



Research paper

Night-time atmospheric degradation of a series of butyl methacrylates

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ABSTRACT

Rate coefficients for the reactions of NO₃ with *n*-butyl methacrylate (*k*₁), *iso*-butyl methacrylate (*k*₂) and *tert*-butyl methacrylate (*k*₃) have been determined at 298 K and atmospheric pressure using the relative rate method. The following rate coefficients ($\times 10^{-15}$ cm³ molecule⁻¹ s⁻¹) were obtained for the first time: *k*₁ = (5.5 ± 2.6), *k*₂ = (5.8 ± 2.8) and *k*₃ = (5.6 ± 2.5).

The NO₃ reactions of these compounds could contribute to the removal of NO_x and as NO_y reservoirs. The potential importance for the tropospheric nitrogen budget of these reactions is discussed and atmospheric lifetimes for the butyl esters are calculated.

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1. Introduction

Methacrylates are used as building blocks to make a wide range of polymers. These polymers are then used as raw materials or components in the manufacture of an extensive range of products, especially when stability, durability, hardness and scratch resistance are needed [1]. It is estimated that worldwide more than three million tons of methacrylates are produced and transformed every year [2].

Methyl methacrylate (MMA) is by far the most produced methacrylate monomer. Its versatility allows it to be used to produce a pure homopolymer (poly-methyl methacrylate) or, in combination with other monomers, a series of polymers with various and valuable properties. Other methacrylate monomers are produced using MMA as a key raw material [3].

n-Butyl methacrylate (*n*-BMA), *iso*-butyl methacrylate (*iso*-BMA) and *tert*-butyl methacrylate (*tert*-BMA) in combination with MMA can be used in many applications, most notably as plastic modifiers and processing aids, in medical equipment and dental objects (fillings, dentures, bridges, dental prosthetics) [4,5]. They are key ingredients in the manufacture of artificial marble and are also found in the composition of many industrial products

including electronics, paper, leather, floor polishes, adhesives and sealants [3].

The production and use of butyl methacrylate isomers in a multitude of applications can result in their release to the environment through various waste streams [5]. The potentially large emissions, high volatility, and toxicity of the butyl methacrylates isomers makes emissions of these compounds into the atmosphere a subject of environmental concern with respect to air quality and human health [6].

In the troposphere, these unsaturated esters are transformed by chemical processes including reaction with OH radicals (during the day-time), with NO₃ radicals (during the evening and night-time hours), reaction with O₃ (both day and night), and potentially also with Cl atoms in coastal, marine and industrial regions (during daylight hours) [7–10].

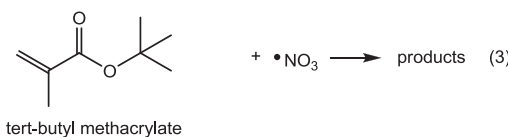
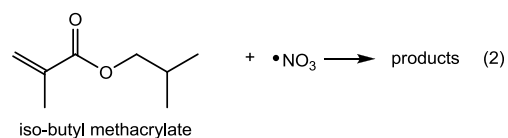
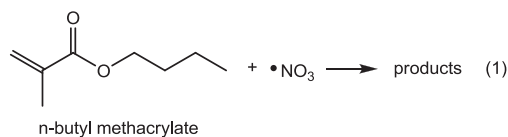
The night-time degradation of unsaturated Volatile Organic Compounds (VOCs) [11] contributes to the removal of NO_x mainly via nitric acid (HNO₃) and particulate nitrate formation [12].

The night-time chemistry of butyl methacrylates has not been very extensively investigated both kinetically and mechanistically. Therefore, knowledge of the rate coefficients for the NO₃-radical initiated oxidation reactions of these unsaturated esters will assist in determining and quantifying the night-time contribution to the impact of this type of compound on the air quality of the troposphere.

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Reported in this study are rate coefficients for the reactions of NO_3 radicals with the three possible isomers of butyl methacrylate: *n*-butyl methacrylate, *iso*-butyl methacrylate and *tert*-butyl methacrylate measured at room temperature and atmospheric pressure using the relative rate technique [13]:



In addition, the products formed under the experimental conditions employed have been investigated and the information used to elucidate atmospheric degradation mechanisms.

The rate coefficient for the reaction of NO_3 with *n*-butyl methacrylate has been studied previously in a static Teflon reactor at 298 K and atmospheric pressure of N_2 using a relative rate technique and gas chromatography (GC) - flame ionization detection (FID) for analysis of the reactants [14]. This work, however, represents the first determination of the rate coefficients for the reactions of NO_3 with *iso*-butyl methacrylate and *tert*-butyl methacrylate. The possible atmospheric implications of the results are discussed.

2. Experimental section

The experiments were performed in a 480 L cylindrical Duran glass vessel (3 m in length, 45 cm in diameter) at (298 ± 2) K and a total pressure of (760 ± 10) Torr synthetic air ($760 \text{ Torr} = 101.325 \text{ kPa}$). The chamber is described in detail elsewhere [15] and only a brief description is given here. The chamber is equipped with an internally mounted White mirror system operated at an optical path length of 48.11 m which is coupled to an FTIR spectrometer (Nicolet 6700) for the acquisition of infrared spectra at a resolution of 1 cm^{-1} .

NO_3 radicals were produced by the thermal dissociation of N_2O_5 prepared in solid form according to a literature method [16]:

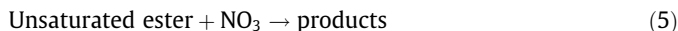


N_2O_5 was added to the premixed reactants in the reactor in multiple stepwise additions by passing air over the surface of solid N_2O_5 in a glass tube placed in a cooling trap at -50°C .

The contents of the reactor were monitored using in situ FTIR, generally, 64 interferograms were co-added per spectrum over a

period of approximately 1 min and 15 such spectra were recorded per experiment.

In the presence of the oxidant, the NO_3 radical, the ester and reference compounds decay through the following reactions:



Provided that the reference compound and the reactant are lost only by reactions (5) and (6), it can be shown that:

$$\ln \left\{ \frac{[\text{Unsaturated ester}]_0}{[\text{Unsaturated ester}]_t} \right\} = \frac{k_{\text{Unsaturated ester}}}{k_{\text{Reference}}} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (1)$$

where $[\text{Unsaturated ester}]_0$, $[\text{Reference}]_0$, $[\text{Unsaturated ester}]_t$ and $[\text{Reference}]_t$ are the concentrations of the unsaturated ester and reference compound at times $t=0$ and t , respectively, and $k_{\text{Unsaturated ester}}$ and $k_{\text{Reference}}$ are the rate coefficients for reactions (5) and (6), respectively.

The initial concentrations typically used in the experiments for the unsaturated esters and reference compounds in ppm (1 ppm = $2.46 \times 10^{13} \text{ molecule cm}^{-3}$ at 298 K and 760 Torr total pressure) were as follows: ~ 4 for *n*-butyl methacrylate; ~ 3.5 for *iso*-butyl methacrylate; ~ 5 for *tert*-butyl methacrylate; 15–20 for 1-butene and ~ 22 for propene.

The reactants were monitored at the following infrared absorption frequencies (in cm^{-1}): *n*-butyl methacrylate at 1168; *iso*-butyl methacrylate and *tert*-butyl methacrylate at 1164; 1-butene and propene at 912.

3. Results

The rate coefficient measurements for the reactions of NO_3 radicals with *n*-butyl methacrylate, *iso*-butyl methacrylate and *tert*-butyl methacrylate were each performed relative to two reference compounds, 1-butene and propene:



The following room temperature rate coefficients were used for 1-butene and propene $k_7 = (1.25 \pm 0.50) \times 10^{-14}$ [11] and $k_8 = (9.54 \pm 3.83) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [17].

Representative plots of the kinetic data for the reactions of NO_3 with *n*-butyl methacrylate, *iso*-butyl methacrylate and *tert*-butyl methacrylate are displayed in Figs. 1–3, respectively. Three

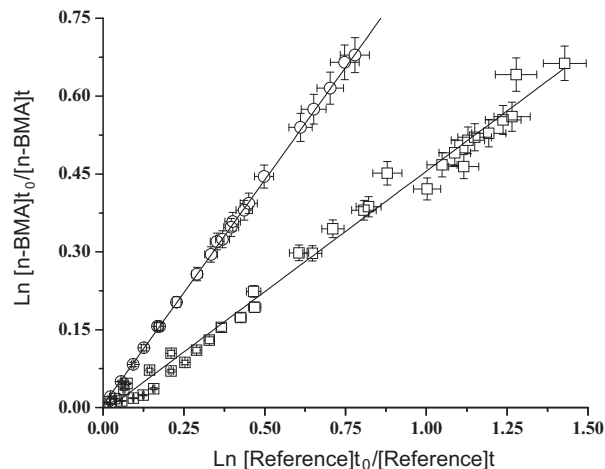


Fig. 1. Plot of the kinetic data for the reaction of NO_3 radicals with *n*-butyl methacrylate (*n*-BMA) measured relative to propene (\circ) and 1-butene (\square) at 298 ± 2 K and atmospheric pressure of air.

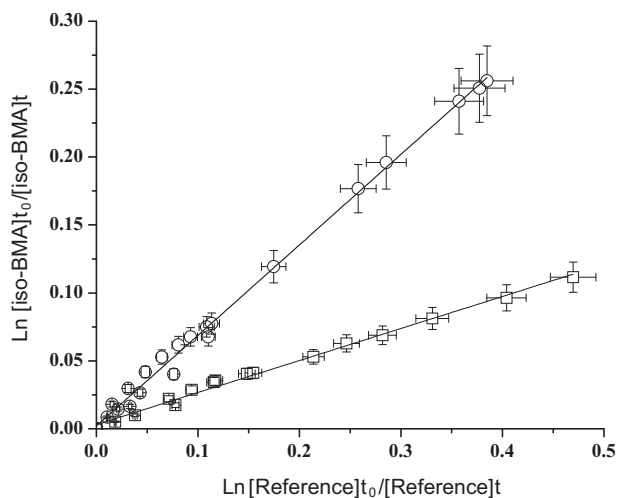


Fig. 2. Plot of the kinetic data for the reaction of NO_3 radicals with *iso*-butyl methacrylate (*iso*-BMA) measured relative to propene (○) and 1-butene (□) at 298 ± 2 K and atmospheric pressure of air.

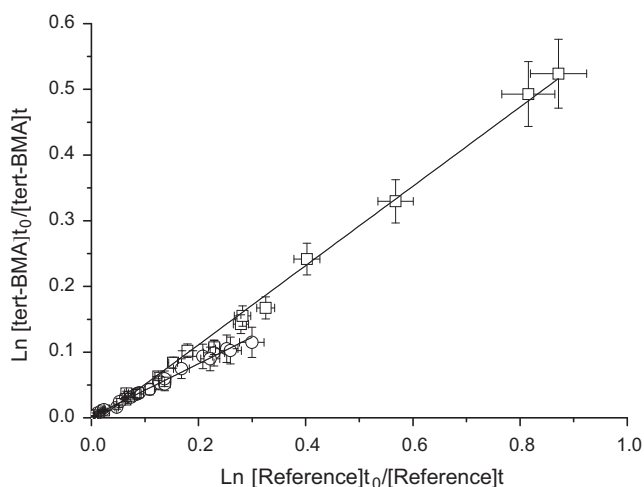


Fig. 3. Plot of the kinetic data for the reaction of NO_3 radicals with *tert*-butyl methacrylate (*tert*-BMA) measured relative to propene (○) and 1-butene (□) at 298 ± 2 K and atmospheric pressure of air.

experiments were performed for each ester and reference compound combination using different Reference/Butyl ester concentration mixing ratios. The reference/butyl ester concentration mixing ratios employed and the individual rate coefficient ratios ($k_{\text{Butylester}}/k_{\text{Reference}}$) determined for each set of experiments are listed in Table 1 together with the absolute values of $k_{\text{Butylester}}$ derived from the rate coefficient ratios using the rate coefficients for the reference reactions listed above. The errors for the $k_{\text{Butylester}}/k_{\text{Reference}}$ ratios given in Table 1 are the 2σ statistical errors from the scatter in the plots shown in Figs. 1–3. The errors quoted for $k_{\text{Butylester}}$ are a combination of the 2σ statistical errors from the linear regression analysis plus an additional error to cover potential uncertainties in the recommended values of the rate coefficients for the reference reactions.

Since consistent results were obtained using two reference compounds (see Table 1) we prefer to give final rate coefficients for the reactions of NO_3 radicals with the unsaturated esters which are averages of all the determinations for that particular reaction. This leads to the following averaged values of the rate coefficients for the reactions:

$$k_1 = (5.5 \pm 2.6) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (5.8 \pm 2.8) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_3 = (5.6 \pm 2.5) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

4. Discussion

4.1. Reactivity trends

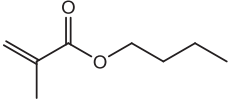
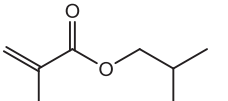
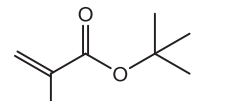
The value of $(5.5 \pm 2.6) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained in this work for the reaction of NO_3 with *n*-butyl methacrylate is in reasonable agreement, within the experimental errors, with the value of $(7.87 \pm 3.86) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ determined by Salgado et al. [14] in a static Teflon reactor at room temperature and atmospheric pressure of N_2 using the relative rate technique and GC-FID for the analysis. For the reactions of NO_3 radicals with *iso*-butyl methacrylate and *tert*-butyl methacrylate, the measurements reported here constitute the first determinations of the rate coefficients. As can be seen in Table 1 the rate coefficients for the reactions of NO_3 with *n*-butyl, *iso*-butyl and *tert*-butyl methacrylate are, within the error limits, the same, the rate coefficient for NO_3 with *iso*-butyl methacrylate being only marginally faster than those for the other two isomers.

Kerdouci et al. [18,19] have recently presented a new SAR method for the prediction of rate coefficients for gas-phase reactions of VOCs with NO_3 radicals. This SAR is based on the parameterization of the molecular structure according to the group-additivity method as frequently used for OH reactions and the current version of the SAR is based on NO_3 kinetic data for 185 organic compounds [19]. The SAR of Kerdouci et al. predicts rate coefficients (in units of $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of 4.60, 4.67 and 4.53 for the reactions of NO_3 with *n*-butyl, *iso*-butyl and *tert*-butyl methacrylate, respectively. These predicted values are in agreement with our experimental results. It should be noted that in the calculation of the rate coefficients using the Kerdouci et al. SAR a value of one was used for the substituent factor $F(\text{RC}(\text{O})-)$ since a value is currently not available for this substituent factor in the Kerdouci et al. SAR. However, this will not unduly affect the calculated values since the factor only influences one of the very minor H-atom abstraction channels in the overall reaction. H-atom abstraction accounts for only 1–2% of the overall reaction of NO_3 with the butyl methacrylate isomers. Hence addition to the double bond entity almost entirely dominates. Interestingly, the Kerdouci et al. SAR predicts *iso*-butyl methacrylate to be marginally faster than the other butyl methacrylate isomers due to the slightly larger contribution from the H-atom abstraction channel in agreement with what we have observed experimentally.

The rates coefficients for the reaction of NO_3 with butyl methacrylates can be compared with those of NO_3 with other alkyl methacrylates. Wang et al. [20] have reported rate coefficients of $(3.6 \pm 1.7) \times 10^{-15}$ and $(4.9 \pm 1.7) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reactions of NO_3 with methyl methacrylate and ethyl methacrylate, respectively, both determined using a relative kinetic method at 298 K and 760 Torr. The value obtained for the reaction of NO_3 with ethyl methacrylate is only marginally but nevertheless lower than the values obtained in this work for reaction of NO_3 with the butyl methacrylate isomers. We could not find kinetic measurements on the reaction of NO_3 with propyl methacrylates in the literature with which a comparison could be made.

Canosa-Mas et al. [21,22] have reported rate coefficients for the reactions of NO_3 with a number of α,β -unsaturated compounds, including esters, using a relative kinetic method at 298 K and 760 Torr in addition to studies on the compounds in a flow tube. They report a value of $(3.70 \pm 0.65) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Table 1
Ratios of concentrations employed of Reference/Butyl ester. Measured rate coefficient ratios, $k_{\text{Butylester}}/k_{\text{Reference}}$, and the rate coefficients for the reactions of NO_3 with the butyl esters at (298 ± 2) K derived from these ratios.

Butyl ester	Reference	[Reference]/[Butyl ester]	$k_{\text{Butylester}}/k_{\text{Reference}}$	$k_{\text{Butylester}}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
 n-butyl methacrylate	Propene	5	0.59 ± 0.01	$(5.6 \pm 2.3) \times 10^{-15}$
	Propene	6	0.57 ± 0.01	$(5.4 \pm 2.2) \times 10^{-15}$
	Propene	5	0.58 ± 0.01	$(5.5 \pm 2.3) \times 10^{-15}$
	1-Butene	4	0.45 ± 0.02	$(5.6 \pm 2.6) \times 10^{-15}$
	1-Butene	5	0.44 ± 0.01	$(5.5 \pm 2.4) \times 10^{-15}$
	1-Butene	3	0.43 ± 0.02	$(5.4 \pm 2.3) \times 10^{-15}$
	Average			$(5.5 \pm 2.6) \times 10^{-15}$
 iso-butyl methacrylate	Propene	6	0.66 ± 0.02	$(6.3 \pm 2.8) \times 10^{-15}$
	Propene	5	0.64 ± 0.02	$(6.1 \pm 2.4) \times 10^{-15}$
	Propene	7	0.61 ± 0.01	$(5.8 \pm 2.1) \times 10^{-15}$
	1-Butene	4	0.47 ± 0.01	$(5.9 \pm 2.4) \times 10^{-15}$
	1-Butene	5	0.44 ± 0.01	$(5.5 \pm 2.2) \times 10^{-15}$
	1-Butene	6	0.42 ± 0.02	$(5.3 \pm 2.0) \times 10^{-15}$
	Average			$(5.8 \pm 2.8) \times 10^{-15}$
 tert-butyl methacrylate	Propene	4	0.60 ± 0.02	$(5.7 \pm 2.1) \times 10^{-15}$
	Propene	6	0.64 ± 0.02	$(6.1 \pm 2.1) \times 10^{-15}$
	Propene	5	0.57 ± 0.01	$(5.4 \pm 2.1) \times 10^{-15}$
	1-Butene	3	0.40 ± 0.01	$(5.0 \pm 2.0) \times 10^{-15}$
	1-Butene	4	0.43 ± 0.01	$(5.4 \pm 2.4) \times 10^{-15}$
	1-Butene	4	0.46 ± 0.02	$(5.8 \pm 2.5) \times 10^{-15}$
	Average			$(5.6 \pm 2.5) \times 10^{-15}$

for the reaction of NO_3 with methyl methacrylate which is in excellent agreement with the value reported by Wang et al. [20]. Apart from methyl methacrylate Canosa-Mas et al. [21,22] did not measure rate coefficients for other alkyl methacrylates.

In the butyl methacrylate isomers the ester entity separates the alkyl groups from the double bond. While the ester group will deactivate the double bond toward electrophilic NO_3 addition, the alkyl groups exert a positive inductive effect which will be different for the different isomers and may compensate to some extent the deactivating effect of the ester entity. Based on the measured rate coefficients for the butyl methacrylate isomers the positive inductive effect of the different isomers does not appear to influence in any way the deactivating effect of the ester. However, when comparing the reported rate coefficient's for the reactions of NO_3 with methyl, ethyl and butyl methacrylates there is a significant increase in reactivity up the fourth carbon atom in the alkyl chain that cannot be attributed to contributions from H-atom abstraction channels but must stem from positive inductive effects from the alkyl chain. It is not expected that inductive effects from the alkyl chain will increase for alkyl chains >4 carbon atoms. The similar rate coefficients for reaction of NO_3 with the butyl methacrylate isomers would seem to confirm this.

Interestingly estimations of the rate coefficients using the Kerdocci et al. SAR for the reactions of NO_3 with the butyl methacrylate isomer alkene analogs, i.e. those obtained on removing the ester moiety, also predict virtually no effect of the alkyl group isomeric structure on the reactivity of the alkenes toward NO_3 apart from small differences arising from the slightly different contributions from the H-atom channels [19]:

$$k_{\text{CH}_2=\text{C}(\text{CH}_3)(\text{CH}_2)_3\text{CH}_3} (2.82 \times 10^{-13}) \sim k_{\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)_2} (3.09 \times 10^{-13}) \\ \sim k_{\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)_3} (3.09 \times 10^{-13})$$

It is not possible to directly compare the reactivity trend of NO_3 toward the butyl methacrylate isomers observed in this work with that of the other tropospheric oxidants, i.e. OH, Cl or O_3 , since presently kinetic data are only available for the reactions of *n*-butyl methacrylate with OH [23], O_3 [24] and Cl [25]. However, the

structure activity relationship (SAR) of Kwok and Atkinson [26] for OH reactions with VOCs predicts similar rate coefficients for the reactions of OH with *n*-butyl methacrylate and *iso*-butyl methacrylate and a slightly slower rate coefficient for the reaction of OH with *tert*-butyl methacrylate the difference arising entirely from slight differences in the contributions from the H-atom abstraction channels. The situation is expected to be similar for the reactions of Cl atoms with the butyl methacrylate isomers where the rate coefficients will be close to the gas kinetic limit in any case.

4.2. Product identification

As has been proposed for the reactions of nitrate radicals with alkenes [11] the reactions of NO_3 with the unsaturated esters will proceed to a large extent *via* addition of the NO_3 radical to the double bond with addition occurring preferentially at the terminal carbon of the double bond in the esters, i.e. generally analogous to the corresponding OH radical reactions [27]. The initially formed nitrooxy-alkyl radicals can decompose to an oxirane plus NO_2 or more probably can add O_2 to form 1,2-nitrooxy-peroxy radicals (see Fig. 4).

The 1,2-nitrooxy-peroxy radicals can react with NO_2 to form unstable 1,2-nitrooxy-peroxynitrates (Fig. 4, channel A) and/or can be reduced by self- and cross-peroxy reactions or reaction with NO_3 to form 1,2-nitrooxy-alkoxy radicals (Fig. 4, channel B where R is the *n*-butyl, *iso*-butyl or *tert*-butyl group).

The reaction of the 1,2-nitrooxy-peroxy radicals with HO_2 could lead to the formation of a 1,2-nitrooxy-hydroperoxide as has been observed in the reaction of NO_3 with isoprene [28,29]. Under the high NO_2 conditions of the present experiments, another potential reaction channel, H-atom migration involving isomerization of the 1,2-nitrooxyalkyl peroxy radicals is highly unlikely and it also remains to be established if they are even feasible at room temperature for the reaction systems under investigation [30,31].

The peroxynitrates formed in channel A are expected to undergo thermal decomposition and ultimately form, at least to a large extent, the corresponding 1,2-nitrooxy-alkoxy radicals. The

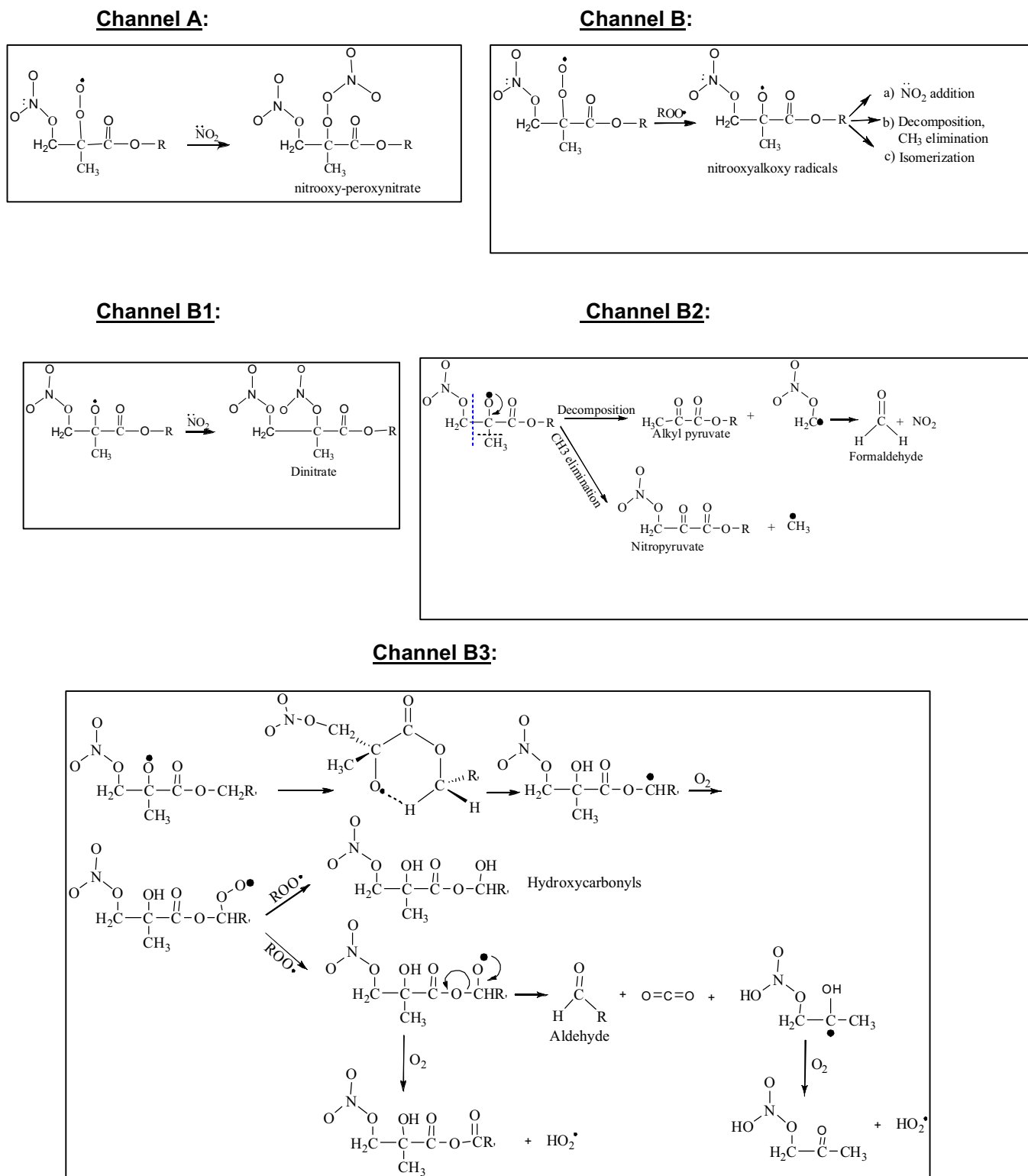


Fig. 4. Simplified pathways (channels A, B, B1, B2, B3) for the addition reaction of NO_3 radical to the double bond of methacrylate esters.

1,2-nitrooxy-alkoxy radicals can (i) react with NO_2 to produce dinitrate compounds (Fig. 4, channel B1), (ii) decompose to give an alkyl pyruvate, formaldehyde and NO_2 or eliminate a $-\text{CH}_3$ group to form a nitrooxy-pyruvate (Fig. 4, channel B2) and finally CH_2O , and (iii) isomerize forming different multifunctional carbonyl, hydroxyl and nitrooxy-containing compounds (Fig. 4, channel B3).

In Fig. 4, channels B1, B2 and B3, R is the $-\text{CH}_2\text{CH}_2\text{CH}_3$, $-\text{CH}(\text{CH}_3)_2$ or $-\text{C}(\text{CH}_3)_3$ group.

To date no product studies on the reactions of NO_3 radicals with *iso*-BMA and *tert*-BMA have appeared in the literature. For the reaction of NO_3 with *n*-butyl methacrylate ($\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$) a qualitative product study using solid phase micro

extraction (SPME)-GC-MS and FTIR spectroscopy to monitor the reactants and products has been reported [14]. In this study, butyl pyruvate was identified as a main product and in the infrared spectra absorption bands consistent with the presence of compounds containing $-\text{OONO}_2$ and $-\text{ONO}_2$ functional groups were observed. The authors also reported butanol as a product but were unable to offer a satisfactory mechanism to explain its formation and considered the route leading to its formation to be of little significance in the reaction of NO_3 with *n*-butyl methacrylate. A product study on the reaction of OH radicals with *n*-BMA using GC-MS has also shown butyl pyruvate to be the major degradation product [32].

Unfortunately, the possible products from the reactions of NO_3 with the butyl methacrylate isomers studied in this work as proposed in the above reaction schemes, i.e. alkyl pyruvates, nitrooxy pyruvates, hydroxycarbonyls, etc., are not commercially available and thus a direct identification and quantification of the products formed in our experiments cannot be made.

Fig. 5 shows a product spectrum in the range $2000\text{--}700\text{ cm}^{-1}$ obtained from the reaction of NO_3 radicals with *n*-butyl methacrylate after subtraction of residual *n*-butyl methacrylate, N_2O_5 , NO_2 and HNO_3 introduced with N_2O_5 to the reactor and also formed from its decomposition. The residual product spectrum displays many of the characteristics that can be seen in the infrared product spectra from the reaction of NO_3 with ethyl methacrylate reported by Salgado et al. [14]. Listed in Table 2 are the main product absorption bands and possible product assignments.

Absorptions at around 1744 ($-\text{NO}_2$ asym. str.), 1284 ($-\text{NO}_2$ sym. str.), 795 ($\text{O}-\text{N}$ str.) cm^{-1} are characteristic of peroxy nitrates [32–34] and are most probably due to formation of a 1,2-nitrooxyperoxy nitrates from the reactions of NO_2 with 1,2-nitrooxyperoxy radicals (Fig. 4, channel A). This reaction will dominate the initial fate of the 1,2-nitrooxyperoxy radicals under the experimental conditions of the present work due to the high levels of NO_2 present in the reaction system, i.e. initially around 4 ppm and increasing to around 15 ppm toward the end of the reaction.

Absorptions at around 1677 ($-\text{NO}_2$ asym. str.), 1284 ($-\text{NO}_2$ sym. str.), 845 ($\text{O}-\text{N}$ str.) cm^{-1} and 743 (NO_2 deformation) cm^{-1} are characteristic for the presence of organic nitrates [34,35]. Here again because of the high levels of NO_2 in the reaction system the most favored fate of the 1,2-nitrooxyalkoxy radicals will be addition of NO_2 to form 1,2-dinitrooxy compounds (Fig. 4, channel B1). The wavenumber range for the $-\text{NO}_2$ symmetric stretch absorption in organic nitrates and peroxy nitrates is quite narrow and similar. The absorption band at around 1884 cm^{-1} is, therefore, probably due to a mixture of both nitrate types.

Table 2

Absorption bands observed in the products studies for the reactions of NO_3 with *n*-butyl methacrylate, *iso*-butyl methacrylate and *tert*-butyl methacrylate.

Absorption band identified (cm^{-1})	Possible product formed
1744	Peroxy nitrates formation
1284	
795	
1677	Organic nitrates formation
1284	
845	
743	
1884	Probably mixture of both nitrate types
1750	Carbonyl absorption
(1260–1200)	Butyl group on the nitrate/peroxy nitrates
1830	Could be due to the carbonyl in the 1-nitroxy-2-peroxy nitrate

It is not possible to tell from the product spectrum if an alkyl pyruvate is being formed (Fig. 4, channel B2 – decomposition) since the carbonyl absorption would be expected around 1750 cm^{-1} and overlap those of the organic nitrates formed in the system. However, the formation of the alkyl pyruvate would be accompanied by formation formaldehyde. No indication for formation of formaldehyde in the reaction system was observed indicating that under the experimental conditions the radicals formed after NO_3 addition to the double bond are probably being effectively trapped as 1,2-nitrooxyperoxy nitrates and 1,2-dinitrooxy compounds.

There are number of relatively strong absorptions in the region $1260\text{--}1200\text{ cm}^{-1}$ for which we have no definite assignment, however, it is quite possible that these are due to butyl group on the nitrate and peroxy nitrate products that we have tentatively identified.

The absorption band at 1830 cm^{-1} is typical for a carbonyl absorption in an acyl peroxy nitrates [33–36] and the presence of electron withdrawing substituents on the carbon positioned alpha to the carbonyl group is known to shift the carbonyl absorptions to even higher frequencies [33]. Salgado et al. [14] have tentatively identified the band at $1829\text{--}1835\text{ cm}^{-1}$, observed in their study on the reaction of NO_3 with ethyl methacrylate, as possibly originating from a peroxyacyl compound, acetone and/or acetoxyaldehyde. Acetone and acetoxyaldehyde can be immediately eliminated since their carbonyl absorptions occur at around 1740

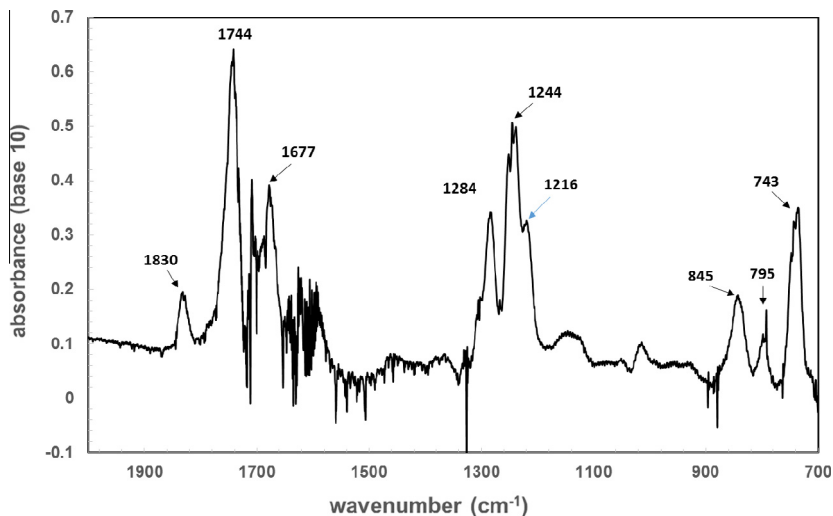


Fig. 5. IR spectrum of the products formed in the reaction of NO_3 radicals with *n*-butyl methacrylate.

and 1780 cm⁻¹, respectively. Given the expected degradation mechanism we can think of no reasonable reaction pathway that would lead to the formation of a peroxyacyl compound. The position of the carbonyl absorption in the 1-nitroxy-2-peroxy nitrate (Fig. 4, channel A) presumed to be formed initially in the reaction of NO₃ with butyl methacrylate is not known. We speculate that the absorption at 1830 cm⁻¹ may be due to the carbonyl in the 1-nitroxy-2-peroxy nitrate; the peroxy nitrate group is electron withdrawing and it is possible there may be some interaction of the NO₂ entity with the CO entity via a six-membered ring that facilitates a shift of the carbonyl absorption to higher frequencies. This is of course presently just conjecture; calculation of the infrared spectrum of the compound may provide some indication of whether or not the speculation is justified.

Very similar residual product spectra have been obtained for the reactions of NO₃ with *iso*- and *tert*-butyl methacrylate. Because of this similarity in product spectra and expected similar reaction pathways, we forego lengthy individual discussions on the products from the reactions of NO₃ with *iso*- and *tert*-butyl methacrylate. In all the reactions systems there is a pronounced slope in the spectrum baseline from 1900 to 4000 cm⁻¹ which is indicative for substantial formation of secondary organic aerosol (SOA).

4.3. Atmospheric implications

The contribution of NO₃ radicals to the atmospheric oxidation of *n*-butyl methacrylate, *iso*-butyl methacrylate and *tert*-butyl methacrylate can be assessed by estimating the lifetimes of these unsaturated esters with respect to reaction with the oxidant. Kinetic data are available for the reaction of *n*-butyl methacrylate with OH radicals [23], O₃ molecules [24] and Cl atoms [25] and allow a direct comparison of the atmospheric lifetime of *n*-butyl methacrylate with respect to oxidation with these oxidants with that of NO₃. Unfortunately, as indicated in the discussion, kinetic data are not available on the reactions of OH radicals, O₃ molecules and Cl atoms with *iso*-BMA and *tert*-BMA.

Tropospheric lifetimes for the reaction of NO₃ with *n*-butyl methacrylate have been calculated using the expression: $\tau_{\text{NO}_3} = 1/k_{\text{NO}_3}[\text{NO}_3]$, where k_{NO_3} is the rate coefficient for the reaction of NO₃ with the unsaturated ester and [NO₃] is the typical atmospheric concentration of the oxidant. The rate coefficients obtained in this work have been used in combination with a 12 h daytime average global tropospheric NO₃ radical concentration of [NO₃] = 5 × 10⁸ molecule cm⁻³ [37] for the lifetime calculations. The estimated tropospheric lifetimes at room temperature of the unsaturated esters with NO₃ radical were calculated to be around 4 days for all three butyl methacrylate isomers.

The reported atmospheric lifetimes for the reactions of *n*-BMA with OH, O₃ and Cl are 2 h, 40 h and 3 days, respectively [23–25], and on the basis of structural similarities the analogous lifetimes for *iso*- and *tert*-butyl methacrylate isomers are expected to be very similar to those of *n*-BMA. The short lifetimes, in the range of few hours, for the OH-initiated degradation, indicate that the butyl methacrylates will be rapidly removed in the gas phase and degraded near to their emissions sources with a potential contribution from Cl-atom mediated oxidation in areas where the Cl-atom concentration is high enough.

Night-time NO₃-initiated degradation of the butyl methacrylates will only play a minor role.

However, some OH radical production can occur at night via OH radical production from RO₂ + HO₂ reactions [38], which will add to the nighttime loss of the unsaturated methacrylates.

Although the reactions of NO₃ with α,β -unsaturated acrylates and methacrylates are slow and the nighttime conversion will be small the potential for their reaction products to act as NO_y reservoirs still needs to be considered. Presently only acyl

peroxynitrates are considered stable enough to accumulate to measurable mixing ratios in the troposphere while alkyl peroxynitrates are quite unstable with thermal lifetimes of a few seconds at room temperature [39]. However, nothing is currently known about the lifetimes of the type of peroxynitrate that will be formed from addition of NO₃ to an α,β -unsaturated carbonyl or ester compound. The continued presence of absorption bands attributable to a peroxynitrate in the product spectrum even at extended reaction times possibly implies that their thermal lifetime is longer than that of alkyl peroxynitrates. However, this needs experimental verification under more controlled conditions and it is not expected that the peroxynitrates from reaction of NO₃ with α,β -unsaturated carbonyls will accumulate in the atmosphere.

The yields of alkyl pyruvates from the reactions of NO₃ with alkyl methacrylates still remain to be quantified, although this is the case the reactions of NO₃ with alkyl methacrylates are not likely to be effective reservoirs for atmospheric nitrogen since NO₂ will be released as a co-product in the oxidation process. Similarly, the formation of 1,2-dinitroxy compounds will only be a very temporary sink since the compounds contain an α -nitrooxy carbonyl entity and photolysis will be an effective atmospheric loss process. Recent studies have shown that the photolysis of compounds containing an α -nitrooxy carbonyl entity are fast and will release NO₂ this photolysis sink being potentially 2–20 times higher than their sink due to reaction with OH [40,41]. All the factors discussed above indicate that NO₃-radical mediated degradation of α,β -unsaturated carbonyls will have little or no effect on the reactive nitrogen species (NO_y) budget [42] and effects if any will be on local scales fairly close to their emission sources.

The non-radical oxidation products of NO₃ + butyl methacrylates reactions will be multi-functional organic nitrates containing alcohol, peroxide or carbonyl groups. These compounds have low vapor pressures and consequently can partition onto atmospheric particles to generate secondary organic aerosol (SOA) [7]. Laboratory experiments have found higher SOA yields from NO₃ + VOC reactions than the corresponding OH reactions and there is also evidence that heterogeneous reactions of aerosol with NO₃ radicals may significantly affect aerosol properties [43].

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