O} \\ || \\ \text{H}_3\text{C}-\text{C}-\text{OH} \end{array}$

$\xrightarrow{\text{O}_2} \begin{array}{c} \text{CH}_3 \text{ O} \\ | \quad || \\ \text{H}_3\text{C}-\text{CH}-\text{C}-\text{O}-\text{O}^\cdot \end{array} \xrightarrow{\text{NO}_2} \begin{array}{c} \text{CH}_3 \text{ O} \\ | \quad || \\ \text{H}_3\text{C}-\text{CH}-\text{C}-\text{O}-\text{O}-\text{NO}_2 \end{array} \text{ (PIBN)}$

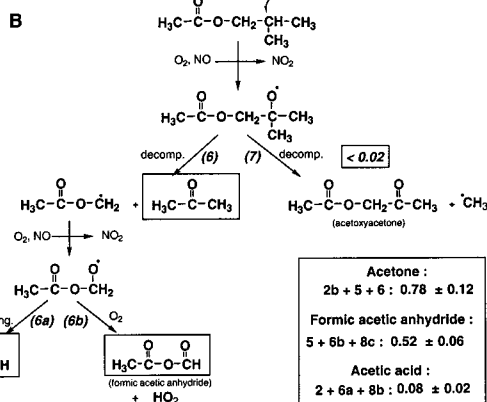
$\xrightarrow{\text{NO}} \begin{array}{c} \text{CH}_3 \text{ O} \\ | \quad || \\ \text{H}_3\text{C}-\text{CH}-\text{C}-\text{O}^\cdot \end{array} \xrightarrow{\text{CO}_2} \begin{array}{c} \text{O} \\ || \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$

$\xrightarrow{\text{isomer. (4)}} \begin{array}{c} \text{O} \quad \text{OH} \quad \text{CH}_3 \\ || \quad | \quad | \\ \text{H}_2\text{C}-\text{C}-\text{O}-\text{CH}-\text{CH}-\text{CH}_3 \end{array} \xrightarrow{\text{O}_2, \text{NO}} \text{NO}_2$

$\xrightarrow{\text{decomp. (5)}} \begin{array}{c} \text{O} \quad \text{O} \\ || \quad || \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{CH} \end{array} + \text{H}_3\text{C}-\text{CH}-\text{CH}_3 \xrightarrow{\text{O}_2, \text{NO}} \text{NO}_2$

$\xrightarrow{\text{O}_2} \begin{array}{c} \text{O} \\ || \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$

$\xrightarrow{\text{decomp.}} \text{HCHO} + \text{CO}_2 + \begin{array}{c} \text{OH} \quad \text{CH}_3 \\ | \quad | \\ \text{CH}-\text{CH}-\text{CH}_3 \end{array} \xrightarrow{\text{O}_2} \begin{array}{c} \text{O} \quad \text{CH}_3 \\ || \quad | \\ \text{CH}-\text{CH}-\text{CH}_3 \end{array}$


$$\begin{array}{c}
 \text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}^+}{\text{C}}-\text{CH}(\text{CH}_3)-\text{CH}_3 \longrightarrow \text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}^+}{\text{C}}-\text{CH}(\text{CH}_3)-\text{CH}_3 \xrightarrow{\text{rearrange}} \text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}^+}{\text{C}}-\text{CH}(\text{CH}_3)-\text{CH}_3 + \text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \\
 \downarrow \text{O}_2 \\
 \text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{OONO}_2 \xrightleftharpoons{\text{NO}_2} \text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{OO}^+ \xrightarrow{\text{NO}} \text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 + \text{CO}_2
 \end{array}$$

The decrease of the slope of formic acetic anhydride at the end of the experiment indicates that this compound is subject to secondary loss processes (see Figure 2). Its reaction with OH radicals is estimated to be slow ($1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ according to the SAR method¹⁶). On another hand, it is well known that anhydrides react easily with water. Hence, we suspect that the main loss process of formic acetic anhydride is hydrolysis with adsorbed water on the walls of the reactor and to a lesser extent hydrolysis in the gas phase. These reactions would lead to the formation of secondary acetic acid and hence would explain the increase of its slope at the end of the experiment (Figure 2).

[illegible]
$$\begin{aligned}
\text{isobutyl acetate} + \text{OH} &\rightarrow \text{acetone} + \text{formic acetic anhydride} & k_1 \quad (1) \\
\text{isobutyl acetate} + \text{OH} &\rightarrow \text{acetone} + \text{acetic acid} & k_2 \quad (2) \\
\text{isobutyl acetate} + \text{OH} &\rightarrow \text{acetone} & k_3 \quad (3) \\
\text{isobutyl acetate} + \text{OH} &\rightarrow \text{acetoxyacetaldehyde} & k_4 \quad (4) \\
\text{formic acetic anhydride} &\rightarrow \text{acetic acid} & k_5 \quad (5) \\
\text{oxyacetaldehyde} + \text{OH} &\rightarrow \text{Products} & k_6 \quad (6) \\
\text{acetic acid} + \text{OH} &\rightarrow \text{Products} & 8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},^{18} \quad (7)
\end{aligned}$$

The constants k_1 to k_6 were adjusted in order to allow the simulated curves to fit the experimental points. The sum of the OH + acetate rate constants is fixed to the overall value of $6.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value was determined in our group from a previous study.⁷ OH concentration was estimated at any time of the experiment using the decrease of the acetate. It was first checked that the reaction of acetate

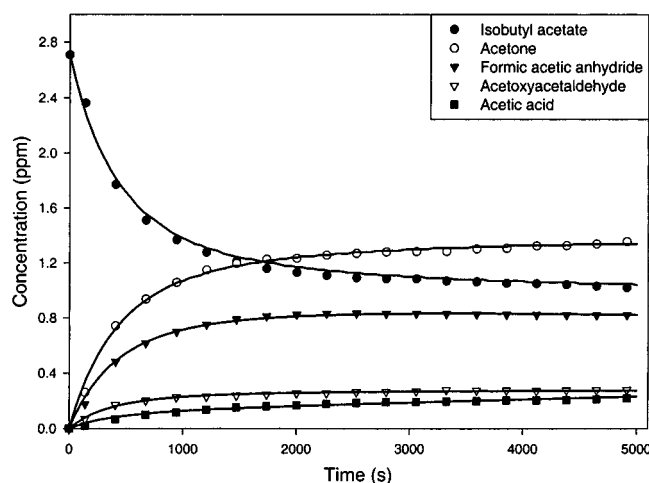


Figure 3. Simulated plots (full curves) and experimental points for the OH-induced oxidation of isobutyl acetate.

TABLE 2: Oxidation Products of Isobutyl Acetate and Their Formation Yields

product	formation yields
acetone	0.78 ± 0.12
formic acetic anhydride	0.52 ± 0.06
acetoxyacetaldehyde	0.18 ± 0.06
acetic acid	0.08 ± 0.02
acetaldehyde	<0.07
acetoxyacetone	<0.02

toward NO_3 radicals, which can be formed by the reaction of NO_2 with ozone, was negligible. Concentrations of NO_3 radicals during the experiments were estimated by measuring N_2O_5 ($\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5$).

Fitted curves are compared to experimental points in Figure 3 and final formation yields of the products are presented in Table 2. These formation yields are averages of the two experiments performed on this acetate. Indicated errors of yields take into account the estimated uncertainties on reactant and product IR absorption band calibrations and the uncertainties on the fitted rate constants. These last uncertainties are determined during the FACSIMILE software fitting procedure. After having calculated the best value of each constant for the fit, the solver makes some further iterations by slightly modifying each fitted constant in order to estimate the sensitivity of

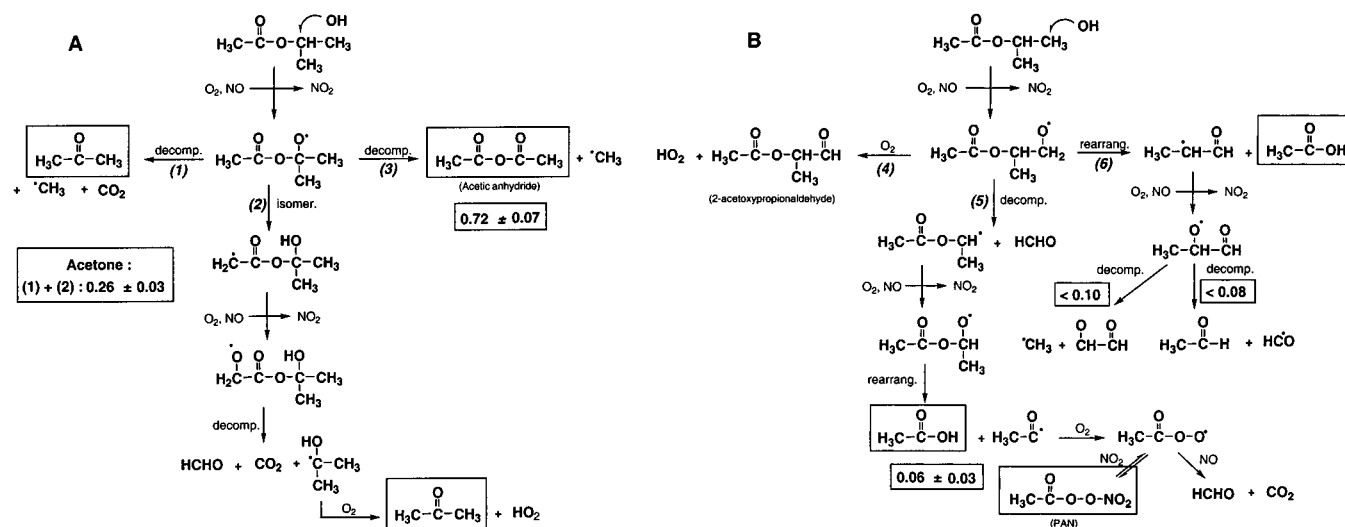
the fit to each of them. Using this information, it calculates final uncertainties for a confidence range of 95% (see FACSIMILE v3.0, Technical Reference). Errors due to the quantification of compounds in infrared spectra have been taken into account, but they are not significant compared to the previous ones. From these data, branching ratios of the channels of OH-induced oxidation of isobutyl acetate were determined (see Scheme 1).

In the oxidation scheme of isobutyl acetate, we were not able to quantify the relative importance of the abstraction sites of OH radicals since some oxidation products can be formed by several of them. For example, acetone can be formed by a decomposition and/or a rearrangement of $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{O}^\bullet)\text{CH}(\text{CH}_3)_2$ radicals (Scheme 1A, channels 2 and 5) and/or a decomposition of $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O}^\bullet)(\text{CH}_3)_2$ radicals (Scheme 1B, channel 6). Nevertheless, in order to have an estimation of their relative importance, some hypothesis can be made using the literature data: Christensen et al.¹⁵ have shown that 65% of the $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{O}^\bullet$ radicals undergo α -ester rearrangement while 35% react with O_2 . Moreover, since acetic acid has a total formation yield of 0.08 ± 0.02 , the branching ratio of the channel 6a on Scheme 1B (which is one of its formation channel) is ≤ 0.08 . Using the branching ratio between the reaction with O_2 and the rearrangement given by Christensen et al.,¹⁵ we can deduce that the channel 6b, which leads to the formation of formic acetic anhydride by the reaction with O_2 of $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{O}^\bullet$ radicals, has a branching ratio ≤ 0.05 . Compared to the total formation yield of this anhydride, this channel is of minor importance. Moreover, since acetaldehyde was not detected in infrared spectra, the channel leading to the coformation of acetaldehyde and acetic acid or formic acetic anhydride by an H-abstraction at the primary carbon of the alkyl function (Scheme 1C, channels 8b and 8c) is also negligible. Therefore, the major formation process of formic acetic anhydride is a decomposition of the $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{O}^\bullet)\text{CH}(\text{CH}_3)_2$ radicals via a C–C bond scission. Similar observations indicate that acetone is mainly formed by the same channel.

No previous mechanistic study has been carried out on isobutyl acetate. Hence, we show here the first results.

Isopropyl Acetate. The mechanism of OH-induced oxidation of isopropyl acetate was investigated by photolyzing CH_3ONO /isopropyl acetate/ NO mixtures. Three experiments were performed and concentration ranges were 6–9 ppm for CH_3ONO ,

SCHEME 3: Oxidation Scheme of Isopropyl Acetate Obtained from the Generally Accepted Process of VOC Oxidation and from the Formation Yields of the Detected Products (framed)



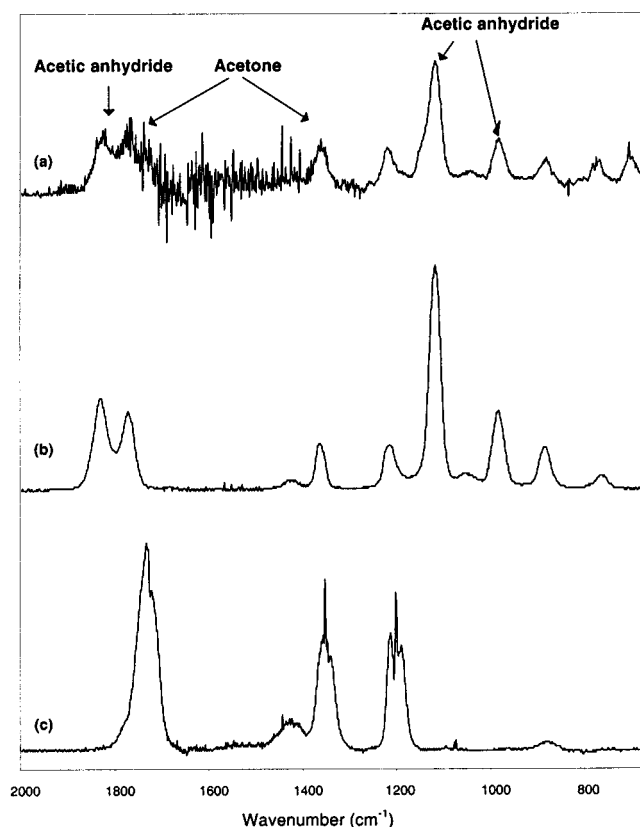


Figure 4. (a) Residual infrared spectrum after the photolysis of CH_3ONO /isopropyl acetate/NO mixture obtained by subtraction of remaining reactants and products arising from CH_3ONO photolysis, compared with reference spectra of (b) acetic anhydride and (c) acetone.

SCHEME 4

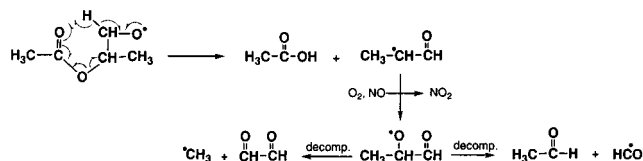


TABLE 3: Oxidation Products of Isopropyl Acetate and Their Formation Yields—Comparison with Previous Studies

product	this work	Tuazon et al. ¹⁰	Le Calvé ¹¹	Kerr and Stocker ⁹
acetic anhydride	0.72 ± 0.07	0.76 ± 0.07	observed	0.10
acetone	0.26 ± 0.03	0.24 ± 0.02	observed	
acetic acid	0.06 ± 0.03	0.09 ± 0.03	observed	
acetaldehyde	<0.08	<0.01		
PAN	0.09 ± 0.03^a	observed		observed
methyl nitrate			observed	observed

^a Upper limit.

2–3 ppm for isopropyl acetate, and 2–3 ppm for NO. From the infrared spectra shown in Figure 4, all main oxidation products of isopropyl acetate were identified. They are acetic anhydride and acetone and to a lesser extent, acetic acid and peroxyacetyl nitrate (PAN). As for isobutyl acetate, formation yields of products were calculated using numerical simulation (see Table 3) and branching ratios of the channels of OH-induced oxidation of isopropyl acetate were deduced (see Scheme 3). Since the formation yield of PAN depends on the ratio NO/NO₂, it was estimated by another method described elsewhere.⁸ As it can be seen in Table 3, the sum of the yields, which is near unity within the experimental uncertainties, reveals that all main oxidation products have been detected.

Acetic anhydride is the major product with a formation yield equal to 0.72 ± 0.07 . It is formed by a decomposition of the $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O}^\bullet)(\text{CH}_3)_2$ radical via a C–C bond cleavage (Scheme 3A, channel 3). To a lesser extent, the decomposition via a C–O bond cleavage and/or an isomerization of this alkoxy radical lead to the formation of acetone (Scheme 3A, channels 1 and 2). Since these channels lead to the same product, we cannot distinguish them.

Moreover, primary formation of acetic acid and PAN was observed, indicating that the α -ester rearrangement of the $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{O}^\bullet)\text{CH}_3$ radical, which is formed by the decomposition of the $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{CH}_2\text{O}^\bullet$ radical, occurs (Scheme 3B, channel 5). Nevertheless, this process is of minor importance since the H-abstraction occurs preferentially at the tertiary carbon instead of at the primary carbon of the alkyl group.

Finally, even if acetaldehyde and glyoxal were not detected in infrared spectra since they react very rapidly with OH radicals ($k_{\text{acetaldehyde}+\text{OH}} = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{\text{glyoxal}+\text{OH}} = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,¹⁹), they could be formed by a β -ester rearrangement of the $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{CH}_2\text{O}^\bullet$ radical (see Scheme 4 and Scheme 3B, channel 6). According to their FTIR detection limits and accounting for secondary reactions with OH, any formation of acetaldehyde and glyoxal would have a molar yield < 0.08 and < 0.10 , respectively, which suggests that these processes are minor.

This study can be compared with the previous ones.⁹⁻¹¹ Tuazon et al.¹⁰ have detected the same oxidation products with formation yields in good agreement with ours (see Table 3). They also observed the formation of PAN but this one was not quantified. The mechanistic study carried out by Le Calvé¹¹ showed acetic anhydride, acetone, and acetic acid as oxidation products, but their formation yields were not precisely determined. Kerr and Stocker⁹ observed the formation of acetone and methyl nitrate as oxidation products of isopropyl acetate. Methyl nitrate is formed conjointly to acetic anhydride by the decomposition of the $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O}^\bullet)(\text{CH}_3)_2$ radicals, which leads to CH_3^\bullet radical formation (Scheme 3A, channel 3). However acetic anhydride was not observed since, according to the authors, it was unlikely to be eluted from the gas-chromatography columns used. From these observations, the authors estimated the branching ratio of the decompositions via a C—C and a C—O cleavages of $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O}^\bullet)(\text{CH}_3)_2$ radicals. They are respectively 0.30 and 0.10. These values are much lower than ours as well than those of Tuazon et al.¹⁰ To understand the origin of this disagreement, it would have been interesting to determine the formation yield of methyl nitrate (due to the oxidation of the acetate) in our study and in the one of Tuazon et al.¹⁰ Unfortunately, it was not possible since the source of hydroxyl radicals (methyl nitrite photolysis) produces large amounts of methyl nitrate, whereas Kerr and Stocker used HONO as OH source. In this previous study, PAN was also detected as a secondary oxidation product. According to the authors, its formation is due to the OH-induced oxidation of acetone and acetic anhydride. However, since these compounds are not very reactive, it seems more probable that PAN is formed as a primary product by the α -ester rearrangement and that its apparent “secondary” formation is due to the very low concentration of NO_2 at the beginning of their experiments.

***tert*-Butyl Acetate.** The mechanism of OH-induced oxidation of *tert*-butyl acetate was investigated by photolyzing a CH₃-ONO/*tert*-butyl acetate/NO mixture (7:2.5:2 ppm). Figure 5 shows a residual spectrum obtained by subtraction of remaining reactants and products arising from methyl nitrite photolysis. Oxidation products are acetone, acetic anhydride, and acetic

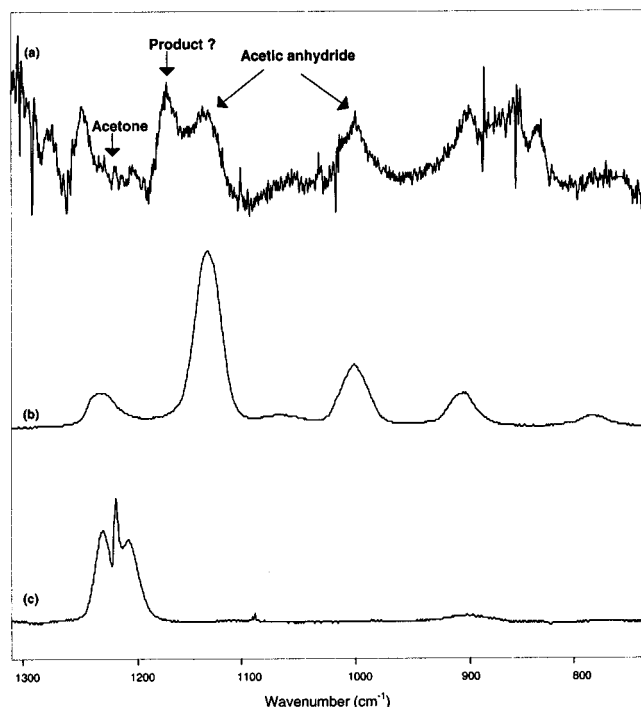


Figure 5. (a) Residual infrared spectrum after the photolysis of $\text{CH}_3\text{ONO}/\text{tert}$ -butyl acetate/ NO mixture obtained by subtraction of remaining reactants and products arising from CH_3ONO photolysis, compared with reference spectra of (b) acetic anhydride and (c) acetone.

acid. In addition, an “unknown product” that absorbs at 1247 and 1170 cm^{-1} was observed. From the commonly admitted process of VOC oxidation, two compounds are suspected: 2-acetoxy-2-methylpropionaldehyde ($\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CH}_3)_2\text{CHO}$) and/or *tert*-butyl glyoxalate ($\text{CHOC}(\text{O})\text{OC}(\text{CH}_3)_3$). However, these two compounds are not commercially available and their syntheses were not successful. Therefore, these hypotheses remain unverified.

Final formation yields of the products are compared to those of the literature in Table 4, and branching ratios of the channels of OH-induced oxidation of *tert*-butyl acetate were deduced (see Scheme 5).

SCHEME 5: Oxidation Scheme of *tert*-Butyl Acetate Obtained from the Generally Accepted Process of VOC Oxidation and from the Formation Yields of the Detected Products (framed)

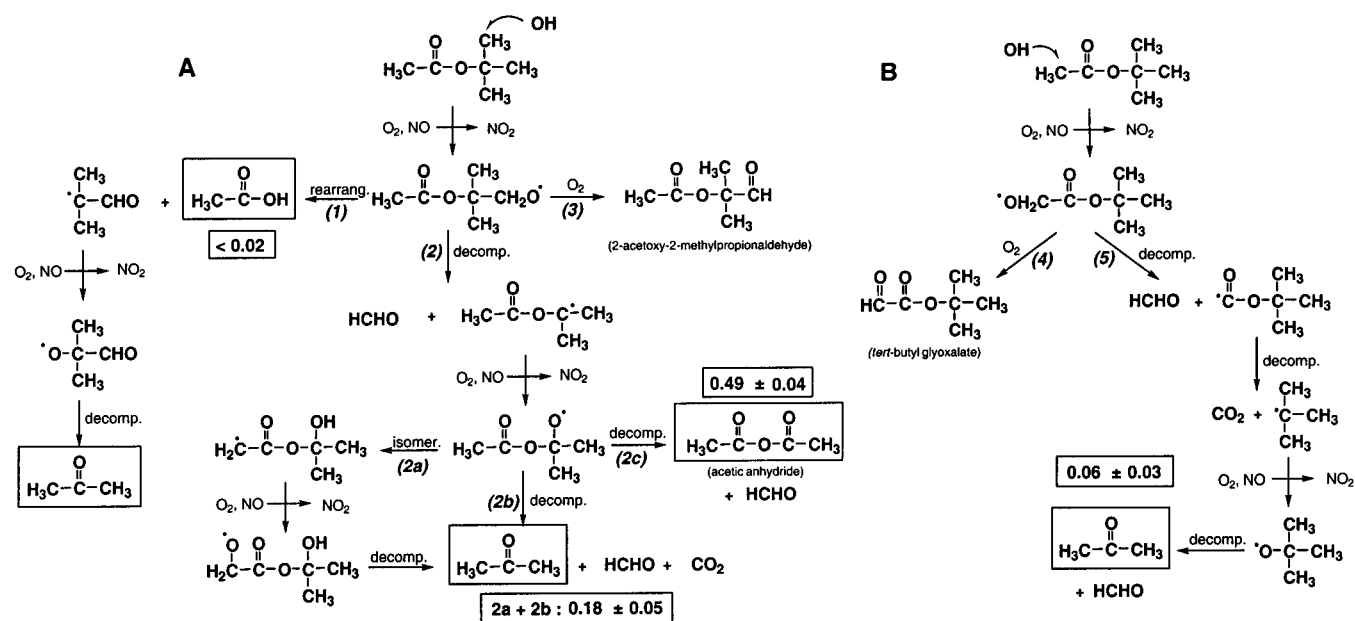


TABLE 4: Oxidation Products of *tert*-Butyl Acetate and Their Formation Yields—Comparison with the Previous Study

product	this work	Tuazon et al. ¹⁰
acetic anhydride	0.49 ± 0.04	0.49 ± 0.05
acetone	0.24 ± 0.04	0.20 ± 0.02
acetic acid	<0.02	<0.07

Even if all oxidation products were not identified, we can observe that the main product is acetic anhydride with a formation yield of 0.49 ± 0.04 . It is formed by a decomposition of the $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CH}_3)_2\text{CH}_2\text{O}^\bullet$ radical followed by a decomposition of the $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O}^\bullet)(\text{CH}_3)_2$ radical via a C—C bond scission (Scheme 5A, channel 2c). Several processes can form acetone, such as decomposition of $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CH}_3)_2\text{CH}_2\text{O}^\bullet$ radicals (Scheme 5A, channels 2a and 2b) and/or $\text{O}^\bullet\text{CH}_2\text{C}(\text{O})\text{OC}(\text{CH}_3)_3$ radicals (Scheme 5B, channel 5). However, using the results obtained for isopropyl acetate oxidation, we were able to distinguish some of them. Hence, as shown in Scheme 5A, an H-atom abstraction from the $-\text{C}(\text{CH}_3)_3$ group can lead, after decomposition of the $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CH}_3)_2\text{CH}_2\text{O}^\bullet$ radical, to the same alkoxy radical as the one obtained after an H-atom abstraction from the tertiary carbon of isopropyl acetate ($\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O}^\bullet)(\text{CH}_3)_2$). Therefore, based on the formation yield of acetic anhydride and the ratio between the C—C and the C—O bond cleavage of the $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O}^\bullet)(\text{CH}_3)_2$ radical obtained for isopropyl acetate (Scheme 3A), we can deduce that the sum of the channels 2a and 2b of the Scheme 5A has a branching ratio of 0.18 ± 0.05 . Acetic acid could be formed conjointly to acetone by a β -ester rearrangement of the $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CH}_3)_2\text{CH}_2\text{O}^\bullet$ radical similar to the one presented in Scheme 4. However, acetic acid was detected only as secondary product, suggesting that this process is negligible. According to the FTIR detection limit, any primary formation of acetic acid would have a molar yield <0.02 .

All these results and observations are in good agreement with those obtained by Tuazon et al.¹⁰ who carried out the only previous study published. Moreover, these authors have not detected acetic acid, which agrees with our results.

Reactivity of OH with Alkyl Acetates. From the oxidation schemes elucidated within this work for isopropyl, isobutyl, and

tert-butyl acetates, some information concerning the first step of the oxidation process, i.e., H-abstraction by OH radicals can be given. For isopropyl acetate, as shown in Scheme 3, OH radicals react preferentially on the $-\text{CH}<$ function ($\sim 98 \pm 10\%$) and to a lesser extent on the $-\text{CH}_3$ one ($\sim 7 \pm 3\%$). However, concerning isobutyl acetate, even if branching ratios of the different attacks of OH could not precisely be quantified, we observe that H-abstraction occurs predominantly on the $-\text{CH}_2-$ function (Scheme 1A) instead of on the $-\text{CH}<$ one (Scheme 1B). This last observation is unexpected since it is common to consider that H-abstraction occurs preferentially on tertiary carbons ($-\text{CH}<$), then on secondary carbons ($-\text{CH}_2-$), and finally on primary carbon ($-\text{CH}_3$) due to the stabilizing effect of the substituted alkyl groups on the radicals R^\bullet . The ester function seems to play a significant role in this behavior. Hence, several authors^{20–22} have studied the temperature dependence of the rate constants for the OH reactions with acetates. They have observed different temperature dependencies at high and low temperatures. This suggests that the dominant overall abstraction mechanism is changing over this temperature range (240–370 K): a direct H-abstraction predominant at low temperatures and an H-abstraction via the formation of an adduct between OH and acetates. This intermediate can either decompose back to reactants or eliminate H_2O predominant at high temperatures. In this case, this adduct would promote hydrogen abstraction from the carbon in the α -position to the acetate function. The formation of such adducts is also strongly suspected for other oxygenated compounds: alcohols, ethers, carbonyl compounds.^{23–26} For ketones in particular, Wallington and Kurylo²⁶ and Franck et al.²⁵ suggest that a six-membered ring adduct promotes the H-abstraction on the carbon in β -position to the carbonyl group. For esters, this hypothesis would be equivalent to the promotion of the H-abstraction on the carbon in the α -position to the acid group, confirming our observations.

It is interesting to notice that for all other acetates for which mechanistic studies have been carried out (methyl,¹⁵ ethyl,^{8,10} isopropyl,^{9–11} *n*-propyl,^{8,9} and *tert*-butyl¹⁰ acetates), this unexpected result could not have been recognized. Indeed, for ethyl and isopropyl acetates, carbons in the α -position were the most branched carbon of the molecule; for *n*-propyl acetate, attacks of OH radicals on carbons located in α and β could not be differentiated; and for methyl and *tert*-butyl acetates, H-abstraction can occur only on one carbon of the alkyl function. So these results on isobutyl acetate are the first experimental confirmation, by a mechanistic study, of the promotion of the H-abstraction on the carbon in the α -position.

For isopropyl and isobutyl acetates, these experimental results were compared with SAR estimations.²⁷ Concerning isopropyl acetate, our observations are in agreement within experimental uncertainties with the SAR calculations since this one estimates that the attack on the tertiary carbon accounts for 88% whereas the one on the primary carbon accounts for 9%. However, the results on isobutyl acetate are not in agreement with estimations that forecast a predominant OH radical attack on the tertiary carbon instead of on the secondary (51% against 39%), whereas our mechanistic study reveals that the predominant attack occurs on the $-\text{CH}_2-$ function. This disagreement reveals that the activation factor given by the SAR estimations to the carbon in the α -position to the ester function is not strong enough. However the new structure–reactivity relationship developed by Neeb²⁸ seems to be more adapted for oxygenated compounds

since it is closer to the experimental results (39% for the tertiary carbon and 51% for the secondary one in the case of isobutyl acetate).

Concerning the reactivity of alkoxy radicals, this study confirms that radicals of the type $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{O}^\bullet)\text{R}$ undergo an α -ester rearrangement leading to acetic acid and PANs as primary products (see oxidation schemes of isopropyl and isobutyl acetates). On the other hand, we observe that β -ester rearrangement is a negligible process compared to the classical ones: unimolecular decomposition, reaction with O_2 and isomerization. These observations confirm the previous studies on esters.^{8,10,14,15} Concerning the branching ratio of the three classical channels, we observe that nonlinear alkoxy radicals predominantly decompose instead of reacting with O_2 and isomerizing. For example, 2-acetoxypropionaldehyde and acetic isobutyric anhydride were not formed by the oxidation of isopropyl and isobutyl acetates (see Scheme 3B and 1A), suggesting that reactions of $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CH}_3)\text{CH}_2\text{O}^\bullet$ and $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{O}^\bullet)\text{CH}(\text{CH}_3)_2$ radicals with oxygen are negligible. Concerning isomerization, even if this process occurs (for example, in Scheme 3A), it is of minor importance compared to decomposition. As it was already discussed in a previous study on linear acetates,⁸ the predominance of decomposition is quite surprising and may be explained by the presence of the oxygenated function. However to understand this phenomenon, further experiments or theoretical calculations on oxygenated alkoxy radicals are necessary.

4. Atmospheric Implications

The main products of the OH-initiated oxidation of three nonlinear acetates were identified as acetic anhydride, acetone, acetic acid, and PAN from isopropyl acetate; acetone, formic acetic anhydride, acetoxyacetaldehyde, acetic acid, and PiBN from isobutyl acetate; and acetic anhydride and acetone from *tert*-butyl acetate. Acids and anhydrides are not very reactive toward OH and other atmospheric oxidants but are highly soluble. Hence, they may be incorporated in rain droplets before reacting in the gas-phase and so may have a significant impact in the aqueous phase, in particular on the acidity of rains. On the contrary, aldehydes have short lifetimes in the gas-phase since they are quickly photolyzed and are very reactive toward OH radicals. They contribute to the formation of photooxidants such as PANs in the atmospheric gas phase. Moreover, aldehydes and PANs are toxic compounds.

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