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Kinetics of the Reactions of NO_3 Radical with Methacrylate Esters

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Abstract

Two different experimental methods (relative rate and absolute rate methods) were used to measure the rate coefficients for the reactions of NO_3 radical with six methacrylate esters: methyl methacrylate (MMA, k_1), ethyl methacrylate (EMA, k_2), propyl methacrylate (PMA, k_3), isopropyl methacrylate (IPMA, k_4), butyl methacrylate (BMA, k_5), isobutyl methacrylate (IBMA, k_6). In the relative rate method, the loss of the esters relative to that of a reference compound was followed in a 7300 L Teflon-walled chamber at (298±2) K and (1000±5) hpa. In the absolute method, the temporal profiles of NO_3 and N_2O_5 were followed using a dual channel cavity ring down spectrometer in the presence of an excess of ester in the 7300 L chamber. The rate coefficients from these two methods (weighted averages) in the units of 10^{-15} cm^3 $molecule^{-1}$ s^{-1} at 298 K are: k_1 = (2.98±0.35); k_2 = (4.67±0.49); k_3 = (5.23±0.60); k_4 = (7.9_1±1.0_0); k_5 = (5.71±0.56); and k_6 = (6.24±0.66). The quoted uncertainties are at the 2σ level and include estimated systematic errors. Unweighted averages are also reported. In addition, the rate coefficient k_7 for the reaction of NO_3 radical with deuterated methyl methacrylate (MMA-D8) was measured using the relative rate method to be essentially the same as k_1. The trends in the measured rate coefficient with the length and nature of the alkyl group, along with the equivalence of k_1 and k_7 strongly suggests that the reaction of NO_3 with the methacrylate esters proceeds via addition to the double bond on the methacrylate group. The present

results are compared with those from previous studies. Using the measured values of the rate coefficients, along with those for reactions of these esters with OH, O_3, and chlorine atoms, the atmospheric lifetimes of methacrylate esters are calculated. We suggest that NO_3 radicals do contribute to the atmospheric loss of these unsaturated esters, but to a lesser extent than their reactions with OH and O_3.

1 Introduction

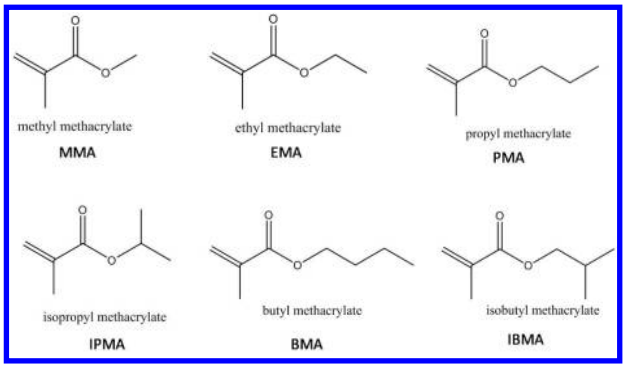
Methacrylate esters are important unsaturated oxygenated volatile organic compounds (OVOCs) used in the production of polymers. They are used extensively for manufacture of industrial products such as resins and plastics. Due to their high volatility, these unsaturated OVOCs may be released into the atmosphere, particularly in industrial areas. For example, more than 5,000 tonnes of methyl methacrylate is produced every year in the European Union. The maximum production capacity in each location methacrylates is estimated to be around 10,000 tonnes per year and release from these facilities are estimated to be between 0.005% to 1.1 % of the production values[1]. If emitted, their atmospheric degradation could lead to surface ozone and aerosols formation.

Once released, these unsaturated OVOCs are degraded in the atmosphere by reaction with various reactive species, which include OH and NO_3 radicals, chlorine atoms and O_3. [2] The nitrate radical, NO_3, is a photochemically unstable radical that is prevalent at night, especially in polluted areas that have large NOx emissions. NO_3 is known to be an important nighttime oxidant for OVOCs in the atmosphere.[3] Therefore, rate coefficients for the reactions of NO_3 radicals with methacrylate esters are needed to assess their atmospheric loss rates, especially at night.

Kinetics and products of reactions of OH radical reactions with acrylates and methacrylates has been the subject of several studies.[4-5] Reactions of several methacrylate

esters with O_3 have also been studied at room temperature.[6-7] Rate coefficients for the reactions of chlorine atoms with methyl methacrylate (MMA) and ethyl methacrylate (EMA) have been reported.[8-9] Several groups[10-13] have measured the rate constants for the reaction of NO_3 with several methacrylates near 298 K via the relative method, often using the reaction of NO_3 with propene as the reference.

In this work, we report the room temperature (298 ± 2K) rate coefficients for the reactions of NO_3 radical with six of the methacrylate esters (shown below): methyl methacrylate (MMA) - k_1; ethyl methacrylate (EMA) - k_2; propyl methacrylate (PMA) - k_3; isopropyl methacrylate (IPMA) - k_4; butyl methacrylate (BMA) - k_5; and isobutyl methacrylate (IBMA) - k_6.



We used two different experimental methods: (1) a relative rate method where the loss of the ester was measured relative to that of a reference compound while competing for a common pool of NO_3 radicals; and (2) a direct method where the temporal profiles of NO_3 and N_2O_5 were measured using cavity ring down spectroscopy to detect NO_3 and N_2O_5 in

an excess of known concentrations of esters. Both N_2O_5 and NO_3 (which are essentially in equilibrium) decay together when NO_3 is lost via its reaction with the hydrocarbon. Therefore, we used a box model consisting of 5 reactions (see later) to simulate the temporal profiles of NO_3 and N_2O_5 and quantitatively compare them (via least squares method) with the observed profiles of these species. The use of these two complementary methods enhances our confidence in the measured rate coefficients. In addition, the rate coefficient of deuterated methyl methacrylate (MMA-D8) with NO_3 radical was also investigated to shed light on the mechanism of the reaction. Using the obtained kinetics data, the atmospheric lifetimes of methacrylate esters towards NO_3 radicals were calculated and compared with those due to loss via reactions with OH radicals, O_3 and chlorine atoms (Cl). The kinetics results also enhance the available database on NO_3 reactions.

2 Experiments and Results

In this section, we will describe our results from the two methods that were used. Because the experimental methods were somewhat different, we will first describe the chamber that was used for both methods followed by the analytical methods that were employed. Subsequently, the obtained data are presented.

2.1 Experimental system: Indoor atmospheric simulation chamber

The kinetic of NO_3 with esters were studied at room temperature (298±2K) in the ICARE-7300L Teflon chamber (Figure1), which has been described in detail.[14-15] We will describe here only the features necessary to understand this study. The chamber was equipped with three key analytical tools: (1) a proton transfer reaction mass spectrometer, which was fed from the center of the chamber, to measure the concentrations of hydrocarbon reactants (and some of the products); (2) a Nicolet 5700 Magna FT-IR spectrometer (which sampled approximately 2m near the center of the chamber) the coupled to a white-type mirror system with roughly 70 passes resulting in an optical path of about 140 m; and (3) a cavity ring down spectrometer fed from the center of the chamber (with its inlet next to that for the PTR-MS) to measure NO_3 and N_2O_5. (We could also estimate the concentration of NO_2 using this system.) All the three analytical tools sampled essentially the same part of the chamber. The contents of the chamber were mixed by two

fans internal to the chamber. In addition, the chamber was equipped with multiple thermocouples to measure temperature and a set of capacitance manometers to measure pressure within the chamber, and a gas handling system to input known amounts of gases into the chamber.

The atmospheric pressure (1000±5hpa) chamber was made of Teflon film and kept dark by shrouding it in a container equipped with black curtains. Purified dry air (relative humidity <3%) was constantly flowed into the chamber. The chamber was flushed with a large flow (about 120L/min) of dry air to clean out the chamber between experiments or to clean it overnight. However, during kinetics studies, a small flow (about 5-10L/min, depending on the sampling flow rate) of purified air was added just to compensate for the continuous withdrawal of gas from the chamber for analysis; such a flow maintained a constant pressure in the chamber that was slightly above ambient. This flow arrangement resulted in a constant slow dilution of the reactants in the chamber. We measured the dilution rate and mixing time in the chamber by injecting a sample of SF_6 (>99.99%, Alpha Gaz) into the chamber and measuring the temporal profile of SF_6 using the in situ FTIR spectrometer. The mixing time (for near complete mixing, >99%) was about 30 seconds, much shorter than the times for reactions studied here, and the dilution rate could be expressed as a first order rate coefficient of around $2.5\times10^{-5}s^{-1}$ (see below).

The gas handling system, external to the chamber, was designed to inject a known volume of a gas into the chamber. We could also inject a known volume of liquid (that

evaporated immediately within the chamber) through a septum into a gas flow that reached the middle of the chamber. Pressures in the gas handling system were measured using calibrated capacitance manometers (0-10 and 0-100 Torr, MKS Baratron).

In the chamber, the organic reactants were detected in real time by using a proton-transfer-reaction time of flight mass spectrometer (PTR-ToF-MS), and the concentrations of N_2O_5 and NO_3 were monitored on line by a two-channel cavity ring down spectrometer (CRDS). The details of these instruments are described in the following sections.

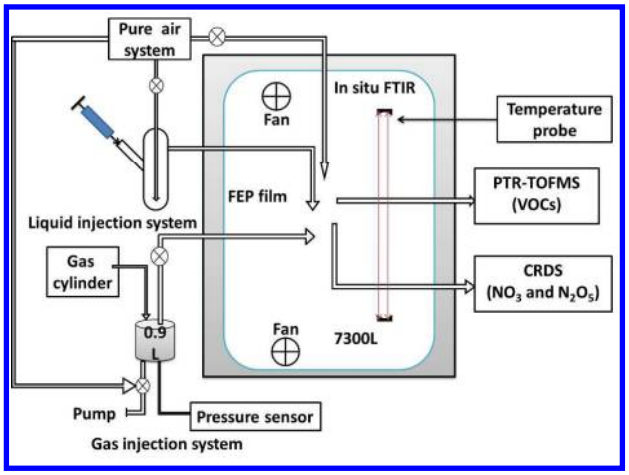


Figure1: Schematic diagram of the 7300 L chamber used to study the reaction of NO_3 radicals with methacrylate esters along with the analytical methods used to detect reactants. The gas inlet system is shown on the left. The gas outlets and the curtains to keep the chamber dark are not shown. The figure is not to scale.

2.1.2 PTR-TOFMS

The high-resolution proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS)[16] (IoniconAnalytik, PTR-ToF-MS 8000) with hydronium ions (H_3O^+) ion source was used to measure methacrylates. The pressure and temperature in the PTR-ToF-MS drift tube was maintained at 2.1 mbar and 333 K. A drift voltage of 400 V was used such that the reduced electric field, E/N, was 98 Td (E is the field strength in V cm^{-1} and N is the number density of gas in molecules cm^{-3}). The flow rate of air from the chamber into the drift tube was approximately 150 mL min^{-1}. The mass resolution of the mass spectrometer, m/Δm, typically ranged from 3500 to 4500. The mass spectral data were analyzed by a PTR-ToF Data Analyzer software[17] and the normalized peak intensities (in counts per second, ncps) were used for calibration and monitoring. The measured signals varied linearly with the concentrations of the hydrocarbon. The detection sensitivities for the hydrocarbons were derived from the slopes of the calibrations plots of the measured signal (ncps) versus the partial pressure of the hydrocarbon (ppbv) (See also Figure S1 in the supporting information). The detection sensitivities (in units of ncps/ppbv, 1ppbv = 2.46×10^{10} molecule cm^{-3} at 298K and 101.3kpa) at their monitored mass are shown in Table 1.

Table 1. A list of specific masses monitored to detect various VOCs using the proton

transfer mass spectrometry. The detection sensitivities are also listed.

	Mass charge ratio (m/z)	Detection sensitivities （ncps/ppbv）
propene	43.05	5.22±0.09
propanal	59.5	7.13±0.09
MMA	101.06	38.9±0.5
d8-MMA	109.09	40.0±0.6
EMA	115.07	5.95±0.47
	87.05	39.2±1.7
PMA	87.05	51.4±0.5
IPMA	87.05	46.8±1.4
BMA	87.05	53.8±2.1
IBMA	87.05	26.1±0.5

2.1.3 CRDS

A two-channel cavity ring down spectrometer operating at 662 nm was used to simultaneously measure the concentrations of NO_3 (in one channel) and N_2O_5 + NO_3 (in another channel). The detection principle and operating characteristics of this instrument has been described in detail elsewhere.[18-21]

The first channel measured the concentration of NO_3. The second, parallel, channel was heated to convert N_2O_5 to NO_3; total NO_3 (which upon quantitative conversion of N_2O_5 to NO_3) was measured and it represents the sum of NO_3 and N_2O_5. The time resolution of the instrument was 1s with detection sensitivities of between 0.4 and 2 ppt for NO_3 and N_2O_5 for 1 second integration, as described in detail by Fuchs et al.[22] The air sample entering the CRDS system was passed through a filter to remove aerosols, which

scatter the 662 nm light and degrade the instrument sensitivity for gas phase measurement. The combined loss of NO_3 and N_2O_5 to the walls of the instrument and the filter located upstream of this same device have been estimated[22-25] to be less than 20% and 4%, respectively, for NO_3 and N_2O_5; these losses are accounted for in calculating the concentrations. The uncertainties in the absorption cross section of NO_3 radical at 662 nm and the ratio of the cavity length to the length over which NO_3 and N_2O_5 are present add to the estimated uncertainties. Based on these factors, the overall (asymmetric) accuracy of the NO_3 and N_2O_5 measurements, respectively, are estimated [26] to be -8% to +11% and from −9% to +12%. Note that the precision of the measurements of NO_3 and N_2O_5 are much better than the quoted absolute uncertainties under the concentration conditions used in the present study (with initial mixing ratios of NO_3 between 500 and 2,500 pptv and initial mixing ratios of N_2O_5 between 8,000 and 25,000 pptv).

2.1.4 Fourier Transform Spectrometer

A commercial Nicolet 5700 Magna FT-IR spectrometer was coupled to a white-type mirror system located away from the walls and close to the center of the chamber. The optical path length within the chamber was about 140 m. The instrument was operated at a resolution of 1 cm^{-1}. The spectra from the instrument were analyzed using the software provided by the vendor. All the details of the instrument and data analyses are given previously.[14-15] The FTS was used to measure SF_6 (934 cm^{-1} - 954 cm^{-1}), hydrocarbons,

and some other species during the course of this study; they are noted when appropriate.

2.2 Chemicals

The purities of chemicals used in the experiments as given by the manufacturer were: methyl methacrylate (MMA, > 99%, TCI), ethyl methacrylate (EMA, >99%, TCI), propyl methacrylate (PMA, >97%, Aldrich), isopropyl methacrylate (IPMA, >98%, TCI), butyl methacrylate (BMA, >99%, TCI), isobutyl methacrylate (IBMA, >98%, TCI), propene (>99%, Air Liquid), and propanal (>98%, Aldrich). The isotopic purity of methyl methacrylate-D8 (MMA-D8 from Apollo Scientific Limited) was quoted to be 99.50 Atom % D. The levels of stabilizers in the samples of esters are noted later. In this study, the NO_3 radicals were produced by the thermal decomposition of N_2O_5 injected into the chamber. Pure N_2O_5 was synthesized by mixing NO with O_3 in a slow flow and collecting N_2O_5 at dry ice temperature, followed by purification, as described by Davidson et al.[27]

2.3 Kinetic study methods and results

As noted earlier, we measured the rate coefficients using two different methods: (a) a relative rate method by following the depletion of a VOC and a reference compound, and (b) an absolute method where the temporal profiles of NO_3 and N_2O_5 in an excess of VOC. For ease of presentation, these two experiments and the obtained results will be presented separately below.

2.3.1 Relative rate method

The experiments were conducted in the chamber (7300L) at atmospheric pressure (1000±5hpa) and at temperature of 298±2K. The depletion of a reactant (each methacrylate esters; hereinafter VOC) and a reference (propene, propanal and MMA) in the presence and in the absence of NO_3 (and N_2O_5 in equilibrium with NO_3 and NO_2) were monitored by PTR-ToF-MS. To account for dilution, as noted earlier, the losses of VOCs in the absence of NO_3 were measured along with the depletion of SF_6 added simultaneously with the VOCs to the chamber. This small decay was essentially first order in the concentrations of VOC and SF_6. The first order rate coefficient for the loss of each reactant in the absence of NO_3 was essentially the same as that for the loss of SF_6; this decay is attributed to dilution caused by the continued injection of dry air into the chamber. The rate first order rate coefficient for the removal of SF_6 and the VOCs, k_d, was $(2.5\pm0.2)\times10^{-5}s^{-1}$. This rate coefficient is essentially what we calculate from the volume flow rates of pure air added to the known volume of the chamber to maintain a constant pressure. The related Figure S2 is given in the supporting information.

Subsequent to these measurements, a sample of N_2O_5 was introduced into the chamber where it dissociated to give NO_3. The rates of depletion of VOCs and reference compound were monitored using the PTR-MS. The VOCs and reference compound are competing for the same pool of NO_3 radicals and are represented by the reactions:

$$\text{VOC}+\text{NO}_3 \xrightarrow{k_{voc}} \text{Products} \qquad \text{(A)}$$
$$\text{Reference}+\text{NO}_3 \xrightarrow{k_r} \text{Products} \qquad \text{(R)}$$

Under these conditions, their relative losses of the VOC and reference compound are given by:

$$\ln\frac{[\text{VOC}]_0}{[\text{VOC}]_t} - k_d t = \frac{k_{VOC}}{k_r}\left(\ln\frac{[\text{Reference}]_0}{[\text{Reference}]_t} - k_d t\right) \qquad \text{(I)}$$

where $[VOC]_0$ and $[VOC]_t$ are the concentration of reactant at initial time t_0 and at time t, $[Reference]_0$ and [Reference] are the concentration of reactant at t_0 and t, k_{voc} and k_r were the rate coefficients for reaction (A) and (R), k_d is the first order rate constant for dilution in the chamber. A plot of $\ln([VOC]_0/[VOC]_t) - k_d t$ versus $\ln([Reference]_0/[Reference]_t) - k_d t$ would be a straight line with a zero intercept and a slope of k_{voc}/k_r. In our experiments, the rate constants of the reactions of the reference compounds with NO_3 radicals were taken to be $k_r(\text{propene}) = (9.5\pm5.5)\times10^{-15}$ $cm^3 molecule^{-1} s^{-1}$ [28], $k_r(\text{propanal}) = (6.3\pm2.6)\times10^{-15}$ cm^3 $molecule^{-1} s^{-1}$ [28], k_r (MMA) $= (2.98\pm0.35)\times10^{-15}$ cm^3 $molecule^{-1} s^{-1}$ (weighted average of the absolute and relative methods from this work; see below). Note that the weighted average for MMA is essentially that measured via the absolute method. The initial concentration of each reactant used in this work is shown in Table 2. A complete summary of the initial concentrations and experimental conditions are given in the supporting information as Table S1.

Figures 2-1 and 2-2 show the loss of the esters relative to propene and MMA, respectively, according to Equation I. For measurement of each rate constant, several

mixtures of the reactant and standard were used and they are all included in the same plots. Clearly, the plots show good linearity for all reactions. These plots were analyzed via linear least squares analyses to obtain the slope of k_{voc}/k_r. The obtained values (average of multiple measurements) of the rate constants are summarized in Table 2.

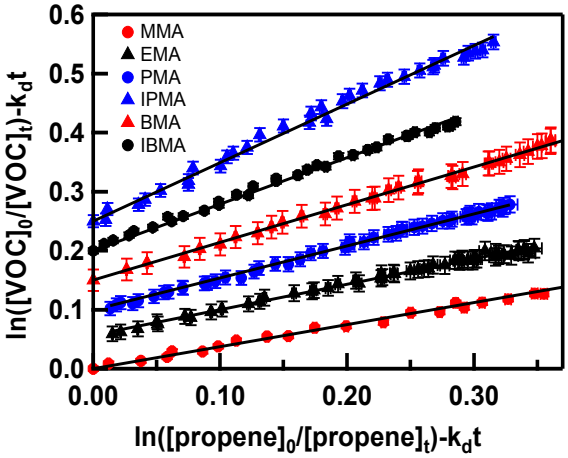


Figure 2-1 Plots of the losses of esters relative to those of propene, which was used as the reference. The losses shown are for: MMA, red filled circles; EMA, black triangles, Y axis offset by 0.05; PMA, blue filled circles, Y axis offset by 0.1; IPMA, blue triangles, Y axis offset by 0.25; BMA, red triangles, Y axis offset by 0.15; IBMA, black filled circles, Y axis offset by 0.20. The linear least squares fits are shown as lines.

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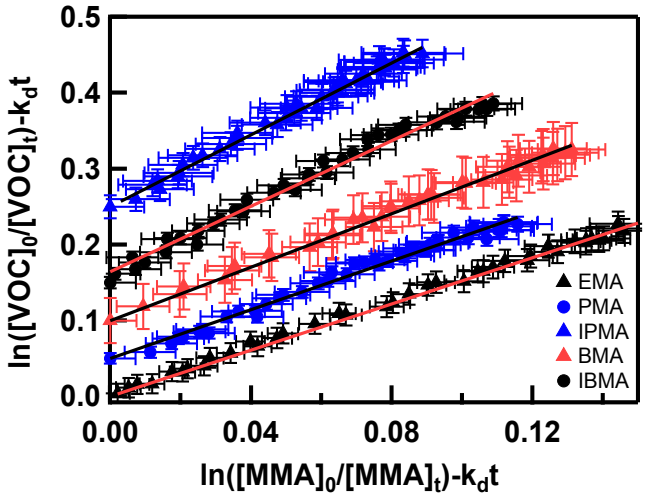

Figure 2-2 Plots of the losses of esters relative to those of MMA used as reference. The specific esters are noted in the legend within the figure (EMA, filled black circles; PMA, blue filled circles, Y axis offset by 0.05; IPMA, blue triangles, Y axis offset by 0.25; BMA, red triangles, Y axis offset by 0.1; IBMA, blue filled circles, Y axis offset by 0.15). The linear least squares fits are shown as lines.

The quoted errors in the rate constant ratios (k_{voc}/k_r) are twice the standard deviation ($2\sigma_{kvoc/kr}$) in the linear least-squares fit of the measured losses to Equation I. In addition to the precision of this ratio, we have included the estimated uncertainty (as given by the IUPAC evaluations) in the rate coefficient ($k_r \pm \sigma_{kr}$) for the reaction of NO_3 with the reference compound.

Table 2. Summary of the results from the relative rate study for reaction of NO_3 with

methacrylate esters at 298±2K.

VOCs	$[VOC]_0$ 10^{12} (molecule cm^{-3})	Ref. Compound	No. of experiments	$\frac{k_{voc}}{k_r} \pm 2\sigma_{(\frac{k_{voc}}{k_r})}$	$k_{voc}\pm2\sigma_{voc}$ 10^{-15} (cm^3 $molecule^{-1}s^{-1}$)
Methyl methacrylate (MMA)	1.13 to 3.40	propene	6	0.37±0.04	(3.52±2.07)
		propanal	2	0.58±0.06	(3.77±1.56)
				Average	(3.6_5±1.3_0)
				Weighted average	(3.6_8±1.2_4)
Ethyl methacrylate (EMA)	1.28 to 2.56	propene	3	0.53±0.05	(5.04±2.95)
		MMA	2	1.55±0.07	(4.62±0.58)
				Average	(4.8_3±1.5_0)
				Weighted average	(4.63±0.57)
Propyl methacrylate (PMA)	1.10 to1.66	propene	3	0.56±0.04	(5.32±3.10)
		MMA	3	1.70±0.16	(5.07±0.76)
				Average	(5.2_0±1.6_0)
				Weighted average	(5.08±0.74)
Isopropyl methacrylate (IPMA)	1.10 to1.65	propene	3	0.91±0.30	(8.65±5.76)
		MMA	3	2.71±0.61	(8.08±2.05)
				Average	(8.3_7±3.0_6)

				Weighted average	$(8.1_4 \pm 1.9_3)$
Butyl methacrylate (BMA)	1.01 to 2.53	propene	3	0.70 ± 0.08	(6.65 ± 3.87)
		MMA	3	1.84 ± 0.12	(5.48 ± 0.74)
				Average	$(6.0_7 \pm 1.9_7)$
				Weighted average	(5.52 ± 0.72)
Isobutyl methacrylate (IBMA)	0.99 to 2.48	propene	3	0.75 ± 0.02	(7.13 ± 4.13)
		MMA	3	1.95 ± 0.23	(5.81 ± 0.96)
				Average	$(6.4_7 \pm 2.1_2)$
				Weighted average	(5.88 ± 0.94)

The number of appropriate significant figures are shown for the averages. The number of significant figures in the reported values are more than what is warranted by the errors, but are shown for completeness. To maintain consistent number of significant figures, some numbers with larger errors are shown with the last digit as a subscript.

2.3.2 Rate coefficients via monitoring temporal profiles of NO_3/N_2O_5 loss using CRDS

The rate coefficients for the reactions of NO_3 radicals with methacrylate esters were also measured by following the temporal profiles of NO_3 and N_2O_5 in an excess of esters. During this process, NO_3 and N_2O_5 are nearly in equilibrium such that one could simply

attempt to fit the temporal profiles to obtain the rate coefficients. However, we fitted the observed profiles to the following set of reactions that occur in the chamber:

$$N_2O_5 \xrightarrow{k_{dc}} NO_3 + NO_2 \qquad (R1)$$

$$NO_3 + NO_2 \xrightarrow{k_f} N_2O_5 \qquad (R1')$$

$$NO_3 \xrightarrow{k_{wall1}} loss \qquad (R2)$$

$$N_2O_5 \xrightarrow{k_{wall\,2}} loss \qquad (R3)$$

$$VOC + NO_3 \xrightarrow{k_{voc}} loss \qquad (R4)$$

First, N_2O_5 was injected into the middle of the chamber. N_2O_5 decomposed immediately in the chamber to give NO_3 and NO_2 and set up an equilibrium with remaining N_2O_5. The temporal variation of NO_3 and N_2O_5 in the chamber were continuously measured using CRDS. The concentrations of NO_3 and N_2O_5 decreased with time as N_2O_5 and NO_3 were lost in the chamber due to wall loss and reaction with impurities.

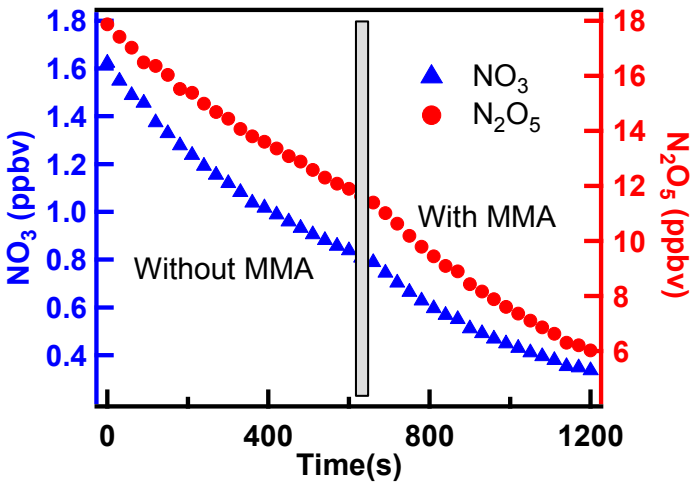

Figure 3 Measured temporal profiles of NO_3 and N_2O_5 mixing ratios in the chamber in the absence (up to the vertical gray bar) and presence of MMA (after the gray bar). The gray bar

indicates the time at which VOCs were injected into the chamber and the time it took for complete mixing. k_{wall1}=0.0065 s^{-1}, k_{wall2}=0.00032 s^{-1}.

Typical observed temporal profiles of NO_3 and N_2O_5 in such experiments after injection of N_2O_5 into the chamber are shown in Figure 3. The measured temporal profiles were fit using a box model that integrated the set of reactions shown above to derive the time dependence of NO_3 and N_2O_5. The fitting was done by minimizing the sum of least squares for both NO_3 and N_2O_5 profiles, by changing the input parameters that included wall loss rates, the equilibrium constant, the rate coefficient for the reaction of NO_3 with VOC as well as the initial NO_2 concentration. First, the data in the absence of VOC was fit to the reaction scheme with VOC concentration set to zero. Using the known values of the rate coefficients for Reactions R1 and R1', the values of k_{wall1}, k_{wall2}, and the initial concentration of NO_2 were derived from the fit. The equilibrium constant was slightly varied to improve the fit, if necessary. The first-order wall loss rate constants of NO_3 and N_2O_5, respectively, k_{wall1} (s^{-1}) and k_{wall2} (s^{-1}). Note that we did not have an accurate independent measure of NO_2 in the chamber since our NO_2 detector (which converted NO_2 to NO by passing it over a hot molybdenum catalyst) also detected N_2O_5. Occasionally, we needed to change the N_2O_5 dissociation rate constant by at most 10% to improve the fit, which reflected the uncertainty in the temperature in the chamber of about 1 K. The equilibrium constant, $k_{eq} = [N_2O_5]/[NO_3][NO_2] = k_f/k_{dc}$, and value of k_{dc}, k_{eq} and k_f at

different temperature were taken from NASA/JPL recommendation.[29]

After about 10 minutes, a sufficient length of time for NO_3 and N_2O_5 observations that enabled an accurate calculation of the equilibrium constant, a known concentration of the VOC was introduced into the chamber and its concentration was measured using PTR-MS and/or FTIR instruments. The concentration of the ester was always much greater than those of N_2O_5 or NO_3 in the chamber. The temporal profile of N_2O_5 and NO_3 measured after 60 s of VOC injection were again fit to minimize the sum of least squares for NO_3 and N_2O_5 decays in the above reaction scheme with only the rate coefficient for the reaction of VOC with NO_3 being the variable As noted earlier, the time for complete mixing was 30 s. The initial concentration of NO_2 was taken to be equal to that calculated just prior to adding the VOC assuming equilibrium between NO_3 and N_2O_5, i.e.,

$$[NO_2]_0 = \frac{[N_2O_5]_0}{[NO_3]_0 k_{eq}} \qquad \text{(II)}$$

Figure 4 shows a fit of the observed temporal profiles of NO_3 and N_2O_5 and the fit of the profiles to the above reaction scheme.

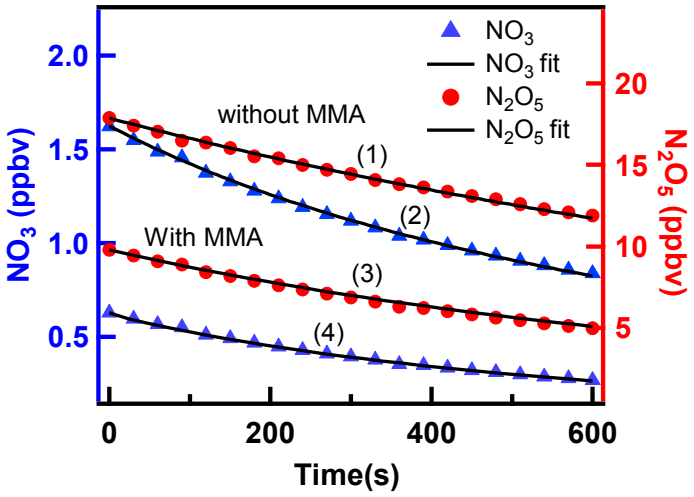

Figure 4: Observed NO_3 and N_2O_5 mixing ratios (circles and triangles) and their simulated temporal profiles (lines) after the injection of VOC into the chamber where NO_3 and N_2O_5 were present at equilibrium. Profile (1) - loss of N_2O_5 without MMA; Profile (2) - loss of NO_3 without MMA; Profile (3) - loss of N_2O_5 with MMA; Profile (4) - loss of NO_3 with MMA. The concentration of MMA was 3.06×10^{12} molecule cm^{-3}. The fits yield a value of $k_{voc} = 2.98 \times 10^{-15}$ molecule^{-1} cm^3 s^{-1}.

Multiple experiments were carried out by varying VOC and initial N_2O_5 concentrations. In some cases, we included additional NO_2 in the chamber before the addition of N_2O_5 (to shift the equilibrium). The uncertainty in obtained value of k(VOC) due to fitting was very small, often much less than 3 %. However, the fits alone do not determine the uncertainty in the precision of our measured rate coefficient. They were obtained the standard deviation of the mean of multiple measurements and including the Student t value for the limited number of measurements. The results of our measurements are given in Table 3.

Table 3. Summary of the experimental conditions for and results from the absolute method to measure the rate constants for reaction of NO_3 with VOCs at 298±2K. The k_{VOC} values shown are those derived from fitting the observed profiles of NO_3 and N_2O_5 to a least squares algorithm.

Compound	T (K)	Initial mixing ratio (ppbv)			k_{VOC} measured[a]	k_{VOC} incl. systematic errors[b]
		VOC	NO_3	N_2O_5	10^{-15} (cm^3 $molecule^{-1}s^{-1}$)	
Propene	296	156.6	0.54	10.16	9.15	
	296	70.0	0.45	9.77	9.97	
					$(9.5_6 \pm 1.3_6)$	$(9.5_6 \pm 1.8_0)$
MMA	295	121.9	0.68	11.05	2.90	
	296	124.3	0.63	9.79	2.98	
	298	363.7	0.78	11.46	2.89	
					(2.92±0.12)	(2.92±0.37)
EMA	298	126.1	0.81	10.85	4.56	
	300	130.1	0.59	6.79	5.09	
	298	333.3	1.13	16.58	4.69	
					(4.78±0.65)	(4.78±0.93)

PMA	297	113.5	0.79	11.15	5.14	
	300	279.7	1.11	10.13	5.77	
	296	113.6	0.83	8.33	5.59	
					(5.50±0.76)	(5.5_0±1.0_0)
IPMA	297	101.6	0.81	10.28	7.94	
	296	86.2	0.91	13.01	7.56	
	300	209.3	0.84	13.69	8.00	
					(7.83±0.56)	(7.8_3±1.1_5)
BMA	299	264.2	1.00	8.80	6.16	
	299	199.2	1.25	11.42	5.86	
	300	251.8	1.10	12.92	6.00	
					(6.00±0.35)	(6.00±0.89)
IBMA	296	142.3	0.77	10.90	6.52	
	297	154.5	1.09	13.00	6.46	
	297	162.6	0.99	9.44	6.82	
					(6.60±0.45)	(6.60±0.94)

[a] Quoted error is at the 95% confidence level and is a measure of the precision of our measurements. It includes Student t-distribution contribution due to the limited number of measurements. To maintain consistent number of significant figures, some numbers with larger errors are shown with the last digit as

a subscript.

[b] The quoted errors include estimated systematic errors as described in the text.

2.4 Error estimation

Relative rate measurements: One of the advantages of relative rate measurements is that uncertainties in absolute concentrations of either reactant do not lead to an error in the measured values since we depend on the relative concentrations changes as the reaction proceeds to derive the rate constant. The concentrations of the reactant, in our case esters, and the reference compound (propene, propanal, or MMA) were measured using the same PTR-ToF-MS system. The calibration plots of the concentration of VOC versus their signals were linear. The precision of the measured signal contributes to the precision of the measured rate constants. The slopes of the plots shown in Figures 2-1 and 2-2 yielded the precision of the measurement. The errors in the values of rate constant ratios (k_{voc}/k_r) are twice the standard deviation ($2\sigma_{kvoc/kr}$) in the least-squares fit of the measured losses to Equation I. In addition to the precision, the main contributor to the accuracy of the measured rate constant is the accuracy of the rate coefficients for the reference reactions. The rate coefficient for the reactions of NO_3 with propene and propanal have been evaluated and we assume the accuracy to be those assessed by the evaluation panels, $k_r(\text{propene})^{28} = (9.5\pm5.5)\times10^{-15}\,\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$, $k_r(\text{propanal})^{28} = (6.3\pm2.6)\times10^{-15}\,\text{cm}^3$

molecule^{-1}s^{-1}. (As noted later, we believe that the uncertainty for the reaction of NO_3 with propene is less than that noted by the evaluation.) We combined the precision of our measured values with the quoted uncertainties in the rate coefficient for the reference reaction to estimate the overall accuracy of the measured rate coefficients.

$$\sigma_{voc} = k_{voc}\sqrt{\left[\frac{2\sigma_{\left(\frac{k_{voc}}{k_r}\right)}}{\frac{k_{voc}}{k_r}}\right]^2 + \left[\frac{\sigma_{k_r}}{k_r}\right]^2} \qquad \text{(III)}$$

Absolute rate constant measurements- The errors in determining the rate coefficients by monitoring the temporal profiles of NO_3 and N_2O_5 arise from the precision in the measurements of NO_3 and N_2O_5, the absolute values of N_2O_5 and NO_3 and the uncertainty in the concentration of the excess reagent, the esters in our study. Ordinarily, the absolute values of the NO_3 reactant would not be needed in an absolute method where NO_3 temporal profile is monitored in an excess of esters. However, in the present study, NO_3 is in equilibrium (or almost in equilibrium) with N_2O_5 and this situation requires absolute concentrations of the NO_3 and N_2O_5. The systematic errors in measurements of NO_3 and N_2O_5 using the CRDS system employed here have been assessed to be -8/+11% for NO_3 and -9/+12% for N_2O_5, as noted earlier. The uncertainty in the fitting, as noted above, is better than 3%. Systematic errors in the measured concentration of the esters are estimated for each compound using the uncertainty of the slope in the calibration plots (<4%) and the uncertainty in measuring ester concentration for the calibration (5%); all at 95%

confidence level. We just added these two errors to get the estimated uncertainty in the concentration of esters in the chamber since they could be correlated. Then, the overall estimated error was calculated by adding in quadrature the fitting error, estimated contribution of absolute concentrations of NO_3 and N_2O_5, the precision of the measurements of k_{VOC}, and the estimated uncertainty in the concentration of the esters. Table 3 lists the uncertainties in the measured values of the rate constants along with the estimated systematic errors.

We measured the rate coefficient for the reaction of NO_3 with propene using the absolute method. Our obtained results are in very good agreement with most of the literature values. This adds further confidence in our measured values of the rate coefficients using the absolute method. We note that most of the reported values for the rate coefficient for the NO_3 reaction with propene in the IUPAC assessment appears to agree reasonably well, though there are a few outliers. We suggest that the error bars given for the reaction of NO_3 with propene in the IUPAC is excessively conservative.

Another potential source of error in the rate coefficient measured using the absolute method is presence of reactive impurities in the sample of the esters. The methacrylates used in the study were the purest we could obtain from commercial vendors (see materials section for purity levels). However, they contained some stabilizers, which could potentially react more rapidly with NO_3 than the esters. The stabilizers used in the methacrylates were normally around 10-20 ppmv, the maximum was about 200 ppmv of

4-Methoxyphenol (MEHQ) in isopropyl methacrylate (IPMA). Stabilizers used with these esters are aromatic compounds with a large side chain containing a saturated group. If MEHQ reacted very rapidly with NO_3, we could indeed overestimate this rate coefficient. Indeed, if the rate coefficient for the reaction of MEHQ with NO_3 were 1 x 10^{-10} cm^3 $molecule^{-1}$ s^{-1} as quoted for other methoxyphenols by Lauraguais et al. [30] we should have measured a value of roughly 2 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1} for IPMA. However, our measured values using the direct and relative methods agree well (see Table 4). Therefore, we do not believe that our reported values were greatly affected by the presence of MEHQ. In case of the other esters, the presence of stabilizers at the quoted levels would contribute at most 20% to the measured value using the direct method. Again, the agreement between the relative and direct method suggests that the contributions of the stabilizer to the measured rate coefficients were not large. We note that the PTR-ToF-MS spectra of each of the esters did not show any measurable hydrocarbons other than the ester. Based on these observations, we conclude that our measured absolute rate coefficients were not significantly influenced by the presence of impurities.

Lastly, we note that the rate coefficients measured here reflect that for the reaction of NO_3 with esters and there is no significant contribution from any possible reaction of N_2O_5 with esters. First, we varied the ratio of NO_3 to N_2O_5 by changing NO_2 and the measured rate coefficients were insensitive to this ratio. Second, the rate coefficients measured using the absolute method agrees with that from the relative method, where some of the reference

molecules are known to be non-reactive towards N_2O_5. Again, in these experiments, the ratios of NO_3 to N_2O_5 were very different and it also varied with the extent of reaction, with no effect on the derived rate coefficients.

3 Discussion

3.1 Comparison of rate coefficients obtained from two methods

We used two different methods to measure the rate coefficients for the reactions of NO_3 with methacrylate esters; they are summarized in Table 4. The rate constants values we measured using the two methods are in good agreement with each other, given the estimated uncertainties in the rate constants. The largest difference is for the reaction of NO_3 with MMA, where the rate coefficients from the two methods differ by about 25%.

We have used weighted average of the two methods, i.e., the absolute and the relate rate methods, to derive the best possible values for the rate coefficients for the reactions of NO_3 with methacrylate esters studies here. They are shown in Table 4.

Table 4 Rate constants values obtained in two methods for the reactions of NO_3 with methacrylate esters.

	Rate constants $k_{voc}(10^{-15}$	Ratio	k_{voc}

	molecule^{-1}cm^{3}s^{-1})		(k_{rm}/k_{ab})	(10^{-15} molecule^{-1}cm^{3}s^{-1})	
	Relative method (k_{rm})	Absolute method (k_{ab})		Unweighted average	Weighted average
MMA(k_1)	(3.68±1.24)	(2.92±0.37)	1.26	(3.30±0.65)	(2.98±0.35)
EMA(k_2)	(4.63±0.57)	(4.78±0.93)	0.97	(4.70±0.55)	(4.67±0.49)
PMA(k_3)	(5.08±0.74)	(5.50±1.00)	0.92	(5.29±0.62)	(5.23±0.60)
IPMA(k_4)	(8.14±1.93)	(7.83±1.15)	1.04	$(7.9_9\pm1.1_2)$ [a]	$(7.9_1\pm1.0_0)$ [a]
BMA(k_5)	(5.52±0.72)	(6.00±0.89)	0.92	(5.76±0.57)	(5.71±0.56)
IBMA(k_6)	(5.88±0.94)	(6.60±0.94)	0.89	(6.24±0.66)	(6.24±0.66)

a. To maintain consistent number of significant figures, some numbers with larger errors are shown with the last digit as a subscript.

Indeed, one could opt to use an unweighted average. Therefore, we have also listed them in the table. We prefer the weighted average mostly to put more weight on the direct method, especially since the quoted uncertainty in the rate coefficient for the reaction of NO3 with propene, a common reference for relative rate studies, is unusually large. This is discussed later.

3.2 Comparison with the kinetic results in literature

Several groups have measured the rate constants of NO_3 radical reactions with MMA, EMA and BMA using relative methods in small chambers (<150L) at room temperature and atmospheric pressure. In their experiments, the initial mixing ratios of the methacrylate esters were in a range of 5-20ppmv. A comparison of rate coefficients determined in this study with the literature data is shown in Table 5. As can be seen in the table, our values are in good agreement with previously reported values, given the reported uncertainties, whenever such comparisons are possible.

Given the reasonably good agreement between various reported studies and a lack of obvious reasons to prefer one study over the other, we suggest that an un-weighted average of all the results be used as recommended values for the rate coefficient. Such average values are also reported in the Table 5. Clearly, there are no previous reports for the rate coefficients for the reactions of NO_3 with PMA, IPMA, and IBMA. However, given the similarities of those compounds with the other methacrylates studied here, it appears that our rate coefficients are also accurate to about 20% and could be used with confidence.

Table 5 Summary of the rate coefficients of NO_3 with MMA, EMA and BMA obtained from literatures and this work.

Reactant	Reference Chemical	k_{VOC} reported $10^{-15}cm^3$ $molecule^{-1}s^{-1}$	Reference
MMA	propene	$(3.7_1 \pm 2.2_2)$[a]	10
	propene	$(3._{51} \pm 2.0_4)$[a]	12
	propene	$(3.6_1 \pm 2.1_0)$[a]	13
	propene	$(3.5_2 \pm 2.0_7)$	This work
	methacrolein	$(3.5_1 \pm 1.0_8)$	13
	1-butene	$(3.7_2 \pm 1.1_5)$	12
	propanal	$(3.7_7 \pm 1.5_6)$	This work
	AM[b]	(2.92±0.37)	This work
		(3.12±0.31)	Weighted average of all work
		(3.53±0.60)	Unweighted average of all work
EMA	propene	$(4.8_1 \pm 2.8_0)$[a]	12
	propene	$(5.7_0 \pm 3.3_1)$[a]	13
	propene	(5.04±2.95)	This work
	1-butene	$(5.0_9 \pm 1.6_1)$	12
	methacrolein	$(5.1_6 \pm 1.5_9)$	13
	MMA	(4.62±0.58)	This work
	AM[b]	(4.78±0.93)	This work

		(4.76±0.44)	Weighted average of all work
		(5.03±0.83)	Unweighted average of all work
BMA	propene	$(8.2_7 \pm 4.8_3)$[a]	13
	propene	$(6.6_5 \pm 3.8_7)$	This work
	1-butene	$(7.5_8 \pm 4.3_6)$	13
	MMA	(5.48±0.74)	This work
	AM[b]	(6.00±0.89)	This work
		(5.78±0.55)	Weighted average of all work
		$(6.8_0 \pm 1.53)$	Unweighted average of all work
PMA		(5.23 ± 0.60)	This work
IPMA		$(7.9_1 \pm 1.0_0)$	This work
IBMA		(6.24±0.66)	This work

[a] The values from the literatures were recalculated by using the rate constant of propene with NO_3 (9.5 ± 5.5) $\times 10^{-15}$ cm^3 $molecule^{-1}s^{-1}$, which was used in our study. Note that these uncertainties are likely to be overestimated because of the large uncertainty quoted by IUPAC. To maintain consistent number of significant figures, some numbers with larger errors are shown with the last digit as a subscript.

[b] Measured from the temporal profiles of NO_3 and N_2O_5, referred to as the absolute method.

3.3 Mechanism and Relationship between structure and reactivity of the methacrylate esters

The rate coefficients for all the methacrylate measured here are roughly in the same range, with the rate coefficient slightly increasing with extent of substitution going from methyl to ethyl to propyl to butyl methacrylate. We observe an increase in the reactivity with the chain length of the alkyl group. $k_{voc}(MMA)<k_{voc}(EMA)<k_{voc}(PMA)<k_{voc}(BMA)$. Further, the isoalkyl methacrylates react a little faster than their normal analogs. This is consistent with the electron donating inductive effect of the substituents (−C(O)OR), consistent with an electrophilic addition mechanism.[31] Such variations are consistent with NO_3 reaction proceeding via electrophilic addition to the double bond in the methacrylate group. These rate constants that have been measured for unsaturated esters, help understand the structure activity relationship (SAR) and complete the parameterization of this family of compounds. We have refrained from calculating SAR relations till data is available for esters. Curiously, however, the isopropyl methacrylate reacts faster than the normal analog while the isobutyl methacrylate reacts with almost the same rate coefficient as the butyl methacrylate. It would be interesting to see if there is enhanced H abstraction in IPMA reaction and leads to HNO_3 as a product.

To further examine this mechanism for the reaction, we studied the reaction of NO_3 with deuterated MMA. The rate coefficients for the reactions of MMA and MMA-D8 with

NO_3 radicals are essentially identical, with k_H/k_D =0.98, as shown in Figure 5. The isotopic purity of the MMA-D8 was high (>99%); therefore, this equality is not due to the deuteration being insufficient. The observed equality of the rate coefficients for the deuterated and non-deuterated MMA further strengthens the expectation that H atom abstraction is insignificant in the reaction of NO_3 with methacrylates.

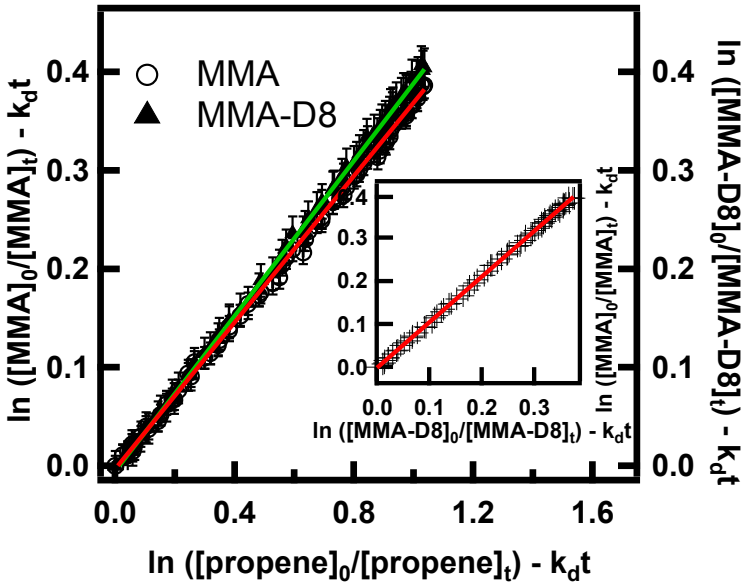

Figure 5: The rates of losses of MMA-D8 relative to those for propene while competing for the same pool of NO_3 radicals. The green line is a fit to the MMA-D8 and the red line is a fit to the MMA data. The inset shows a similar plot for the loss of MMA relative that for MMA-D8, with a slope of essentially unity showing the both deuterated and non-deuterated MMA react with NO_3 with the same rate coefficient, i.e., $k_1 \approx k_7$.

Furthermore, in our experiments, we deduced NO_2 was not produced after NO_3 was removed. Figure 6 shows the observed NO_3 and N_2O_5 profiles in the presence of MMA. Simulation of these profiles where we include a yield of NO_2 of unity is shown as the

dashed line. Clearly, we cannot fit the data to a scheme where NO_2 is produced from the reaction with a large yield. If NO_2 were the product of the reaction, we would expect a production of one NO_2 for each NO_3 lost, unless there is stoichiometric removal of NO_2 by a peroxy radical formed by the NO_3 reaction with the methacrylate ester that reacts very rapidly with NO_2 to form a stable nitrate. Since, we cannot rule out the formation of such a nitrate, we cannot unequivocally rule out the formation of NO_2 as a product of the reaction. Future studies in a chamber that were constrained by an accurate measurements of NO_2 and total NO_y would be useful in constraining the branching ratio toward NO_2 or organic nitrate production, even if the former were small. Similarly, a simulation of the all the subsequent reactions would be useful when the majority of the stable products are identified and quantified.

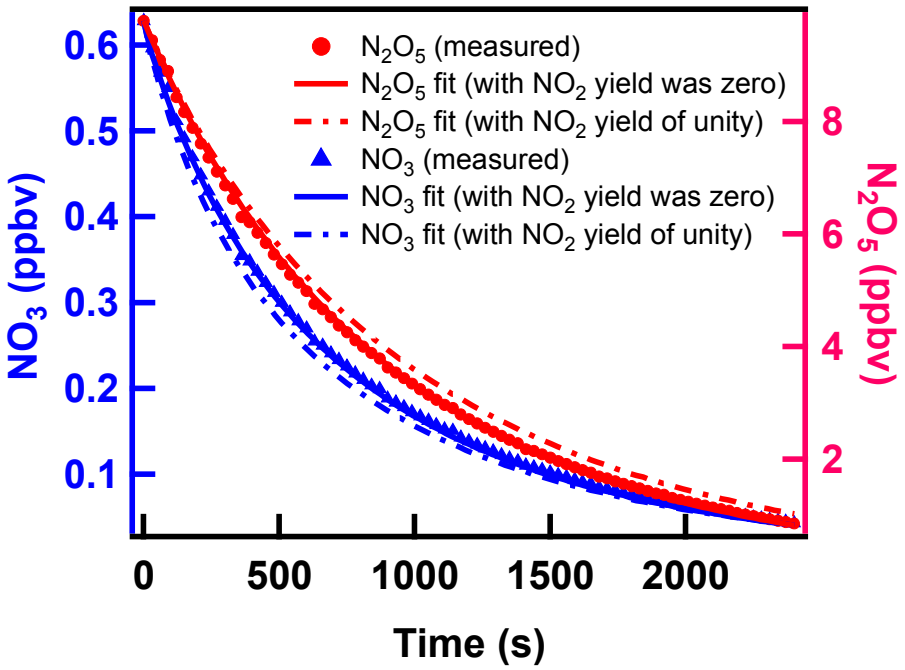

Figure 6 Experimental and simulated results for NO_3 and N_2O_5 profiles from chamber experiment ($MMA+NO_3$) when NO_2 was set as a product of unit yield in the modeled reaction scheme.

Based on these observation we suggest that, the atmospheric oxidation mechanism of NO_3 reactions with unsaturated carbonyl group compounds proceeds mostly via electrophilic addition to the C=C double bond.

3.4 Atmospheric implication

Once emitted into the atmosphere, the studied methacrylate esters are removed mainly through their reactions with reactive species such as OH, NO_3, O_3 and chlorine atoms. The lifetimes for the removal of the esters were calculated using nominal concentrations of the reactive radicals and ozone in the lower troposphere. Note that these lifetimes are nominal values and are expected to be location and time dependent. The

lifetimes were calculated using the equation:

$$\tau = \frac{1}{k_{voc+x}[x]} \qquad \text{(IV)}$$

where k_{voc+x} is the rate coefficient for the reaction of the oxidant with the methacrylate ester and [x] is the nominal representative atmospheric concentration of the oxidants. Tropospheric concentrations of OH, NO_3, O_3 and chlorine atoms that could be expected were used in the calculations to approximate the loss of esters in the troposphere. Here we take their concentrations to be: [Cl]=1×10^4 molecule cm^{-3} [32], [OH] = 1×10^6 molecule cm^{-3} [33], [NO_3] = 5×10^8 molecule cm^{-3} [34], [O_3] = 1×10^{12} molecule cm^{-3} (~40 ppbv). Note that NO_3 concentration in locations where esters are emitted (such as urban plumes) can be much larger [35]. However, the lifetimes would still be many days such that the esters would be dispersed. Therefore, the calculated atmospheric lifetimes of the methacrylate esters summarized in Table 6 would be reasonably representative of the removal processes for these esters.

The atmospheric lifetimes for methacrylate esters due to reaction with OH radicals are roughly a few hours, followed by that due to loss via reaction with ozone of ~40 hours. Clearly, the reaction of NO_3 would contribute only about 5% to the overall lifetime. However, in dark areas with large NOx emissions, the loss via reaction with NO_3 could be significant compared to that via reaction with OH. However, the abundances of NO_3 are closely related to those of O_3 since it is formed by the reaction of NO_2 with O_3.

Therefore, clearly, both the reaction of O_3 and NO_3 will contribute significantly at night when the NOx emissions are high.

Table 6. Summary of rate constants and estimated atmospheric lifetimes of methacrylate esters with respect to their reactions with OH, NO_3, O_3 and Cl at (298±2)K and atmospheric pressure.

	Rate constants (cm^3 $molecule^{-1}s^{-1}$)				Lifetime (hours)			
	k_{OH}	k_{NO3}	k_{O3}	k_{Cl}	τ_{OH}	τ_{NO3}	$\tau_{O3}{}^{i}$	τ_{Cl}
MMA	$(4.2)\times10^{-11}$ [b,c,d]	$(2.98)\times10^{-15}$ [a]	$(7.51)\times10^{-18}$ [d]	$(2.17)\times10^{-10}$ [f]	6.6	186	37	128
EMA	$(4.58)\times10^{-11}$ [c]	$(4.67)\times10^{-15}$ [a]	$(7.68)\times10^{-18}$ [e]	$(2.71)\times10^{-10}$ [f]	6.1	119	36	103
PMA		$(5.23)\times10^{-15}$ [a]				106	~40	
IPMA		$(7.91)\times10^{-15}$ [a]				70	~40	
BMA	$(7.08)\times10^{-11}$ [c]	$(5.71)\times10^{-15}$ [a]		$(3.72)\times10^{-10}$ [f,g]	3.3	97	~40	75
IBMA		$(6.24)\times10^{-15}$ [a]				89	~40	

Assuming [OH] = 1×10^{6} molecule cm^{-3} [33], [NO_3] = 5×10^{8} molecule cm^{-3} [34], [O_3] = 1×10^{12} molecule cm^{-3} (~40 ppbv), and [Cl] = 1×10^{4} molecule cm^{-3} [32].

a This work.

b,c,d are from references 3, 4, and 5: Value reported by ref. d is roughly a factor of 2 lower than that reported by ref. b and c. We used the average value from ref. b and c.

e from reference 7, f from reference 36, and g from reference 9.

i. When the rate coefficients for the reactions of esters with ozone were not available, we have assumed it to be roughly the same as that for MMA.

Supporting Information.

Table S1-S2, a complete summary of the initial concentrations and experimental conditions for the relative rate method and absolute rate methods; Figure S1, Calibration of each reactants and references in PTR-ToF-MS; Figure S2, the first order decay rate of SF_6 and MMA in the absence of NO_3; Figure S3, experimental and simulated results for NO_3 and N_2O_5 profiles from absolute rate method experiments.

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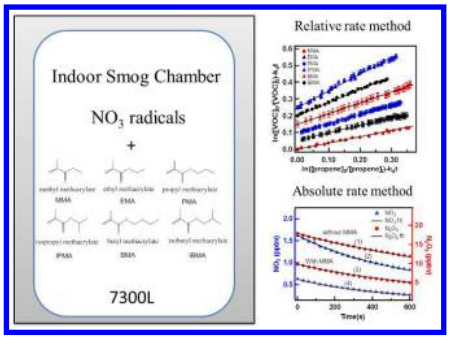
715 TOC Graphic

716



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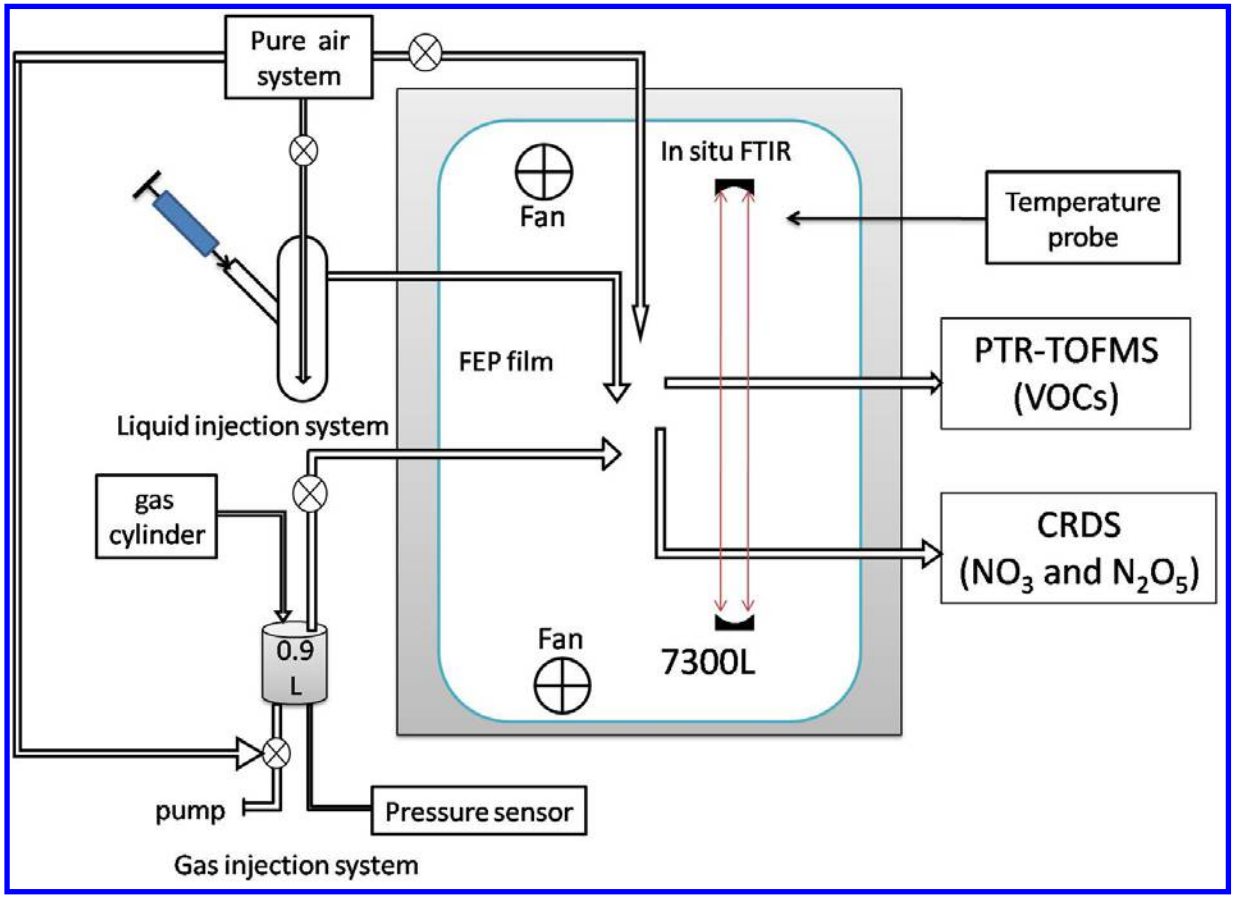
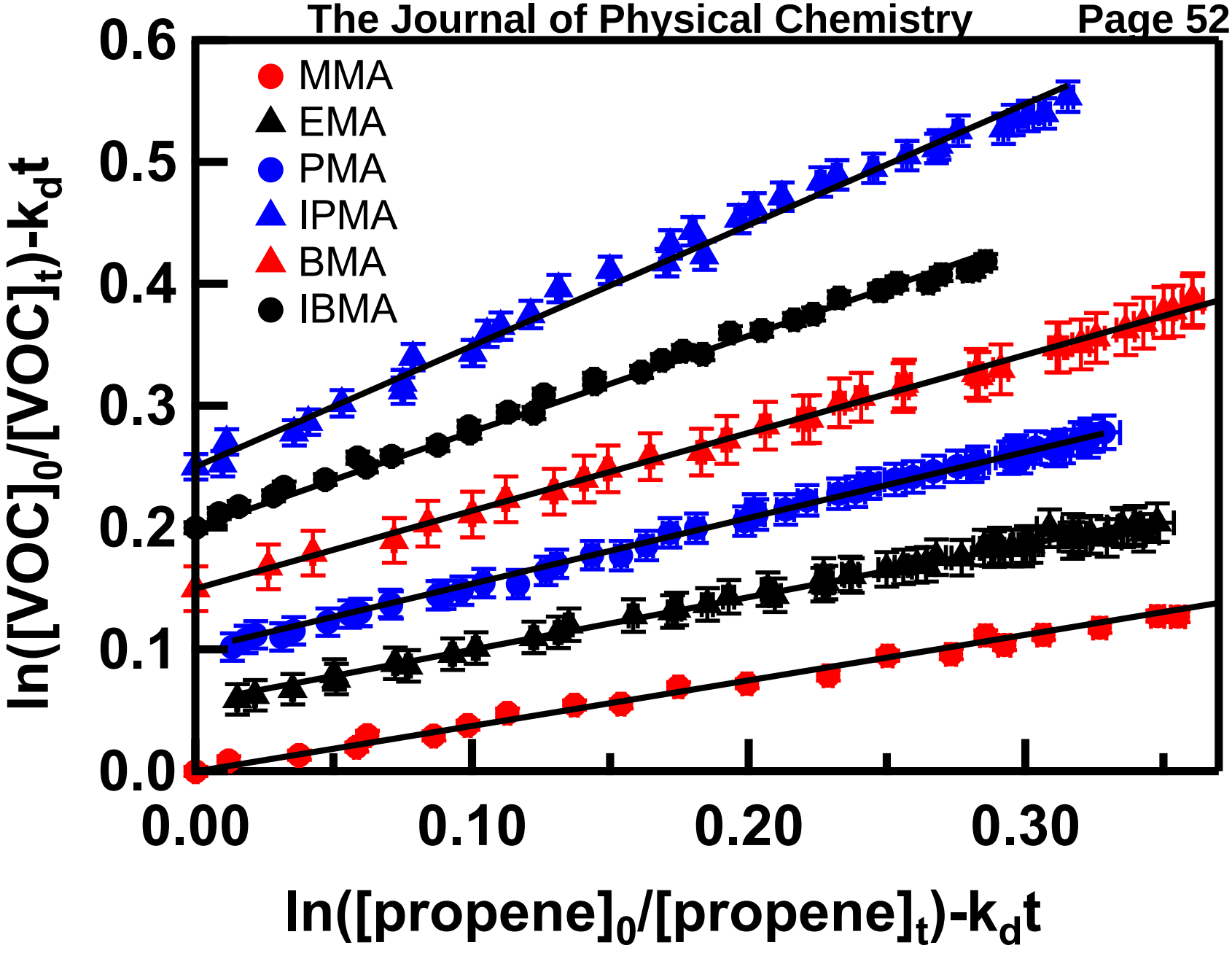

Pure air system
In situ FTIR
Fan
Temperature probe
FEP film
PTR-TOFMS (VOCs)
Liquid injection system
gas cylinder
CRDS (NO_3 and N_2O_5)
0.9 L
Fan
7300L
pump
Pressure sensor
Gas injection system

Figure 1



ACS Paragon Plus Environment

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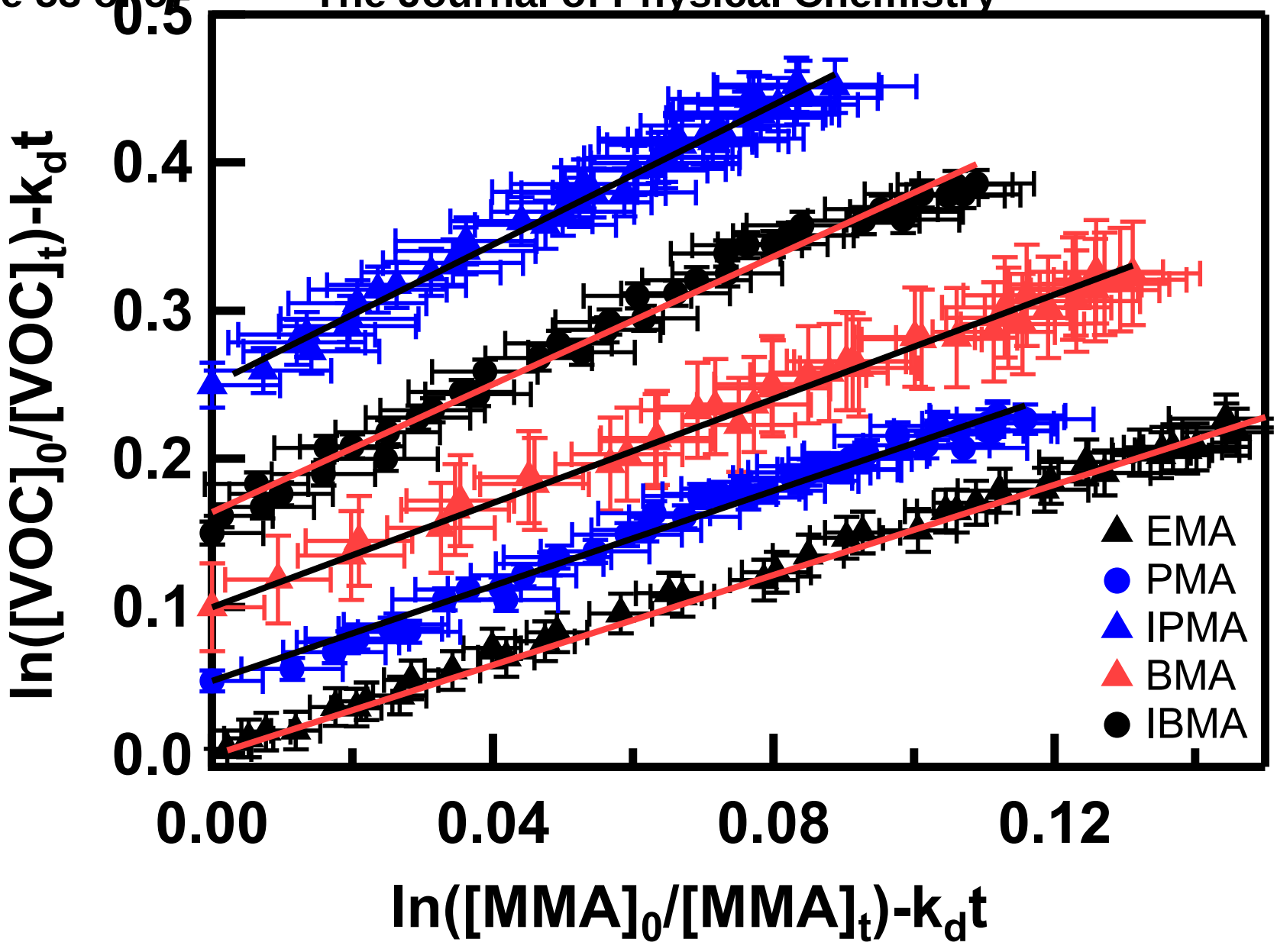
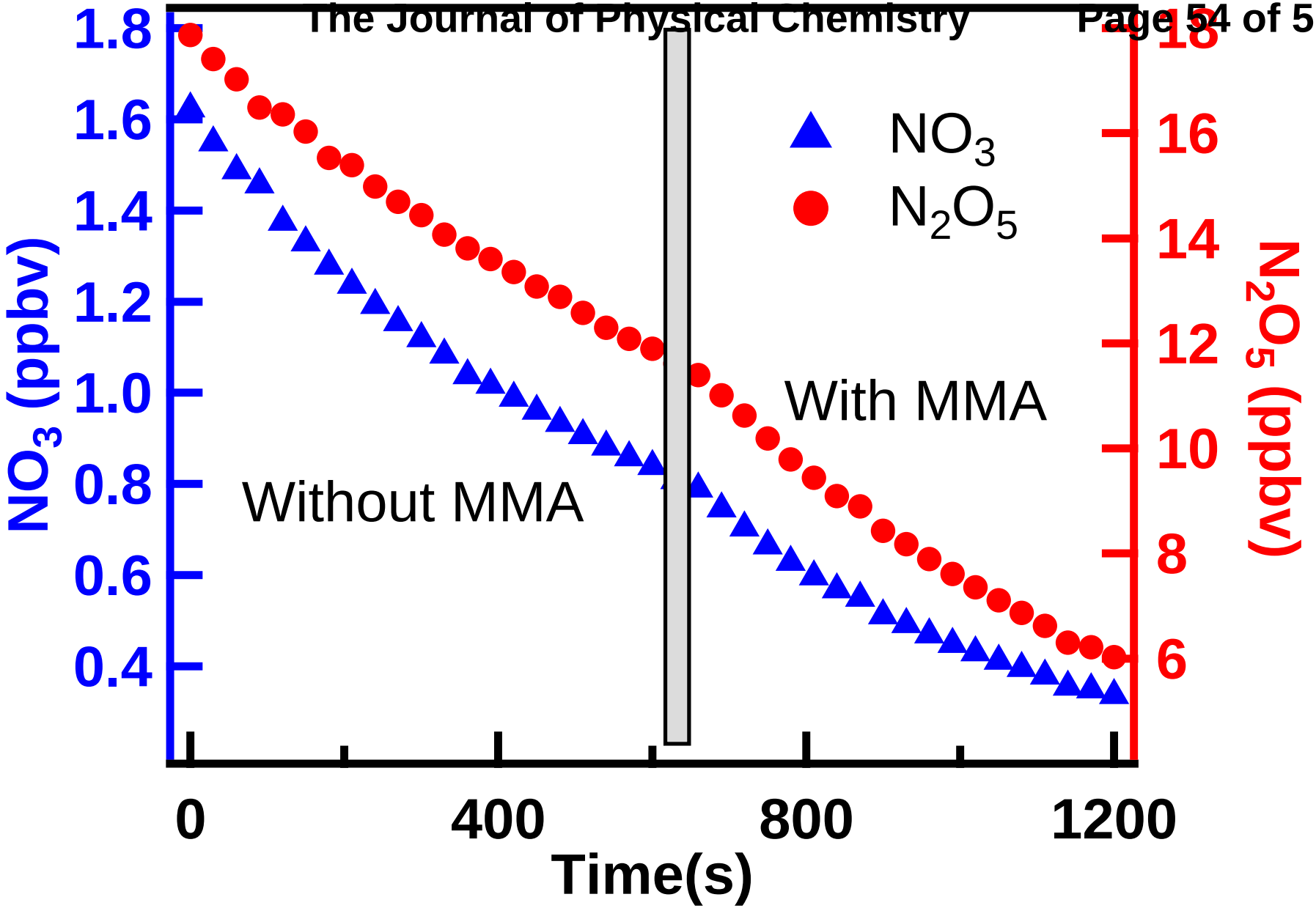

0.5
0.4
0.3
0.2
0.1
0.0
0.00
0.04
0.08
0.12
ln([VOC]0/[VOC]t)-kdt
ln([MMA]0/[MMA]t)-kdt
EMA
PMA
IPMA
BMA
IBMA

Figure 2-2



ACS Paragon Plus Environment

Figure 3

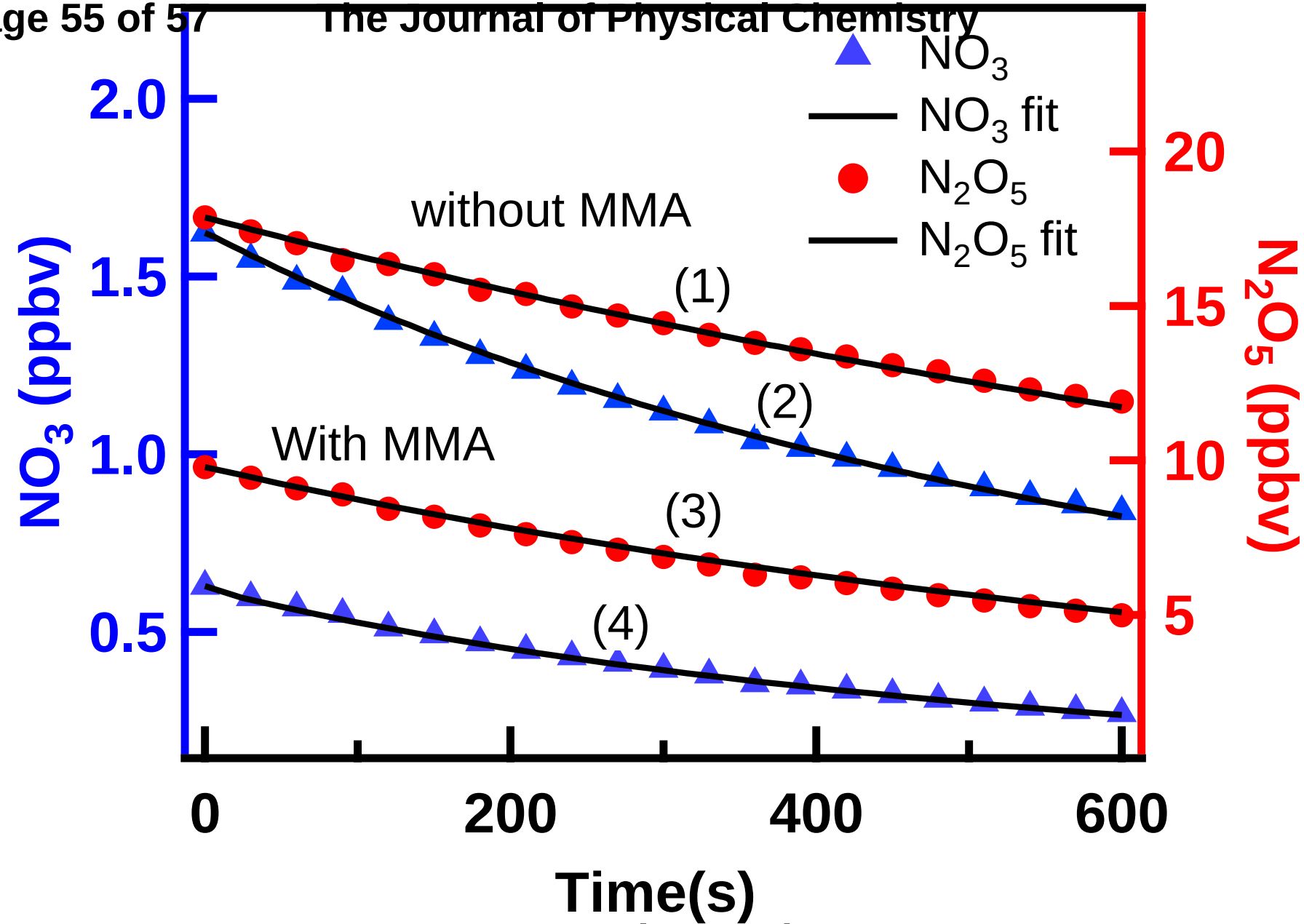

NO3
NO3 fit
N2O5
N2O5 fit
without MMA
With MMA
(1)
(2)
(3)
(4)
NO3 (ppbv)
N2O5 (ppbv)
2.0
1.5
1.0
0.5
20
15
10
5
0
200
400
600
Time(s)

Figure 4

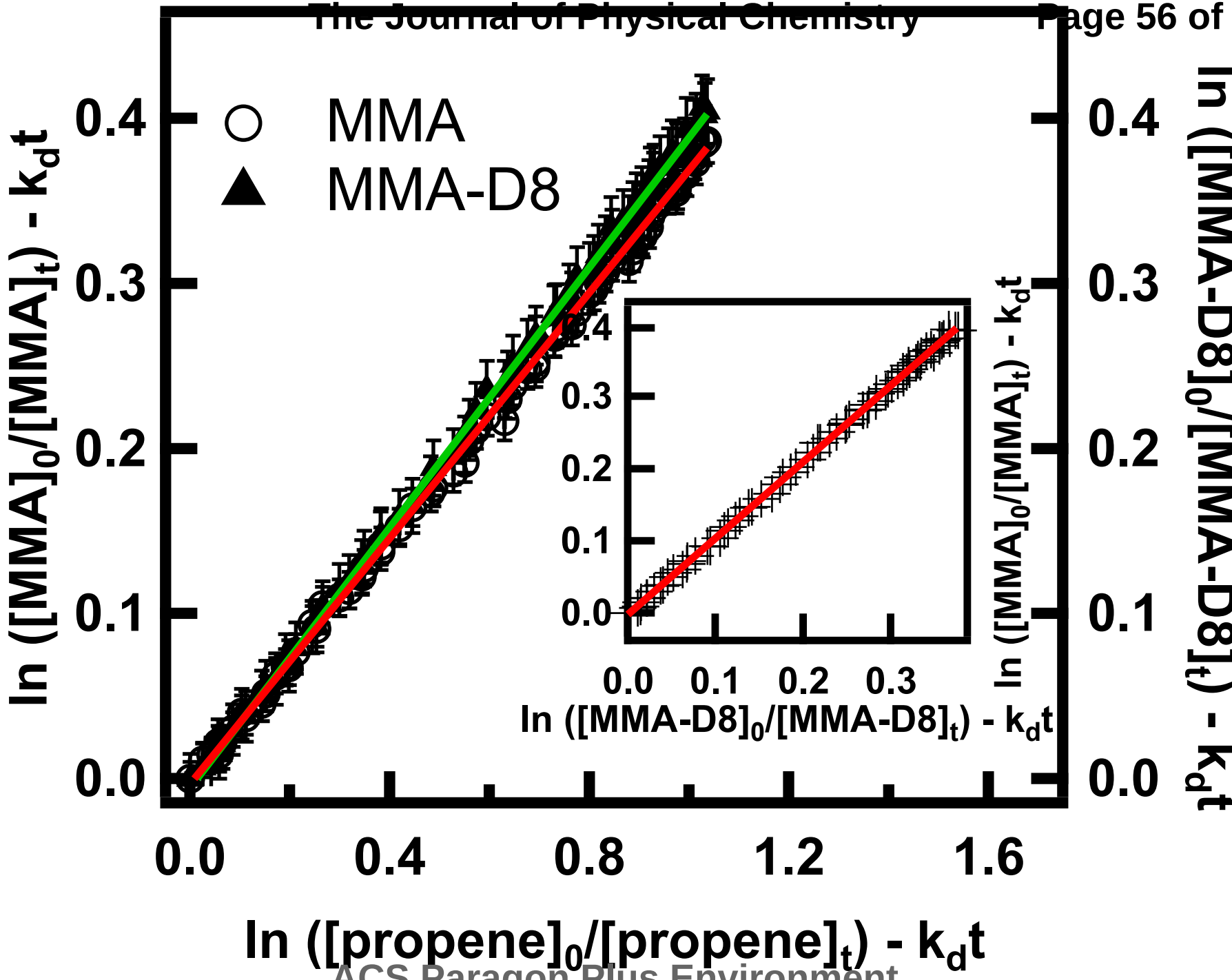


Figure 5

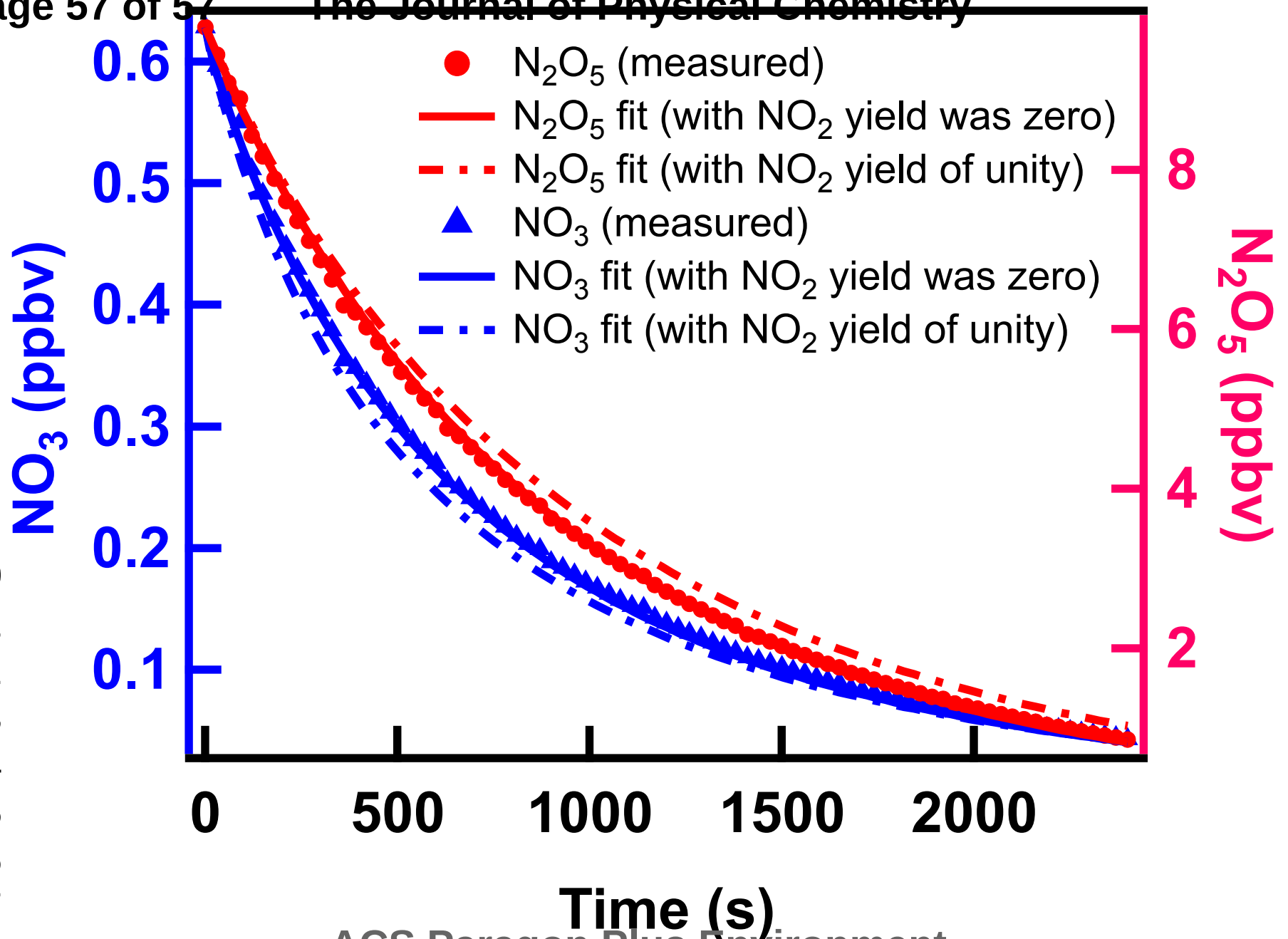


Figure 6