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Photodegradation of butyl acrylate in the troposphere by OH radicals: kinetics and fate of 1,2-hydroxyalcoxy radicals

María B. Blanco[a] and Mariano A. Teruel[a]*

The rate constant of the reaction of OH radicals with butyl acrylate was studied for the first time using an atmospheric simulation chamber at 298 K and ~750 Torr of air or nitrogen. The decay of the organics was followed using a gas chromatograph with a flame ionization detector (GC-FID), and the rate constant was determined using a relative rate method with different references. The obtained average value of $(1.80 \pm 0.26) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} is in agreement with previous determinations of the rate constants of OH radicals with acrylates and methacrylates in the literature. Additionally, product identification under atmospheric conditions was performed for the first time by the GC-MS technique. Butyl glyoxalate was observed as the degradation product in accordance with the addition of OH to the less substituted carbon atom of the double bond, followed by decomposition of the 1,2-hydroxyalkoxy radicals formed. Room temperature rate coefficient was used to estimate the atmospheric lifetime of the ester studied. Reactivity trends are discussed in terms of the substituent effects and the length of the hydrogenated chain of the ester. The atmospheric persistence of BUAC was calculated taking into account the experimental rate constant obtained. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: reaction rate constant; butyl acrylate; OH radicals; unsaturated VOCs; troposphere

INTRODUCTION

Acrylate esters containing a double bond and functional carboxyl group are used chiefly as a monomer or co-monomer in making acrylic and modacrylic fibers. They are used in formulating paints and dispersions for paints, inks, and adhesives, in making cleaning products, antioxidant agents, amphoteric surfactants as well as in making aqueous resins and dispersions for textiles and papers. Butyl acrylate (BUAC) is a very useful feedstock for chemical syntheses, because it readily undergoes addition reactions with a wide variety of organic and inorganic compounds.[1,2]

Substantial amounts of unsaturated oxygenates are continually introduced into the atmosphere and the kinetics and degradation pathways under atmospheric conditions of many of these compounds are still largely unknown. The atmospheric degradation of these compounds will be initiated mainly by chemical reaction with OH and NO_3 radicals and O_3 molecules contributing to tropospheric ozone production and the formation of other secondary photo-oxidants in polluted areas.[3]

In order to assess the impact of these species on air quality, kinetic, and mechanistic information on their tropospheric degradation is therefore needed.

Up until now, studies on the atmospheric chemistry of unsaturated esters have not been very extensive. Limited data are available in the literature on the gas-phase reactions of a few unsaturated esters.[4–7]

In this work, we report the rate coefficient for the reaction of OH radicals with BUAC:

$$OH + CH_2 = CHC(O)O(CH_2)_3CH_3 \rightarrow \text{Products} \qquad (1)$$

Experiments were conducted using the relative rate method with different OH sources and reference compounds at room temperature and atmospheric pressure of air or nitrogen.

To the best of our knowledge, this work provides the first kinetic study for the reaction cited above (1) under atmospheric conditions. In addition, our work aims to better define the reactivity of the $CH_2{=}CHR$ compounds toward OH radicals as an extension of our previous work involving $O(^3P)$ additions to haloalkenes,[8–10] OH addition to methacrylates and acrylates[5,7] and OH radicals and Cl atoms additions to other unsaturated VOCs.[11] In this sense, the results are also discussed in terms of the substituent effects to the double bond and the length of the hydrogenated chain of the ester on the reactivity of the olefinic carbon. The atmospheric lifetime of BUAC was calculated taking into account the experimental rate constant obtained.

Finally, product studies using the GC-MS technique under atmospheric conditions were carried out for the first time for the reaction of OH radical with the ester studied, therefore the degradation pathway of BUAC in the atmosphere is also postulated.

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* *Departamento de Fisicoquímica, Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina.*
E-mail: mteruel@fcq.unc.edu.ar

[a] *María B. Blanco, Mariano A. Teruel*
Departamento de Fisicoquímica, Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

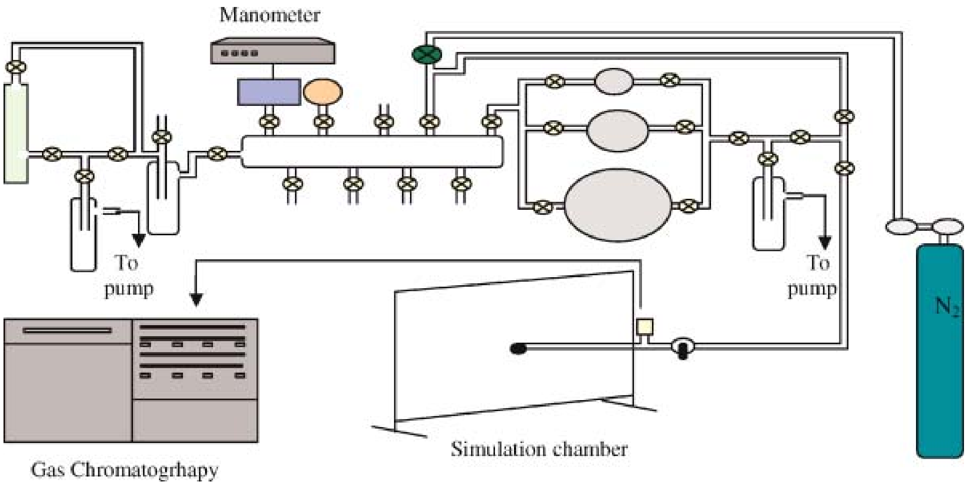

Figure 1. Schematic diagram of the simulation chamber apparatus used in the OH + BUAC reaction study

EXPERIMENTAL

The experimental set-up consisted of a 80 L Teflon bag located in a wooden box with the internal walls covered with aluminum foil, and operated at atmospheric pressure (750 ± 10) Torr and (298 ± 1) K. The schematic diagram of the simulation chamber employed in this work is shown in Fig. 1.

Measured amounts of the organic reactants were flushed from calibrated bulbs into the reaction chamber with a stream of ultra pure air. The bag was then filled to its full capacity at atmospheric pressure with N_2 or ultra pure air. Before each set of experiments the Teflon bag was cleaned by filling it with a mixture of O_2 and N_2 which was irradiated for 15–25 min using four germicidal lamps (Philips 30 W) with a UV emission at 254 nm, to produce O_3. After this procedure, the bag was cleaned again by repeated flushing with N_2 and checked before performing the experiments by gas chromatography (GC) to verify that there were no observable impurities.

The initial concentrations used in the experiments were in the range of 136–282 ppm (1 ppm $= 2.46 \times 10^{13}$ molecule cm^{-3} at 298 K and 760 Torr of total pressure) for BUAC, 155–263 ppm for diethyl ether and *n*-pentane used as reference compounds, 251–289 ppm for methyl nitrite, 336–379 ppm for NO, and 100 μL for H_2O_2.

Methyl nitrite (CH_3ONO) in the presence of NO/O_2 was used to generate OH radicals by its photolysis using a set of black lamps (Philips 30 W) surrounding the Teflon bag, according to the following reactions:

$$CH_3ONO + hv \rightarrow CH_3O + NO \qquad (2)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad (3)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (4)$$

These lamps provide UV radiation with a λ maximum around 360 nm.

H_2O_2 was used as an alternative source of OH radicals by direct UV photolysis with germicidal lamps emitting at 254 nm (Philips 30 W) surrounding the Teflon bag, according to the following reaction:

$$H_2O_2 + hn \rightarrow 2OH \qquad (5)$$

In the present work, typically four of these lamps were used to produce OH radicals and the time of photolysis varied from 3 to 35 min.

Periodically, gas samples were removed from the Teflon bag using calibrated gas syringes. The organics were monitored by gas chromatography (Shimadzu GC-14B) coupled with flame ionization detection (FID), using a Porapak Q column (Alltech, 2.3 m) held from 160 to 240 °C.

The analytical technique employed for qualitative identification of the products formed after irradiation was GC-mass spectrometry on a Shimadzu GC-MS QP 5050 spectrometer equipped with a 30 m–0.12 mm DB-5 MS column.

The chemicals used were: N_2 (AGA, 99.999%), synthetic air (AGA, 99.999%), BUAC (Aldrich, 99%), diethyl ether (Fluka 99%), *n*-pentane (Mallinckrodt, 99.9%) and H_2O_2 (Ciccarelli 60 wt%) were degassed by repeated freeze-pump-traw cycling. CH_3ONO was synthesized by the dropwise addition of 50% H_2SO_4 to a saturated solution of sodium nitrite in methanol and was purified by vacuum distillation until a sample of 99% purity was obtained, confirmed by IR spectroscopy and GC-FID.

RESULTS

Relative rate coefficient for the reactions of OH radicals with BUAC was determined by comparing the OH reaction rate with the unsaturated ester to that with the reference compounds

$$OH + BUAC \rightarrow Products \quad k_{ester} \qquad (6)$$

$$OH + reference \rightarrow Products \quad k_{ref} \qquad (7)$$

Provided that the reaction with OH is the only significant loss process for both, reactant and reference compounds, then it can be shown that

$$\ln([BUAC]_0/[BUAC]_t) = (k_{ester}/k_{ref}) \times \ln([ref]_0/[ref]_t) \qquad (8)$$

where the subscripts 0 and *t* indicate concentrations before irradiation and at time *t*, respectively. Plots of $\ln([BUAC]_0/[BUAC]_t)$ *versus* $\ln([ref]_0/[ref]_t)$ should yield straight lines with slope k_{ester}/k_{ref}.

The rate constants for the reaction of OH with BUAC studied here was measured at (298 ± 1) K and atmospheric pressure, relative to the rate constant of OH with *n*-pentane or diethyl

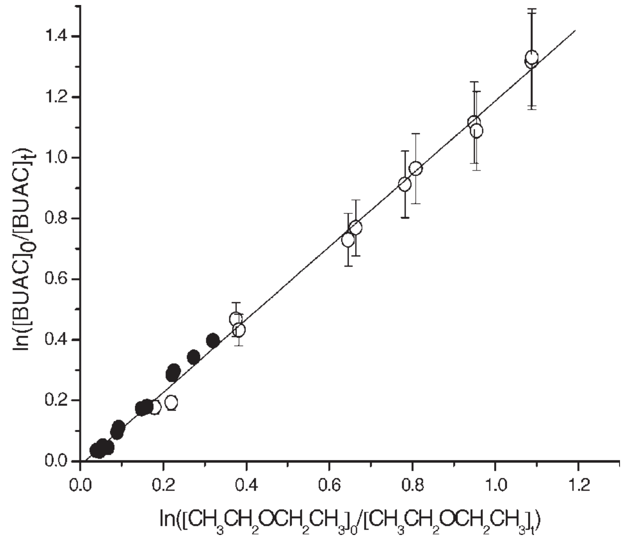

Figure 2. Relative rate data for the OH reaction with butyl acrylate using diethyl ether as reference compound at 298 K and atmospheric pressure of N_2 (○) and air (●)

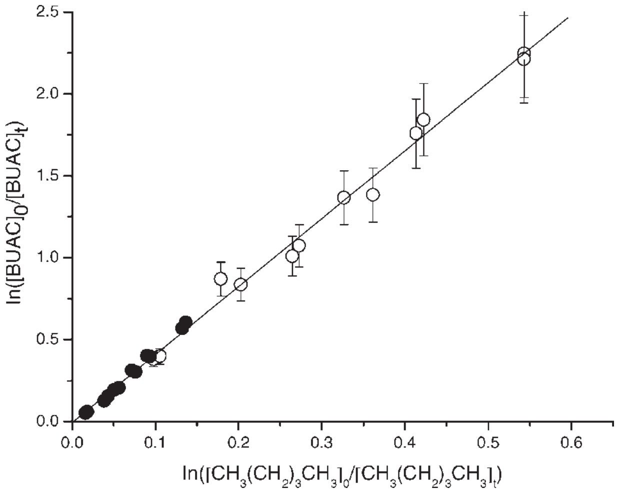

Figure 3. Relative rate data for the OH reaction with butyl acrylate using *n*-pentane as reference compound at 298 K and atmospheric pressure of N_2 (○) and air (●)

ether. The mixtures of the esters and references with CH_3ONO/NO or H_2O_2 were stable in the dark when left in the chamber for about 1 h. Moreover, in the absence of CH_3ONO/NO or H_2O_2, photolysis of the mixtures (BUAC and references in air or nitrogen) for more than 1 h shown negligible decrease in the concentrations.

By using this technique, the rate constant for the reaction studied was obtained from Eqn (8). The data were fitted to a straight line by the linear least-squares procedure. Figures 2 and 3 show the plot of ln([BUAC]$_0$/[BUAC]$_t$) *versus* ln([ref]$_0$/[ref]$_t$), for the reaction (1) using diethyl ether and *n*-pentane as reference compounds, respectively. For each organic reactant studied, several runs were performed for the rate constant determination; however for the sake of clarity, only one example is presented in Figs. 2 and 3. The rate constants of the reaction of OH with the references used in this work were taken as $(3.98 \pm 0.13) \times 10^{-12}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ for *n*-pentane[12] and $(1.36 \pm 0.11) \times 10^{-11}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ for diethyl ether at 298 K.[13]

The rate constant obtained by averaging the values from different experiments in the absolute terms was the following:

$$k_1 = (1.80 \pm 0.26) \times 10^{-11}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$$

The linearity of the data points and the fact that the plots show practically zero intercepts suggest that the contribution of secondary reactions is negligible. This fact is supported also by obtaining the same results using different sources of OH radicals as well as using nitrogen or synthetic air as bath gases. In Table 1, the rate constant ratios are given along with the derived rate constant for the OH reaction with BUAC.

The uncertainties are a combination of the 2σ statistical errors from the linear regression analysis and a contribution to cover errors in the rate constants of the reference hydrocarbons.

DISCUSSION

To the best of our knowledge, no kinetic data on the reactions of OH radicals with BUAC have been reported. The present study, thus, is the first measurement of the rate constant of the reaction (1) and therefore no direct comparison with the literature can be made.

However, it is interesting to compare the reactivity of BUAC toward OH radicals with the corresponding alkene and other unsaturated esters, since it has been postulated that unsaturated VOCs react via similar addition mechanisms.[3,14] In Table 2, the room temperature rate constants of the reactions of OH radicals

Table 1. Reactant concentrations, slopes k/k_{ref} and the obtained rate constants for the reaction of OH radicals with *n*-butyl acrylate at 298 K in 760 Torr of air or N_2

Precursor of OH	Bath gas	[Ester]$_0$ (ppm)	Reference	[Ref]$_0$ (ppm)	$k_{reactant}/k_{reference}$	$k_{reactant}$ (cm^3 molecule^{-1} s^{-1})
H_2O_2	N_2	136	Diethyl ether	155	1.29 ± 0.02	$(1.75 \pm 0.17) \times 10^{-11}$
H_2O_2	N_2	165	Diethyl ether	263	1.35 ± 0.08	$(1.84 \pm 0.26) \times 10^{-11}$
CH_3ONO	Air	282	Diethyl ether	192	1.36 ± 0.04	$(1.85 \pm 0.20) \times 10^{-11}$
H_2O_2	N_2	265	*n*-Pentane	179	4.41 ± 0.11	$(1.76 \pm 0.10) \times 10^{-11}$
CH_3ONO	Air	192	*n*-Pentane	230	4.44 ± 0.14	$(1.77 \pm 0.11) \times 10^{-11}$
CH_3ONO	Air	212	*n*-Pentane	204	4.63 ± 0.11	$(1.84 \pm 0.10) \times 10^{-11}$
					Average	$(1.80 \pm 0.26) \times 10^{-11}$

with BUAC are showed together with other unsaturated esters and the corresponding 1-hexene and *n*-hexane obtained from the literature. It is possible to observe that the rate coefficients of the esters with OH radicals, including OH + BUAC reaction, are close to the corresponding alkene (OH + 1-hexene) reaction in the order of 10^{-11} cm^3 molecule^{-1} s^{-1}. The same tendency was also previously observed by Le Calve *et al*. for unsaturated acetates and in our previous work for the reactions of methacrylates.[16,7] The rate coefficients of unsaturated esters with OH radicals are in general slightly lower than for the corresponding alkenes. This observation is consistent with the negative inductive effect of the —C(O)O— group on the double bond, indicating that the reactions of OH with unsaturated esters proceeds essentially by OH addition to the C=C double bond.[7]

On the other hand, H-substitution by electron-donor groups like —CH_3 or other alkyl groups in the olefin increases the reactivity toward the electrophilic attack of OH radicals. This can be observed comparing the higher reactivity of methacrylates ($CH_2{=}C(CH_3)R$) over the acrylates ($CH_2{=}CHR$), i.e., $k_{CH_2=C(CH_3)COO(CH_2)_3CH_3} > k_{CH_2=CHCOO(CH_2)_3CH_3}$, $k_{CH_2=C(CH_3)COOCH_2CH_3} > k_{CH_2=CHCOOCH_2CH_3}$, and $k_{CH_2=C(CH_3)COOCH_3} > k_{CH_2=CHCOOCH_3}$. This effect can be attributed to the electron-donor capacity of the CH_3 radical, which increases the charge density on the carbon atom next to the double bond, as well as the polarizability of the π electrons, leading to an increase in the rate constant value consistent with the electrophilic character of the OH radical.

The reactivity of BUAC toward OH radicals can be compared also with their corresponding saturated ester

$$OH + CH_3CH_2C(O)O(CH_2)_3CH_3 \rightarrow \text{products} \tag{9}$$

Unfortunatly, no kinetic data exist reaction (9). However, the room temperature rate constants of the reactions

$$OH + CH_3CH_2C(O)O(CH_2)_2CH_3 \rightarrow \text{products} \tag{10}$$

$$OH + CH_3C(O)O(CH_2)_4CH_3 \rightarrow \text{products} \tag{11}$$

were reported previously to be $k_{10} = 7.4 \times 10^{-12}$ and $k_{11} = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[17,18] The rate coefficient of the reaction (9) is expected to be close to the values of k_{10} and k_{11} (around 7×10^{-12} cm^3 molecule^{-1} s^{-1}). This value is considerably lower than the rate coefficient determined in this work for reaction (1), 1.8×10^{-11} cm^3 molecule^{-1} s^{-1}, providing evidence that both lead to products following different reaction mechanisms (e.g., addition to the C=C double bond for BUAC and H-atom abstraction for $CH_3CH_2C(O)O(CH_2)_3CH_3$).[3,19–21]

Product identification

Further experiments were also conducted to identify reaction products under similar conditions to the kinetic experiments for reaction (1). The main product was butyl glyoxalate in accordance with that obtained previously for the OH addition reaction to methacrylates.[7] We observed the ions with $m/e = 29$, 41, and 57 characteristic of butyl glyoxalate. The reaction products found, together with the observed reactivity trends, confirm that the reaction proceeds via an addition mechanism of the OH radical to the double bond similar to that proposed by Atkinson for the OH radical addition to alkenes.[19,20] The 1,2-hydroxyalkyl radical is oxidized and further reduced in the presence of O_2 and NO to give the 1,2-hydroxyalkoxy radical. This radical decomposes leading mainly to the corresponding glyoxalate and formaldehyde, as shown in the following reaction scheme:

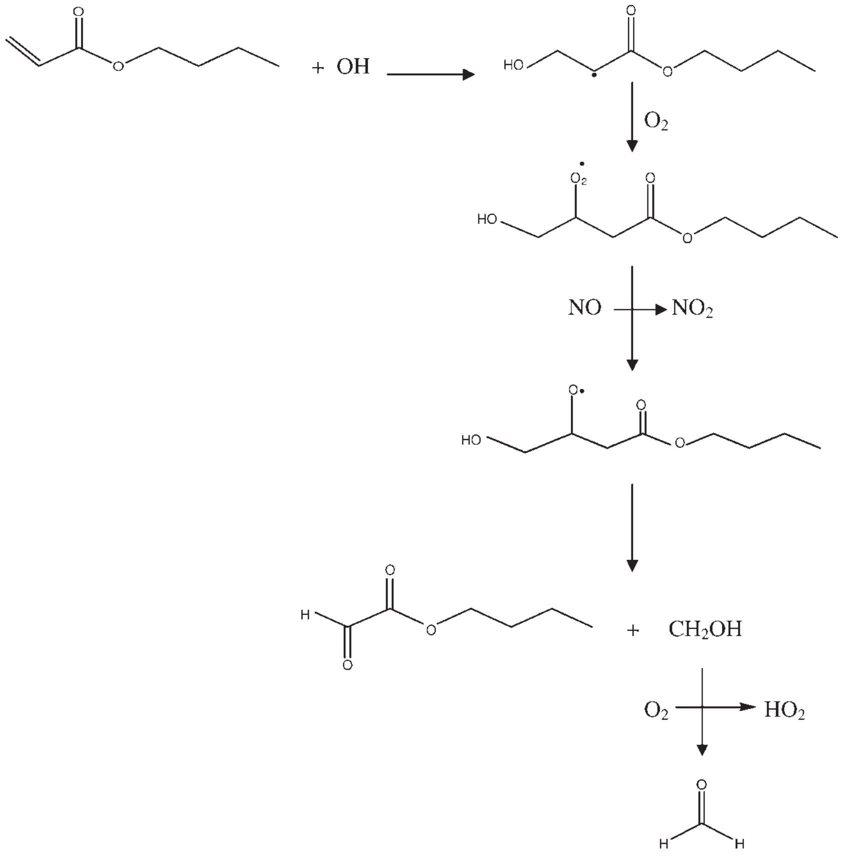

Table 2. Comparison of the rate constants of the reactions of different $CH_2{=}CHR$, $CH_2{=}(CH_3)R$ and *n*-hexane with OH radicals under atmospheric pressure and 298 K

VOC	$k_{OH} \times 10^{11}$ (cm^3 $molecule^{-1}$ s^{-1})
$CH_2{=}CHC(O)OCH_3$	1.3[a]
$CH_2{=}CHC(O)OCH_2CH_3$	1.7[a]
$CH_2{=}CHC(O)O(CH_2)_3CH_3$	1.8[b]
$CH_2{=}C(CH_3)C(O)OCH_3$	4.2[c]
$CH_2{=}C(CH_3)C(O)OCH_2CH_3$	4.6[c]
$CH_2{=}C(CH_3)C(O)O(CH_2)_3CH_3$	7.1[c]
$CH_2{=}CHCH_3$	3.0[d]
$CH_2{=}CHCH_2CH_3$	3.0[d]
$CH_2{=}CH(CH_2)_3CH_3$	1.7[d]
$CH_3(CH_2)_4CH_3$	0.7[d]

[a] Reference.[5]
[b] This work.
[c] Reference.[7]
[d] Reference.[15]

According to the products observed, the main fate of the 1,2-hydroxyalcoxy radicals formed seems to be the decomposition channel, where the OH preferably attacks the terminal carbon of the double bond.[22] We did not find dihydroxycarbonyl compounds or hydroxycarbonyl acids as reaction products. Therefore, we can conclude that other channels such as isomerization or reaction with O_2, respectively, proposed by Atkinson for alkenes,[19,20] are negligible for BUAC under our experimental conditions.

Regarding nitrate formation in the reactions of NO with 1,2-hydroxyalkyl, 1,2-hydroxyperoxy, and 1,2-hydroxyalcoxy radicals, we did not see any organic nitrate formation, hence addition of NO to such radicals is negligible under our experimental conditions.

The atmospheric lifetime, τ_x, of the BUAC was calculated through the expression: $\tau_x = 1/k_x[OH]$. Unfortunately, no kinetic data are available for the reactions of BUAC with other tropospheric oxidants like O_3 molecules NO_3 radicals or Cl atoms. A tropospheric lifetime of 8 h is calculated, assuming a 12 h average concentration of OH of 2×10^6 molecule cm^{-3}.[23] This lifetime indicates that BUAC is likely to be rapidly removed in the gas phase, the reaction with OH being the major loss process for the unsaturated ester. Loss by photolysis can be considered negligible since it is photolytically stable in the actinic region of the electromagnetic spectrum.

The short lifetime of a few hours indicates that BUAC, like other acrylates and methacrylates will be oxidized close to the emission sources. Consequently, this emissions will have mainly a local impact concerning the photochemical smog production. The products formed from the OH-initiated degradation are mainly carbonyl compounds, which are net sources of HO_x (OH, HO_2) radicals that enhance photo-oxidation formation.

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