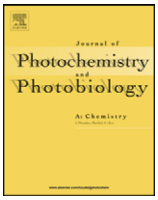
Journal of Photochemistry and Photobiology A: Chemistry 204 (2009) 75–81

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Kinetics and reaction mechanism in the oxidation of ethyl formate in the presence of NO_2: Atmospheric implications

Fabio E. Malanca*, Juan C. Fraire, Gustavo A. Argüello

INFIQC (CONICET) – Departamento de Fisicoquímica – Facultad de Ciencias Químicas – Universidad Nacional de Córdoba – Ciudad Universitaria – (5000) Córdoba – Argentina

ARTICLE INFO

Article history:
Received 29 July 2008
Received in revised form 30 January 2009
Accepted 12 February 2009
Available online 28 February 2009

Keywords:
Atmospheric oxidation
Ethyl formate
Peroxynitrates
Kinetics mechanism

ABSTRACT

The mechanism for the Cl-initiated oxidation of ethyl formate (EF) has been determined in the presence of NO_2. The Cl atom initiates the oxidation mainly at two different sites of the molecule; one corresponds to the H-atom abstraction on the carbon atom in the α-position of the oxygenated carbonylic group $(62 \pm 7)\%$ and the second to the H-atom on the carbonylic group $(44 \pm 5)\%$. The quantification of products, within experimental uncertainties, accounts for the complete disappearance of EF. The attack of Cl atoms to the methyl group, if occurring at all, should provide for less than $(2 \pm 1)\%$.

The progress of the reaction was followed by FTIR. The oxidation reaction carried out in the presence of NO_2 led to the formation of formic acid, peroxyacetyl nitrate ($CH_3C(O)OONO_2$), ethyl nitrate ($CH_3CH_2ONO_2$), acetic formic anhydride ($CH_3C(O)OC(O)H$), 1-(nitrooxy) ethyl formate and the new peroxynitrate, peroxy ethoxyformyl nitrate ($CH_3CH_2OC(O)OONO_2$, PEFN), whose thermal stability at room temperature was also measured.

1. Introduction

Esters are an important class of oxygenated volatile organic compounds present in almost any plant and are emitted naturally to the atmosphere. Esters are also formed in the atmosphere as products of the oxidation of alcohols and ethers and some of the new biofuels may represent potential emission sources of precursors. Esters are also used as food flavorings and in perfumes.

Ethyl formate (EF, $CH_3CH_2OC(O)H$) is produced by many fruit and vegetables being an important flavoring component. It occurs naturally in a variety of products, including essential oils of grasses, beer, rice, beef and cheese and volatile components of grapes and wine [1,2]. It has shown insecticidal, fungicidal, larvicidal and pesticidal properties [3–5]. Due to its intrinsic advantage of being volatile, EF has been used for fumigation of commodities and for pests associated with dried fruit [3–5]. Even a commercial product containing EF has been registered as a grain fumigant for farm storages [6]. Besides, it has been found to be formed in the photo-oxidation of diethyl ether with yields between 66 and 92% [7,8].

Therefore, the knowledge of the oxidation mechanisms of formates in the atmosphere is of relevance. Atmospheric degradation of methyl formate has been already reported. The oxidation mechanism in the presence and in the absence of NO_x at room temperature, was investigated by Wallington et al. [9] using a smog chamber. Within that study, the authors determined that chlorine atoms (the laboratory surrogate for the OH radical) react with methyl formate via attack at both groups in the molecule; the methyl group (45%) and the formate group (55%). *tert*-Butyl formate studies were also reported, though in that case, the main goal beyond the oxidation itself, was the investigation of new peroxinitrates formed through the degradation of fuel additives [10]. Other formates have been studied. The determination of the absolute rate constant for the reaction of chlorine atoms, that initiates the oxidation mechanism has been reported for ethyl, *n*-propyl and *n*-butyl [11,12]. For ethyl formate, previous reports on the overall rate constant for the gas phase reaction with chlorine atoms:

$$CH_3{-}CH_2{-}O{-}C(O)H + Cl^{\bullet} \rightarrow \text{products} \qquad (1)$$

come from Notario et al. [11], Sellevåg and Nielsen [13] and Wallington et al. [12]. Their reported values were: 1.34×10^{-11}, 1.10×10^{-11} and $9.57 \times 10^{-12}\ \text{cm}^3\ \text{molec}^{-1}\ \text{s}^{-1}$, respectively. Though the rate constant for this reaction has been exhaustively measured and deserved three papers, there was neither indication about the Cl atom attack's site nor quantification of the different channels.

Reaction kinetics of the oxidation of EF in the presence and in the absence of NO_2 at 298 K is presented in this paper using chlorine atoms to initiate the oxidation. Reaction (1) provides the precursors that in the atmosphere react with O_2 and lead to the formation of peroxy radicals which, by analogy to some other peroxy radicals, can react with atmospheric trace components such as NO and NO_2.

---

* Corresponding author. Tel.: +54 351 433 4169; fax: +54 351 433 4188.
E-mail address: fmalanca@fcq.unc.edu.ar (F.E. Malanca).

1010-6030/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2009.02.015

There are three possible paths for the initiation reaction:

$$CH_3–CH_2–O–C(O)H + Cl^\bullet \rightarrow CH_3–CH^\bullet–O–C(O)H + HCl \qquad (1a)$$

$$CH_3–CH_2–O–C(O)H + Cl^\bullet \rightarrow CH_3–CH_2–O–CO^\bullet + HCl \qquad (1b)$$

$$CH_3–CH_2–O–C(O)H + Cl^\bullet \rightarrow {}^\bullet CH_2–CH_2–O–C(O)H + HCl \qquad (1c)$$

In this work we analyzed these three paths, and quantified their yields through the products formed in the degradation reactions carried out in the presence of NO_2 added. This study will also show the formation of nitrates, in particular a new peroxy nitrate, ethyl carbonic nitric peroxy anhydride ($CH_3CH_2OC(O)OONO_2$) according to the IUPAC nomenclature, that we will refer as peroxy ethoxyformyl nitrate (PEFN) whose thermal stability is studied.

2. Experimental

2.1. Chemicals

Commercially available samples of ethyl formate (Riedel-de Haën), NO (AGA) and O_2 (AGA) were used. Oxygen was condensed while flowing at atmospheric pressure through a trap immersed in liquid air. It was then pumped under vacuum several times and transferred to a glass bulb whilst the trap was still immersed in liquid air. NO_2 was prepared adding O_2 to NO and further purification. Cl_2 was synthesized by direct reaction between HCl and $KMnO_4$ in a nitrogen flow and collected in a trap immersed in liquid air and further distillation.

2.2. Methods

In order to identify and quantify the products formed in the oxidation of EF, a standard IR gas cell (22.0 cm in length) in the optical path of a FTIR was employed. In all the cases, the assays were carried out at room temperature (298 K).

Photolyses of mixtures of EF (3.0–5.0)/Cl_2 (0.5–2.0)/NO_2 (0.5–2.0)/O_2 (1000) mbar were carried out in the IR gas cell using black lamps, that provide wavelengths longer than 330 nm.

In order to quantify both, the disappearance of EF and the appearance of products at any time, the following sequence was performed. First, a calibrated reference spectrum of pure EF was used for subtraction of any particular spectrum (analyzing simultaneously all the IR bands and not a particular feature). The same procedure was repeated for NO_2. The resulting spectrum contains therefore only the products at that particular time. Then, formic acid, peroxyacetyl nitrate, and PEFN were quantified by subtraction, in that order, of calibrated reference spectra analyzing the peaks at 637, 1163 and 1223 cm^{-1}, respectively. Ethyl nitrate and acetic formic anhydride were quantified using the values of integrated absorption bands reported previously: 1.09×10^{-17} cm molec^{-1} (between 800 and 900 cm^{-1} for the nitrate) and 5.99×10^{-17} cm molec^{-1} (between 1005 and 1095 cm^{-1} for the anhydride) [14,15]. The yields informed in the mechanism correspond to the average for all the points collected at the different times. The standard deviations associated with these mean values are also reported.

Since the photo-oxidation reactions in the presence of NO_2 lead to the formation of peroxynitrates, and since we identified a new one, a special run was carried out to obtain substantial quantities of this product using a 5 L glass round flask. The progress of this reaction was followed by IR analysis taking small samples from the reactor and bringing them into the IR cell connected on-line. The photolysis was stopped when the infrared absorption bands characteristic of NO_2 (1602 cm^{-1}) were no longer present. The mixture obtained was subsequently distilled to obtain a fraction containing high-peroxynitrate concentration which was condensed in liquid air and pumped off to eliminate the non-condensable fraction (O_2). The excess of reactant and the other products formed (ClNO, CO_2, PAN, and HC(O)OH) were eliminated by fractional distillation. The remaining sample contained finally PEFN and formic acid and was no longer manipulated.

3. Results and discussion

3.1. Mechanism of photo-oxidation initiated by Cl-atoms

Fig. 1 shows the infrared spectra obtained in the photolysis of a mixture containing EF (3.0 mbar), Cl_2 (0.5 mbar), NO_2 (0.5 mbar) and O_2 (1000 mbar). The first and the second traces were obtained before and after 40 min of photolysis, respectively. The next trace shows the products, where some of their characteristic peaks have been marked for identification, and was obtained subtracting to the second trace EF and NO_2, scaled to appropriate factors. The subtraction of reference spectra of formic acid HC(O)OH (1105 and 637 cm^{-1}) and peroxy acetyl nitrate (PAN) (1163 and 1302 cm^{-1}) to the third trace leads to the fourth one, where it is possible to identify other products such as nitrosyl chloride, ClNO (1789 and 1809 cm^{-1}) and nitric acid, HNO_3 (1325 cm^{-1}). The peaks observed at 1223 and 790 cm^{-1} were assigned to PEFN, whose reference spectrum, obtained as will be discussed later, is shown in the fifth trace. The subtraction of this peroxynitrate as well as HNO_3 and ClNO to the fourth trace leads to the sixth one, where it is observed the formation of acetic formic anhydride ($CH_3C(O)OC(O)H$), 1045 cm^{-1}, and ethyl nitrate ($CH_3CH_2ONO_2$), 1659 cm^{-1} (reference spectrum shown in the seventh trace). The subtraction of both products leads to the last trace showing clearly the presence of another substance. As it can be seen, the residual absorbance (peaks at 1758, 1686, 1295, 1162, 1098 and 833 cm^{-1}) is not negligible. Possible candidates for these absorptions derive from the following: indication of infrared bands near 600 cm^{-1}, corresponding to C–Cl bonds, is absent leading to the assumption that no other chlorinated (aside from ClNO) product is formed.

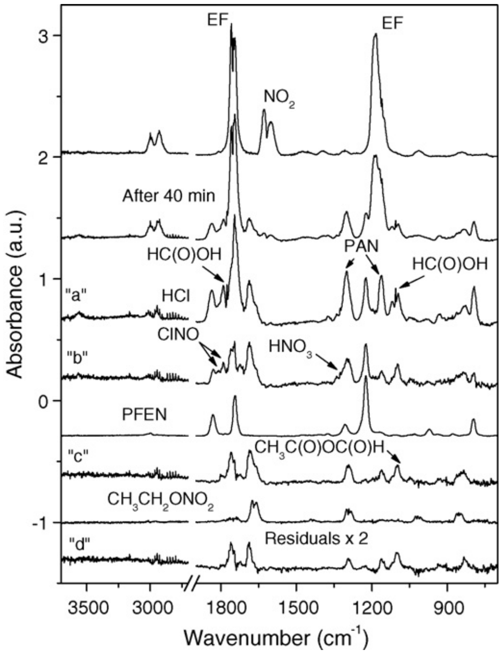


Fig. 1. Photo-oxidation of ethyl formate in the presence of NO_2. From top to bottom: before irradiation; after 40 min of photolysis; reaction products (“a”); “b” = “a”–HC(O)OH–PAN; PEFN reference spectrum (see text for details); “c” = “b”–ClNO–HNO_3–PEFN; ethyl nitrate ($CH_3CH_2ONO_2$) reference spectrum; “d” = “c”–$CH_3C(O)OC(O)H$–$CH_3CH_2ONO_2$.

Table 1
Relative yield for H-atom abstraction.

Comparison of the branching ratios for H-abstraction from selected volatile organic compounds (VOCs)

VOC	Radical	Relative rate of H-atom abstraction	Ref.
$CH_3OCH_2CH_2CH_3$	$CH_3OCH^{\bullet}CH_2CH_3$	80%	[18]
	$CH_3OCH_2CH^{\bullet}CH_3$	9.5%	
	$\mathit{CH_2^{\bullet}OCH_2CH_2CH_3}$	*9.6%*	
	$\mathit{CH_3OCH_2CH_2CH_2^{\bullet}}$	*1.4%*	
$\mathbf{CH_3CH_2O}CH_2CH_2CH_2CH_3$	$CH_3CH_2OCH^{\bullet}CH_2CH_2CH_3$	47.3%	
	$\mathbf{CH_3CH^{\bullet}O}CH_2CH_2CH_2CH_3$	**38.5%**	
	$CH_3CH_2OCH_2CH^{\bullet}CH_2CH_3$	6.9%	
	$CH_3CH_2OCH_2CH_2CH^{\bullet}CH_3$	5.6%	
	$\mathit{CH_3CH_2OCH_2CH_2CH_2CH_2^{\bullet}}$	*0.8%*	
	$\boldsymbol{CH_2^{\bullet}CH_2O}\mathit{CH_2CH_2CH_2CH_3}$	*0.8%*	
$CH_3OCH_2CH(OH)CH_3$	$CH_3OCH^{\bullet}CH(OH)CH_3$	59%	
	$CH_3OCH_2C(OH)^{\bullet}CH_3$	35%	
	$\mathit{CH_2^{\bullet}OCH_2CH(OH)CH_3}$	*4.9%*	
	$\mathit{CH_3OCH_2CH(OH)CH_2^{\bullet}}$	***0.8%***	
$(OH)CH_2CH_2OCH_2CH_2CH_2CH_3$	$(OH)CH_2CH^{\bullet}OCH_2CH_2CH_2CH_3$	57%	
	$(OH)CH_2CH_2OCH^{\bullet}CH_2CH_2CH_3$	21%	
	$(OH)CH^{\bullet}CH_2OCH_2CH_2CH_2CH_3$	13%	
	$(OH)CH_2CH_2OCH_2CH^{\bullet}CH_2CH_3$	4.4%	
	$(OH)CH_2CH_2OCH_2CH_2CH^{\bullet}CH_3$	*3.5%*	
	$\mathit{(OH)CH_2CH_2OCH_2CH_2CH_2CH_2^{\bullet}}$	*0.9%*	
$CH_3C(O)CH_2CH_2CH_3$	$CH_3C(O)CH_2CH^{\bullet}CH_3$	76%	[19]
	$CH_3C(O)CH^{\bullet}CH_2CH_3$	18%	
	$\mathit{CH_3C(O)CH_2CH_2CH_2^{\bullet}}$	*3.5%*	
	$\mathit{CH_2^{\bullet}C(O)CH_2CH_2CH_3}$	*2%*	
$CH_3\mathbf{OC(O)H}$	$CH_3\mathbf{OC(O)^{\bullet}}$	**55%**	[9]
	$CH_2^{\bullet}OC(O)H$	45%	
$\mathbf{CH_3CH_2OC(O)H}$	$\mathbf{CH_3CH^{\bullet}OC(O)H}$	**(62 ± 8)%**	**This work**
	$\mathbf{CH_3CH_aOC(O)^{\bullet}}$	**(45 ± 5)%**	
	$\mathbf{CH_2^{\bullet}CH_2OC(O)H}$	**(2 ± 1)%**	

The italicized species denote primary radicals; the bold moieties correspond to those appearing in the ethyl formate.

The absorbance at 1758 cm^{-1} indicates a C=O and the band at 1686 cm^{-1} could be ascribed to the characteristic band of the asymmetric NO_2 stretch in nitrates [16,17]. We are thus led to the conclusion that possibly an acyl nitrate could be present. This assumption is consistent with our proposed mechanism and will be proved later.

The formation of the products presented in Fig. 1 could be explained with the sequence of reactions initiated by the hydrogen abstraction by Cl atoms from EF, followed by reaction of the radical formed with O_2 to give peroxy radicals ($RO_2^{\bullet}$) (*e.g.* Ref. [18]) and their subsequent reactions with NO_2. A detailed reaction mechanism (comprising all the possible products) is shown in Schemes 1a and b. The presence of NO in the reaction schemes is a consequence of NO_2 photolysis, simultaneous to that of Cl_2, because of irradiation with black lamps.

The hydrogen abstraction of EF by chlorine atoms could, a priori, occur at three different sites of this molecule (reactions (1a)–(1c)). Nevertheless, the quantification carried out for all the products formed, accounts for the total EF reacted if only channels "a" and "b" are considered. Should channel "c" occur, its contribution would be limited to less than 1–3% of the EF reacted, according to our experimental errors. Table 1 shows the relative importance of H-atom abstraction for volatile organic compounds, [9,18,19] where it can be seen that for terminal carbon atoms, abstraction is around 1%; much lower than abstraction from carbonylic or methylenic groups. These results agree with ours, as we will discuss later.

The radicals formed, in the presence of O_2 could lead to the formation of $CH_3CH(O–O^{\bullet})OC(O)H$ (R_a), $CH_3CH_2OC(O)O_2^{\bullet}$ (R_b) and $HC(O)OCH_2CH_2O_2^{\bullet}$ (R_c), which should react mainly with NO_2 to form peroxynitrates (RO_2NO_2):

$$RO_2^{\bullet} + NO_2 \leftrightarrows RO_2NO_2 \qquad (2)$$

or with NO [20]

$$RO_2^{\bullet} + NO \rightarrow RO^{\bullet} + NO_2 \qquad (3a)$$

$$RO_2^{\bullet} + NO \rightarrow RONO_2 \qquad (3b)$$

Peroxynitrates exist in equilibrium with NO_2 and $RO_2^{\bullet}$ radicals (reaction (2)). The structure of the $RO_2^{\bullet}$ radicals determine the stability of the peroxy nitrate, being peroxyacyl nitrates relatively stable [21,22] and consequently liable to be observed in our system.

On the other hand, reaction (3) proceeds mainly through the formation of alkoxy radicals (reaction (3a)) being reaction (3b) only a minor channel according to Wallington et al. [20].

The path "a" in Scheme 1 shows the reactions following the formation of $CH_3CH(O–O^{\bullet})OC(O)H$ radicals. As stated, this radical could react with NO_2 or NO; however, the rate constants for these reactions have not been reported so far. We could expect them to be similar to the rate constants for reactions of peroxy radicals having similar structure (for example, *iso*-propyl peroxy radical, $(CH_3)_2CHO_2^{\bullet}$):

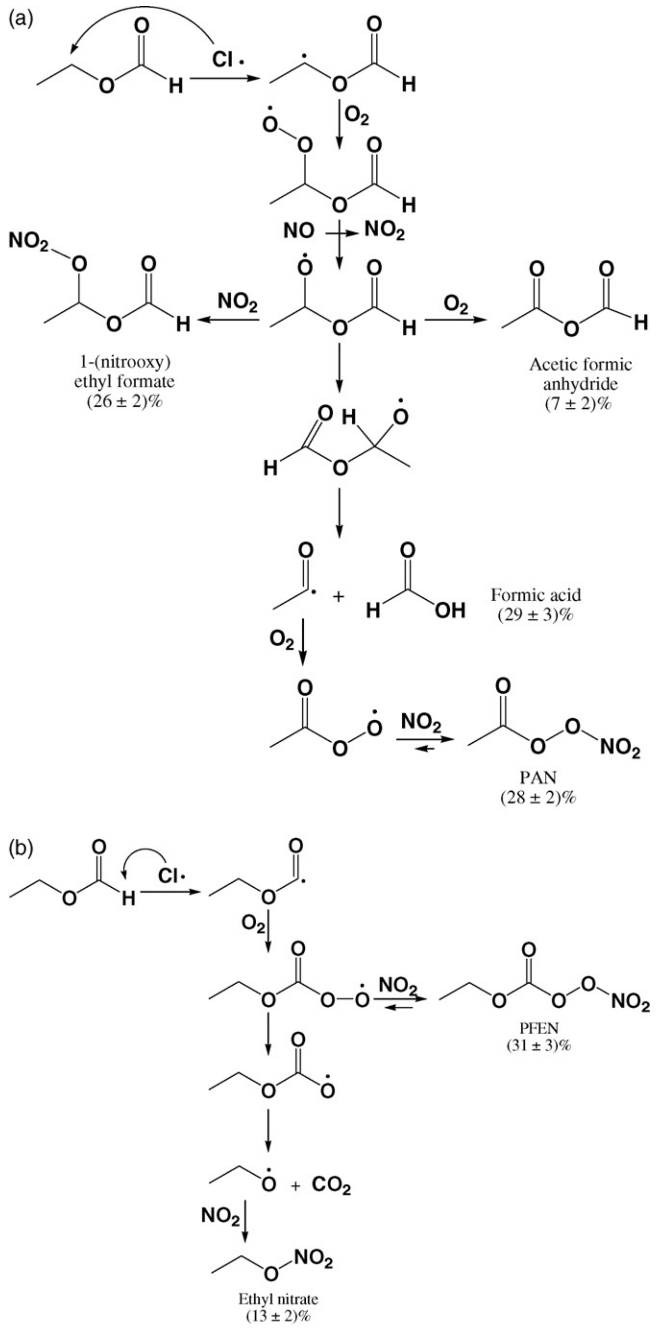
$$(CH_3)_2CHO_2^{\bullet} + NO_2 \rightarrow (CH_3)_2CHO_2NO_2 \qquad (4)$$

$$(CH_3)_2CHO_2^{\bullet} + NO \rightarrow (CH_3)_2CHO^{\bullet} + NO_2 \qquad (5a)$$

$$(CH_3)_2CHO_2^{\bullet} + NO \rightarrow (CH_3)_2CHONO_2 \qquad (5b)$$

whose rate at 298 K are $k_4 = 5.65 \times 10^{-12}$, $k_{5a} = 9.0 \times 10^{-12}$, $k_{5b} = 5.0 \times 10^{-14}$ cm^3 $molec^{-1}$ s^{-1} [23–25].

Within this assumption reaction (5b) is negligible compared with reactions (4) and (5a) [20]. Consequently, $CH_3CH(O–O^{\bullet})OC(O)H$ could react with NO_2 to form the peroxynitrate ($CH_3CH(O–O–NO_2)OC(O)H$) or with NO to form the alkoxy radical $CH_3CH(O^{\bullet})OC(O)H$. The structure of the peroxynitrate is that of an alkyl peroxynitrate (is not an acyl peroxynitrate), which are quite unstable and have thermal lifetimes of the order of



Scheme 1. Oxidation mechanism of EF in presence of NO_2. Only the major paths are represented as branches “a” and “b”.

seconds at room temperature and atmospheric pressure [21], and therefore it could decompose to re-form NO_2 and peroxy radicals (reaction (2)). Therefore, the major channel to reaction for these peroxy radicals ($CH_3CH(O–O^\bullet)OC(O)H$) is

$$CH_3CH(O–O^\bullet)OC(O)H + NO \rightarrow CH_3CH(O^\bullet)OC(O)H + NO_2 \quad (6)$$

There are several reaction paths for alkoxy radicals; reaction with O_2, NO_2, rearrangement and/or decomposition. In general, unimolecular decomposition leads to a breakdown of the carbon chain with generation of more reactive short-chain carbonyl compounds. On the other hand, reaction with O_2 or NO_2 lead to a preservation of the carbon chain and the production of less reactive and more highly substituted oxygenated species [26].

Rearrangement and decomposition seems to be the major channel for this alkoxy radical, as can be seen from the products obtained, 29% formic acid and 28% PAN (Scheme 1a). The difference between the yields for both products is within the experimental error. This kind of rearrangement, α-ester rearrangement, appears to be specific to this class of substituted oxy radicals. As other papers already expose (Ref. [26] and references cited therein) the reaction involves transfer of a hydrogen atom in a five-membered transition state from the alkyl chain of an ester to the carbonyl group in the acid function, and many studies indicate that this should occur in any ester that has hydrogen atoms available on the α-carbon of the alkyl chain [26]. Table 2 summarizes the relative yields for α-ester rearrangements for a number of selected radicals [9,27–29]. It can be seen that, irrespective of the radical considered, the rearrangement is important in all cases acquiring very broad limits.

Table 2
Relative yields for α-ester rearrangement for alkoxy radicals.

Comparison of the α-ester rearrangement, pathway relative importance for alkoxy radicals		
Radical	Relative rate	Ref.
$CH_3C(O)OCH_2O^\bullet$	65%	[27]
$HC(O)OCH_2O^\bullet$	33%	[9]
$CH_3C(O)OCH(O^\bullet)CH_3$	75%	[28]
$CH_3C(O)OCH(O^\bullet)CH_2CH_3$	10–15%	[28]
$C_2H_5C(O)OCH_2O^\bullet$	60%	[29]
$CH_3CH(O^\bullet)OC(O)H$	**(29 ± 3)%**	**This work**

The reaction of $CH_3CH(O^\bullet)OC(O)H$ with O_2 leads to acetic formic anhydride formation and explains 7% of the EF disappearance. Within the assumption that $CH_3CH(O^\bullet)OC(O)H$ could be considered similar to 2-propoxy radical ($(CH_3)_2CHO^\bullet$), reactions (7) and (8) provide rate constants for the reactivity of this radical towards O_2 and NO_2 of

$$(CH_3)_2CHO^\bullet + O_2 \rightarrow (CH_3)_2C{=}O + HO_2^\bullet \quad (7)$$

$$(CH_3)_2CHO^\bullet + NO_2 \rightarrow (CH_3)_2CHONO_2 \quad (8)$$

$k_7 = 6.9 \times 10^{-15}$ and $k_8 = 3.5 \times 10^{-11}\ \mathrm{cm^3\ molec^{-1}\ s^{-1}}$, respectively [24,30]. Being the NO_2 concentration around $(5–0.6) \times 10^{16}$ and $[O_2]$ equal to $2.5 \times 10^{19}\ \mathrm{molec\ cm^{-3}}$, and considering the ratio $\nu_8/\nu_7 = (k_8 \times [NO_2])/(k_7 \times [O_2])$ as a test indicative of the relative importance of reaction (8), we can obtain $\nu_8/\nu_7 = (17-2) \times 10^5/1.7 \times 10^5 \approx (10-1)$. These numbers reflect what it can be seen in Scheme 1; that is, on the one hand, both reactions are running in the system and on the other hand, the yield of acetic formic anhydride is lower than the yield of nitrate. In turn, the presence of the nitrate is consistent with the observation of the last IR spectrum in Fig. 1, which was quantified using the average integrated absorption cross-section for the asymmetric NO_2 stretch, reported by Tuazon et al. [17] and Atkinson et al. [31] of $(2.5 \pm 0.2) \times 10^{-17}\ \mathrm{cm\ molec^{-1}}$ for many organic nitrates.

Finally, other possible reactions for $CH_3CH(O^\bullet)OC(O)H$ radicals are the direct decomposition without rearrangement, which could occur through three possible paths:

$$CH_3–CH(O^\bullet)–O–C(O)H \rightarrow CH_3C(O)H + HC(O)O^\bullet \quad (9a)$$

$$CH_3–CH(O^\bullet)–O–C(O)H \rightarrow CH_3^\bullet + HC(O)OC(O)H \quad (9b)$$

$$CH_3–CH(O^\bullet)–O–C(O)H \rightarrow CH_3^\bullet + CO_2 + HC(O)H \quad (9c)$$

Fig. 1 does not show evidence of peaks corresponding to either acetaldehyde ($CH_3C(O)H$), formic anhydride ($HC(O)OC(O)H$) or formaldehyde ($HC(O)H$) (expected at 1353 and 2724; 1829 and 1775; 1505 and 2801 $\mathrm{cm^{-1}}$, respectively). Besides the mass balance derived for all the stable products (see below) fully accounts for the total EF reacted. Consequently, the decomposition, if it occurs at all, is a minor path in this system. A similar comparison to that presented in the analysis of the relative importance of reactions (7) and (8) (always within the assumption that $CH_3CH(O^\bullet)OC(O)H$

and 2-propoxy radicals share common properties) could be carried out to compare ν_9 and ν_7. Meunier et al. [32] determined the ratio $k_{\text{decomposition}}/k_{\text{reaction}}$ as equal to $(2.9 \pm 0.3) \times 10^{16}\,\text{cm}^{-3}$ molecule. Using this value for k_9/k_7, the ratio $\nu_9/\nu_7 = k_9/(k_7 \times [O_2])$ gives 1.2×10^{-3} thus providing a good indication for the non-observation of direct decomposition products. This is, in turn, entirely consistent with the results reported by Meunier et al., [32] who observed that the major path for 2-propoxy radicals is the reaction with O_2, and those obtained by Cavalli et al. [29] in the study of oxidation of dibasic esters, who determined that, for dimetyl succinate oxidation in the presence of NO, the decomposition channel of alkoxy radicals is negligible.

Summarizing, the quantification of products obtained from the hydrogen abstraction of the methylene group gives an overall yield for the EF reacted equal to (62 ± 7)% (see Scheme 1a).

Scheme 1b shows the mechanism resulting from the abstraction of the carbonylic H-atom. Two products could be formed in the reaction sequence; PEFN and ethyl nitrate ($CH_3CH_2ONO_2$). As mentioned previously, peroxyacyl nitrates are relatively stable, and consequently it should be expected the formation and detection of this type of compounds. The quantification of both products accounts for about (44 ± 5)% of the EF disappearance.

The identification and quantification of PEFN required sample quantities substantially higher than those used in the kinetic measurements. We proceeded to its bulk synthesis using the 5 L glass round flask and putting in there EF (9.3)/Cl_2 (2.1)/NO_2 (4.0)/O_2 (1000) mbar. Once filled, soft UV radiation was allowed and the progress in the synthesis was followed by taking small fractions at specific times that were analyzed by IR spectroscopy. The photolysis was stopped when the infrared absorption bands of NO_2 were negligible. The sample was distilled under vacuum separating the highly volatiles first (−80 °C). The remnant fraction contained only PAN, PEFN and formic acid. PAN was eliminated by further distillation and formic acid was subtracted from calibrated spectra. The resulting spectrum is the reference spectrum of PEFN shown in Fig. 1. Calculations were also carried out to obtain the IR spectrum of the PEFN with the Gaussian 03 package. The results are shown in Fig. 2 where a very good correspondence is observed with the experimental spectrum not only regarding the bands position but also the relative intensities. The frequency of the carbonylic stretch was used as base for the scaling. Though this calculated spectrum does not definitely prove that the experimental spectrum corresponds to a unique species, the set of arguments put forward along this paper speak for only PEFN.

In order to verify that formic acid is formed from the rearrangement of alkoxy radicals, photolysis of EF/Cl_2/O_2 was carried out (*i.e.* in the absence of NO_2).

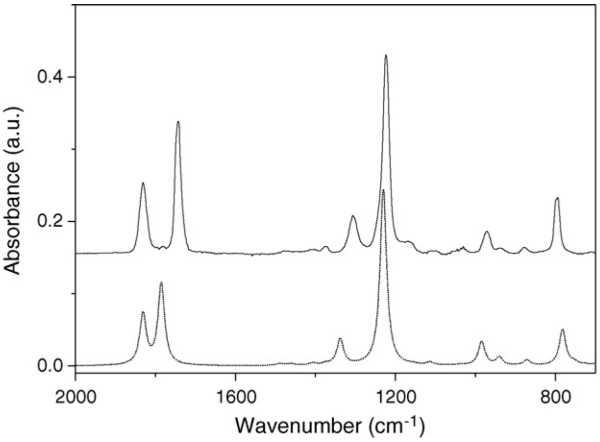


Fig. 2. Experimental (solid) and calculated (dotted) IR spectra of PEFN.

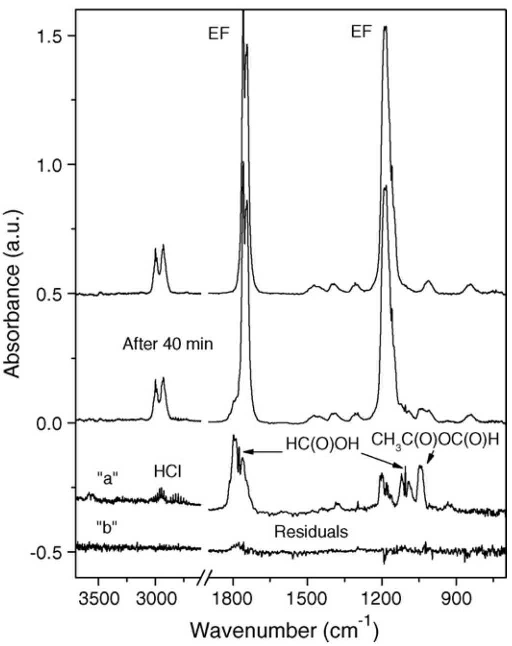


Fig. 3. Photo-oxidation of ethyl formate in the absence of NO_2. From top to bottom: before irradiation; after 40 min of photolysis; reaction products (“a”); “b” = “a”–HC(O)OH–$CH_3C(O)OC(O)H$.

Fig. 3 shows the infrared spectra collected in the photolysis of a mixture containing EF (3.0 mbar), Cl_2 (0.5 mbar), and O_2 (1013 mbar). First and second traces correspond to the spectra of the mixture before and after 40 min photolysis. The product's spectrum, shown in the third trace, was obtained by subtracting the second to the first trace, appropriately scaled. The following trace shows the residual spectrum, which was obtained through subtraction of formic acid and acetic formic anhydride, respectively. The remaining signals observed in the residual spectrum show minor absorbances that could be consequence of successive subtractions. A broad comparison with the residual spectrum of Fig. 1, where we clearly identified the presence of a substance, indicates that in this case, we can reasonably speak of aleatory noise only.

The quantification of formic acid leads to a yield of (27 ± 2)%, which is coincident, within our uncertainties, with the results obtained in the photolysis with NO_2. This can be rationalized taking into account that formic acid is formed, in both cases, through a rearrangement of the $CH_3CH(O^\bullet)OC(O)H$ radical, *i.e.* this process is not dependent on the addition of any gases to the system. The yield of acetic formic anhydride (13 ± 2)%, higher than the observed in the presence of NO_2 (7 ± 2)%, is a consequence of the fact that the reaction of the radical with NO_2 is faster than with O_2. Therefore, when the photolysis is carried out in the absence of NO_2, the product formed through reaction with O_2 (acetic formic anhydride) increases.

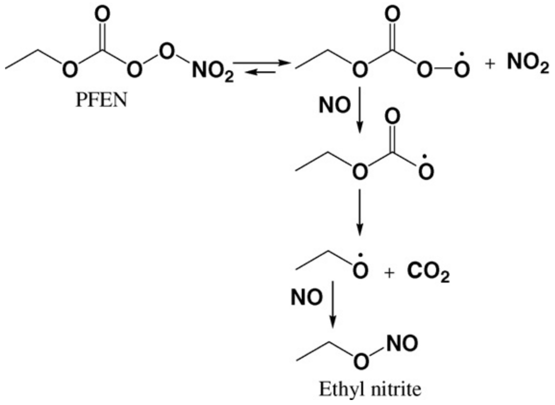
There are other possible reactions that could take place with the radicals involved in the formation of PEFN; but given the high concentration of NO_2, the equilibrium is strongly shifted so as to lower the radical concentration. Besides, if some of these radicals had the chance to react and generate their subsequent products, these could in turn react with Cl atoms and some of them with rate constants even higher that those of the parent molecules (for instance, formaldehyde reacts with Cl atoms with a rate constant of $7.5 \times 10^{-11}\,\text{cm}^3\,\text{molec}^{-1}\,\text{s}^{-1}$ [33] as compared to reaction (1)). These possible molecules have therefore been explicitly deleted from the mechanism shown in Scheme 1.

Table 3
Selected infrared absorption bands of different hydrogenated peroxy acyl nitrates.

R	R–C(O)OONO$_2$							Ref.
	Wavenumber (cm^{-1})							
CH$_3$	1842	1741	1302		1163	930	792	[35]
CH$_3$O	1835	1748	1308	1237		928	799	[10]
C$_2$H$_5$	1834	1739	1300		1043	990	793	[21,31]
C$_2$H$_5$O	**1831**	**1744**	**1308**	**1224**		**973**	**796**	**This work**
C$_6$H$_5$	1805	1739	1300	1229	1185	989	790	[34]
C$_6$H$_5$O	1844	1746	1310	1216		982	798	[21]

4. Thermal decomposition of PEFN

The study of the thermal decomposition of peroxynitrates has been usually carried out "on the fly"; that is, adding NO to the mixture obtained in the photolysis (*i.e.* the mixture comprising all the products and reactants), especially by authors that use big chambers (*e.g.* Refs. [10,21,34]). Therefore, the purity of the compound, whose thermal decomposition is studied, is not a limiting constraint as long as no side reactions are present. The sample that we obtained after the synthetic method used, contained PEFN and formic acid. The concentration of the latter did not change with time proving that there was no reaction among them. The reference spectrum of pure PEFN plotted in Fig. 1 comes from the subtraction of formic acid as impurity. The characteristic IR bands corresponding to the molecule strongly suggest that we are in the presence of a peroxynitrate. Table 3 summarizes the infrared absorption bands of a series of peroxynitrates [10,21,31,34,35]. As it can be seen, it is clear the similarity between the corresponding bands. Another proof of the identity of PEFN derives from the observation of the rate of disappearance of all the peaks assigned to it, when NO in excess is added to the sample. NO sequesters irreversibly the radicals [24] formed in the decomposition (as Scheme 2 shows) and all the IR bands (with the exception of the band at 796 cm^{-1}, which is a superposition of the decrease caused by PEFN decomposition and the increase of its decomposition product –ethyl nitrite-) decrease with the same rate thus definitely proving that all peaks correspond to the same compound. In Fig. 4 we have included the IR spectra of the mixture containing PEFN before it decomposes and that corresponding to complete decomposition. The third trace in the figure corresponds to their ratio, rather than the difference between the first two traces, that clearly shows as positive peaks the substances that were consumed and as negative ones, the substances that were formed through decomposition. According to Scheme 2, CH_3CH_2ONO is expected to be the main product of the decomposition and this is confirmed by comparing the negative bands with the reference spectrum of ethyl nitrite shown in the last trace.



Scheme 2. Sequence of reactions for the thermal decomposition of PEFN in the presence of NO.

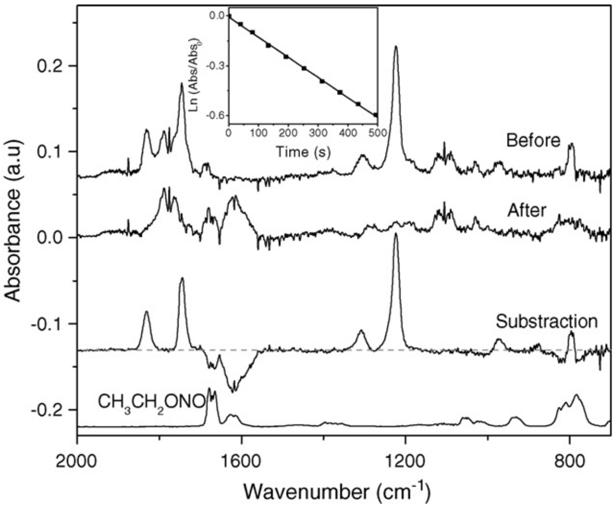


Fig. 4. Thermal decomposition of PEFN. From top to bottom: before; after complete PEFN decomposition; direct subtraction (the bands pointing upwards correspond to the decomposed substance, and the bands pointing downward correspond to the products generated); last trace corresponds to the reference spectrum of ethyl nitrite (CH_3CH_2ONO) which is a product of PEFN decomposition. The insert shows the first order decay of PEFN at room temperature. The pseudo-first order rate constant was obtained through the fitting to the experimental points.

The insert in Fig. 4 shows the first order decay curve for the thermal decomposition of PEFN in the presence of NO (4.0 mbar) at 298 K. The slope obtained by linear regression corresponds to a rate constant of $1.2 \times 10^{-3}\ s^{-1}$. A comparison between this value, and those corresponding to other acyl peroxynitrates (PAN among them) is shown in Table 4 [10,21,36]. A brief analysis reveals that the value reported for PEFN is within the expected for other peroxyacyl nitrates. Another comparison suggests that the rate constant increases by the inclusion of oxygen into the alkyl group of the molecule (compare rows 1–2; 3–4; and 5–6 of the table).

5. Atmospheric implications

As mentioned, ethyl formate has extensive uses as fumigant, pesticide, larvicide, among others, and could even be formed in the atmospheric degradation of some alcohols and ethers extensively used besides its possible formation as reaction product of biodiesels. Therefore, it could be present in the atmosphere, and the knowledge of its degradation mechanism is relevant. EF could react with OH radicals leading, in the presence of atmospheric components (especially O_2 and NO_2), to the formation of nitrates ($CH_3CH_2ONO_2$ and $CH_3CH(ONO_2)OC(O)H$) and peroxynitrates (PAN and PEFN).

The stability of nitrates is high, and peroxyacyl nitrates are relatively stable at low temperatures. Consequently, PEFN which has a rate constant of the order of other peroxynitrates could also be formed and transported in the atmosphere, especially if it reaches the regions of the free troposphere where lower temperatures further stabilize this molecule. Though the motivation of the present study was to improve the knowledge of peroxynitrates,

Table 4
Thermal rate constants of peroxyacyl nitrates R–C(O)OONO$_2$.

R	$k_{(298\,K)}$ ($\times 10^3\ s^{-1}$)	Ref.
CH$_3$	0.40	[36]
CH$_3$O	0.84	[10]
C$_2$H$_5$	0.35	[21]
C$_2$H$_5$O	**1.3**	**This work**
C$_6$H$_5$	0.31	[21]
C$_6$H$_5$O	0.53	[21]

further studies on stability and temperature dependence should be done in order to better understand the chemistry of this particular molecule.

Acknowledgements

Financial support from CONICET, SECYT-UNC and FONCYT, is gratefully acknowledged.

References

[1] J.M. Desmarchelier, Ethyl formate and formic acid: occurence and environmental fate, Postharvest News Inf. 10 (1999) 7–12.

[2] T. Hiroyasu, C. Shibanuma, H. Ishii, R. Yamada, C. Nakamura, Studies on the sugars organic acids and volatile compounds in grape-berries, Tech. Bull. Fac. Hortic., Chiba Univ. 20 (1972) 51–60.

[3] T. Simpson, V. Bikoba, E.J. Mitcham, Effects of ethyl formate on fruit quality and target pest mortality for harvested strawberries, Postharvest Biol. Technol. 34 (2004) 313–319.

[4] T. Simpson, V. Bikoba, C. Tipping, E.J. Mitcham, Ethyl formate as a postharvest fumigant for selected pest of table grapes, J. Econ. Entomol. 100 (2007) 1084–1090.

[5] L.E. Vincent, D.L. Lindgren, Hydrogen phosphide and ethyl formate: fumigation of insects infesting dates and other dried fruits, J. Econ. Entomol. 65 (1972) 1667–1669.

[6] V.S. Haritos, K.A. Damcevski, G. Dojchinov, Toxicological and regulatory information supporting the registration of VAPORMATE^{TM} as a grain fumigant for farm storages, in: E.J. Wright, M.C. Webb, E. Highley (Eds.), Australian Postharvest Technical Conference, CSIRO Stored Grain Research Laboratory, Canberra, 2003, pp. 193–198.

[7] J. Eberhard, C. Müller, D.W. Stocker, J.A. Kerr, The photo-oxidation of diethyl ether in smog chamber experiments simulating tropospheric conditions. Products studies and proposed mechanism, Int. J. Chem. Kinet. 25 (1993) 639–649.

[8] T.J. Wallington, S.M. Japar, Atmospheric chemistry of diethyl ether and ethyl *tert*-butyl ether, Environ. Sci. Technol. 25 (1991) 410–415.

[9] T.J. Wallington, M.D. Hurley, T. Maurer, I. Barnes, K.H. Becker, G.S. Tyndall, J.J. Orlando, A.S. Pimentel, M. Bilde, Atmospheric oxidation mechanism of methyl formate, J. Phys. Chem. A 105 (2001) 5146–5154.

[10] F. Kirchner, L.P. Thuener, I. Barnes, K.H. Becker, B. Donner, F. Zabel, Thermal lifetimes of peroxynitrates occurring in the atmospheric degradation of oxygenated fuel additives, Environ. Sci. Technol. 31 (1997) 1801–1804.

[11] A. Notario, G. Le Bras, A. Mellouki, Absolute rate constants for the reactions of Cl atoms with a series of esters, J. Phys. Chem. A 102 (1998) 3112–3117.

[12] T.J. Wallington, M.D. Hurley, A. Haryanto, Kinetics of the gas phase reactions of chlorine atoms with a series of formates, Chem. Phys. Lett. 432 (2006) 57–61.

[13] S.R. Sellevág, C.J. Nielsen, Kinetic study of the reactions $CH_2ClCH_2Cl + OH$, $CH_3C(O)CH_3 + Cl$ and $HC(O)OCH_2CH_3 + Cl$ by the relative rate method, Asian Chem. Lett. 7 (2003) 15–20.

[14] S. Langer, E. Ljungström, Rates of reactions between the nitrate radical and some aliphatic alcohols, J. Chem. Soc., Faraday Trans. 91 (1995) 405–410.

[15] B. Picquet-Varrault, J.F. Doussin, R. Durand-Jolibois, O. Pirali, P. Carlier, C. Pittschen, Kinetic and mechanistic study of the atmospheric oxidation by OH radicals of allyl acetate, Environ. Sci. Technol. 36 (2002) 4081–4086.

[16] J.M. Roberts, The atmospheric chemistry of organic nitrates, Atmos. Environ. 24A (1990) 243–287.

[17] E.C. Tuazon, R. Atkinson, Product study of the gas-phase reaction of isoprene with the OH radical in the presence of NO_x, Int. J. Chem. Kinet. 22 (1990) 1221–1236.

[18] C. Espada, P.B. Shepson, The production of organic nitrates from atmospheric oxidation of ethers and glycol ethers, Int. J. Chem. Kinet. 37 (2005) 686–699.

[19] E. Jiménez, B. Ballesteros, E. Martínez, J. Albaladejo, Tropospheric reaction of OH with selected linear ketones: kinetic studies between 228 and 405 K, Environ. Sci. Technol. 39 (2005) 814–820.

[20] T.J. Wallington, P. Dagaut, M.J. Kurylo, UV absorption cross sections and reaction kinetics and mechanisms for peroxy radicals in the gas phase, Chem. Rev. 92 (1992) 667–710.

[21] F. Kirchner, A. Mayer-Figge, F. Zabel, K.H. Becker, Thermal stability of peroxynitrates, Int. J. Chem. Kinet. 31 (1999) 127–144.

[22] M. Manetti, F.E. Malanca, G.A. Argüello, Thermal decomposition of trifluoromethoxycarbonyl peroxy nitrate, $CF_3OC(O)O_2NO_2$, Int. J. Chem. Kinet. 40 (2008) 831–838.

[23] H. Adachi, N. Basco, Reactions of isopropylperoxy radicals with NO and NO_2, Int. J. Chem. Kinet. 14 (1982) 1125–1138.

[24] R. Atkinson, D.L. Baulch, R.A. Cox, J.N. Crowley, R.F. Hampson Jr., J.A. Kerr, M.J. Rossi, J. Troe, Summary of evaluated kinetic and photochemical data for atmospheric chemistry, IUPAC Subcommittee on Gas Kinetic data evaluation for atmospheric chemistry. Web Version (Dec. 2001) 1–56.

[25] J.M. Chow, A.M. Miller, M.J. Elrod, Kinetics of the $C_3H_7O_2 + NO$ reaction: temperature dependence of the overall rate constant and the i-$C_3H_7ONO_2$ branching channel, J. Phys. Chem. A 107 (2003) 3040–3047.

[26] J.J. Orlando, G.S. Tyndall, T.J. Wallington, The atmospheric chemistry of alkoxy radicals, Chem. Rev. 103 (2003) 4657–4689.

[27] L.K. Christensen, J.C. Ball, T.J. Wallington, Atmospheric oxidation mechanism of methyl acetate, J. Phys. Chem. A 104 (2000) 345–351.

[28] B. Picquet-Varrault, J.F. Doussin, R. Durand-Jolibois, P. Carlier, FTIR spectroscopic study of the OH-induced oxidation of two linear acetates: ethyl and *n*-propyl acetates, Phys. Chem. Chem. Phys. 3 (2001) 2595–2606.

[29] F. Cavalli, I. Barnes, K.H. Becker, FT-IR kinetic and product study of the OH radical and Cl-atom-initiated oxidation of dibasic esters, Int. J. Chem. Kinet. 33 (2001) 431–439.

[30] R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson Jr., J.A. Kerr, M.J. Rossi, J. Troe, Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry: supplement V, IUPAC Subcommittee on gas kinetic data evaluation for atmospheric chemistry, J. Phys. Chem. Ref. Data 26 (1997) 521–1013.

[31] R. Atkinson, E.C. Tuazon, S.M. Aschmann, Atmospheric chemistry of 2-pentanone and 2-heptanone, Environ. Sci. Technol. 34 (2000) 623–631.

[32] N. Meunier, J.F. Doussin, E. Chevallier, R. Durand-Jolibois, B. Picquet-Varrault, P. Carlier, Atmospheric fate of alkoxy radicals: branching ratio of evolution pathways for 1-propoxy, 2-propoxy, 2-butoxy and 3-pentoxy radicals, Phys. Chem. Chem. Phys. 5 (2003) 4834–4839.

[33] G.S. Tyndall, T.J. Wallington, M.D. Hurley, W.F. Schneider, Rate coefficient for the reaction of hydroxymethyl radicals with chlorine and infrared spectra of chloromethanol and dichloromethanol, J. Phys. Chem. 97 (1993) 1576–1582.

[34] F. Caralp, V. Foucher, R. Lesclaux, T.J. Wallington, M.D. Hurley, Atmospheric chemistry of benzaldehyde: UV absorption spectrum and reaction kinetics and mechanisms of the $C_6H_5C(O)O_2$ radical, Phys. Chem. Chem. Phys. 1 (1999) 3509–3517.

[35] P.W. Bruckmann, H. Willner, Infrared spectroscopic study of peroxyacetyl nitrate (PAN) and its decomposition products, Environ. Sci. Technol. 17 (1983) 352–357.

[36] P.D. Lightfoot, R.A. Cox, J.N. Crowley, M. Destriau, G.D. Hayman, M.E. Jenkin, G.K. Moortgat, F. Zabel, Organic peroxy radicals: kinetics, spectroscopy and tropospheric chemistry, Atmos. Environ. 26A (1992) 1805–1961.