PCCP

A kinetic study of the reactions of NO_3 with methyl vinyl ketone, methacrolein, acrolein, methyl acrylate and methyl methacrylate

Carlos E. Canosa-Mas,[a] Sinéad Carr,[a] Martin D. King,[a] Dudley E. Shallcross,[b] Katherine C. Thompson[a] and Richard P. Wayne[a]*

[a] *Physical and Theoretical Chemistry Department, South Parks Road, Oxford, UK OX1 3QZ*
[b] *Centre for Atmospheric Science, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*
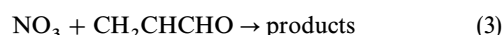
Absolute and relative-rate techniques have been used to obtain rate coefficients for the reactions: $NO_3 + CH_3C(O)CHCH_2 \rightarrow$ products (1), $NO_3 + CH_2C(CH_3)CHO \rightarrow$ products (2), $NO_3 + CH_2CHCHO \rightarrow$ products (3), and $NO_3 + CH_2CHC(O)OCH_3 \rightarrow$ products (4). The reaction $NO_3 + CH_2C(CH_3)C(O)OCH_3 \rightarrow$ products (5), has been investigated by a relative-rate method only. The rate coefficients obtained by the relative-rate method at $T = 296 \pm 2$ K and $P = 760$ Torr are $k_1 = (4.7 \pm 1.7) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, $k_2 = (3.7 \pm 1.0) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, $k_3 = (1.1 \pm 0.4) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, $k_4 = (1.0 \pm 0.6) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} and $k_5 = (3.6 \pm 1.3) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. The rate coefficients determined by the discharge-flow technique at low pressure ($P = 1–10$ Torr) and at $T = 293–303$ K are $k_1 = (3.2 \pm 0.6) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, $k_2 = (9.6 \pm 2.0) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, $k_3 = (8.9 \pm 2.8) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, $k_4 = (1.9 \pm 0.4) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. The discrepancy between the values obtained from the relative-rate technique and the absolute technique are discussed and explained in terms of interference in the absolute study caused by secondary chemistry and fast-reacting impurities. Product studies reveal that methyl glyoxal is a product of reactions (1) and (2) along with peroxymethacryloyl nitrate (MPAN) for reaction (2) in air. A diurnally varying boundary-layer model suggests that reaction (2) is an important loss process for methacrolein and that it can lead to the generation of OH at night.

Introduction

Vegetation provides a major source of reactive carbon entering the Earth's atmosphere.[1] Estimates for the total emissions of biogenic species range from 430 to 830 Tg yr^{-1}.[1] Isoprene (C_5H_8) is a hemiterpene emitted by many plants and trees;[1] estimated total emissions range from 250 to 450 Tg yr^{-1}. Isoprene therefore constitutes about half the total biogenic emissions, and the higher end of the estimated range of emissions is comparable with the emission of methane.[2] Emissions of isoprene are known to fall to zero at night and, since isoprene reacts extremely quickly with the major daytime oxidant, the OH radical, its night-time concentration is usually small or zero.[1] It is now widely recognised that the nitrate radical (NO_3) could be the dominant oxidant for a number of species, particularly unsaturated ones.[3] Although NO_3 reacts rapidly with isoprene, the nitrate radical is rapidly photolysed during the day and can only build up to significant concentrations during the night, so that the two species are in anti-phase. During the day, the OH-initiated oxidation of isoprene yields methyl vinyl ketone ($CH_3C(O)CHCH_2$) and methacrolein ($CH_2C(CH_3)CHO$) as the major primary products.[4] Both methyl vinyl ketone and methacrolein are sufficiently long lived that they will persist into the night and can therefore interact with NO_3. The purpose of the work reported in this paper was to study the kinetics of the reactions of NO_3 with methyl vinyl ketone and methacrolein:

$$NO_3 + CH_3C(O)CHCH_2 \rightarrow \text{products} \qquad (1)$$

$$NO_3 + CH_2C(CH_3)CHO \rightarrow \text{products} \qquad (2)$$
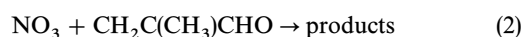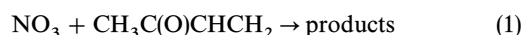
In addition, the reaction between NO_3 and three other α,β-unsaturated-carbonyl compounds (acrolein, CH_2CHCHO; methyl acrylate, $CH_2CHC(O)OCH_3$; and methyl methacrylate, $CH_2C(CH_3)C(O)OCH_3$) have also been investigated:

$$NO_3 + CH_2CHCHO \rightarrow \text{products} \qquad (3)$$

$$NO_3 + CH_2CHC(O)OCH_3 \rightarrow \text{products} \qquad (4)$$

$$NO_3 + CH_2C(CH_3)C(O)OCH_3 \rightarrow \text{products} \qquad (5)$$

Rate coefficients have been determined using the relative-rate technique for reactions (1)–(5), and also by the absolute discharge-flow method for reactions (1)–(4). Studies of the reaction products were carried out for processes (1) and (2). The atmospheric implications of these reactions are discussed in the context of a diurnally varying planetary boundary layer model.[5]

Experimental

Relative-rate experiments

The relative-rate technique was used to study reactions (1)–(5). The experiments were carried out at atmospheric pressure using a 56 l PTFE-lined bag housed in an insulating, dark cabinet. The decay of the substrate and a reference compound was monitored in the presence of NO_3. The relative concentrations of the substrate and reference compounds were determined by gas chromatography with flame-ionisation detection (Perkin Elmer, GC 8500 series). The reaction mixture was sampled by expanding it into an evacuated 1 cm^3 stainless-steel sample loop and injecting it onto a column packed with

Table 1 Summary of rate coefficients obtained from the relative rate experiments[a]

Substrate	Reference	Ratio	k_s/cm³ molecule⁻¹ s⁻¹
Methyl vinyl ketone	Ethene	2.53 ± 0.59	$(4.7 \pm 1.7) \times 10^{-16}$
Methacrolein	Propene	0.40 ± 0.05	$(3.7 \pm 1.0) \times 10^{-15}$
Acrolein	Ethene	6.09 ± 1.30	$(1.1 \pm 0.4) \times 10^{-15}$
Methyl acrylate	Ethene	0.56 ± 0.25	$(1.0 \pm 0.6) \times 10^{-16}$
Methyl methacrylate	Propene	0.39 ± 0.06	$(3.6 \pm 1.3) \times 10^{-15}$

[a] The rate coefficients used for the reactions of NO_3 with propene and ethene were $(9.3 \pm 1.9) \times 10^{-15}$ and $(1.85 \pm 0.24) \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹, respectively.

Chromosorb 102 (Alltech) by means of a 10-port gas-sampling valve (Alltech). The temperature of the column was modified for each mixture to give optimum peak separation. The initial concentrations of substrate and reference compound were varied with respect to each other between limits of 4.0×10^{15} and 1.0×10^{16} molecule cm⁻³, to test for interference from secondary reactions. The organic reagents were added simultaneously to the bag and allowed to mix for at least one hour. The thermal decomposition of N_2O_5 was used as the source of NO_3 radicals. Five or six additions of N_2O_5 were made to the mixture of organic reagents in the bag, a chromatogram of the mixture being recorded after each addition. An internal standard was used to allow for dilution due to the N_2O_5 additions. The internal standard used for experiments with methacrolein was n-pentane, whereas methane was used as the internal standard for all other substrates studied. The rate constants for the reaction of NO_3 with pentane and methane are 8.7×10^{-17} cm³ molecule⁻¹ s⁻¹ [6] and $\leqslant 3.9 \times 10^{-19}$ cm³ molecule⁻¹ s⁻¹,[7] respectively, so that little or no reaction would be expected. All relative-rate experiments were performed at $T = 296 \pm 2$ K using nitrogen as the bath gas.

Discharge-flow (absolute) experiments

A conventional discharge-flow system[8] was used to determine absolute rate constants for reactions (1)–(4). The decay of NO_3 as a function of time was monitored using optical absorption at $\lambda = 662$ nm. The absolute concentration[8] of NO_3 was found by titrating NO_3 with NO in the reaction

$$NO_3 + NO \rightarrow 2NO_2$$

$$(k_{298\,K} = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^9 \qquad (6)$$
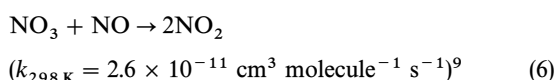
An effective absorption cross section $\sigma_{662\,nm} = (1.5 \pm 0.2) \times 10^{-17}$ cm² molecule⁻¹ was determined. Nitrate radicals were generated by the reaction of F atoms with anhydrous nitric acid

$$F + HNO_3 \rightarrow HF + NO_3$$

$$(k_{298\,K} = 2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^9 \qquad (7)$$
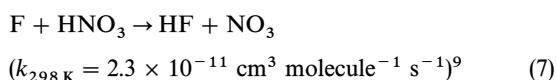
The minimum detectable $[NO_3]$ was found to be *ca.* 5×10^{11} molecule cm⁻³, for a signal-to-noise ratio of unity and a 10 s integration time. Nitrogen dioxide, a possible product of reactions (1)–(4), was monitored by laser-induced fluorescence (LIF), the excitation being provided by an argon-ion laser (Coherent Innova 70) operating at $\lambda = 488$ nm with a power of *ca.* 0.6 W. The LIF signal was calibrated daily by admitting a known amount of NO_2. The signal varied linearly with $[NO_2]$. The detection limit of the system was 5×10^9 molecule cm⁻³ in the absence of any quenching species other than He, for a signal-to-noise ratio of unity and a time constant of 5 s. The experiments were performed at low pressures (1–10 Torr) and at $T = 293$–303 K. Pseudo-first order conditions were employed for all kinetic studies, the organic species being in at least a ten-fold excess over NO_3. The carrier gas used was helium.

Materials

Acrolein (90%, containing $\leqslant 10\%$ H_2O and cyclic dimer, with hydroquinone stabiliser), pentane (99+%), methacrolein (95%, inhibited with 0.1% hydroquinone), methyl vinyl ketone (99%, inhibited with 0.1% acetic acid and 0.05% hydroquinone), methyl methacrylate (99%, 10–100 ppm hydroquinone monoethyl ether stabiliser) and propene (99+%) were supplied by Aldrich. Ethene (99.8%), methane (99.5%) and methyl acrylate (99%, 0.02% 4-methoxy-phenol stabiliser) were supplied by BDH. Volatile impurities were removed from the organic reagents by repeated freeze–pump–thaw cycles and for the discharge-flow experiments, trap-to-trap distillation was also performed Nitrogen (99%, BOC) and oxygen (99%, BOC) were passed through a phosphorus pentoxide trap to remove water. N_2O_5 was prepared in advance and stored at liquid nitrogen temperatures until used. The preparation consisted of allowing NO_2 to react with O_3. A 3% mixture of O_3 was made by passing O_2 through a conventional ozoniser (Argentox). NO_2 (BDH 99%) was trapped at 196 K, any volatile impurities were pumped off, and the NO_2 was allowed to warm up in a stream of the O_3 mixture. After passing through a 3 l mixing volume, the N_2O_5 formed and any remaining NO_2 was trapped in a second trap at 196 K. The process was repeated until N_2O_5 (determined by FTIR spectroscopy) contained only minor amounts of NO_2 and HNO_3. Nitric acid (BDH, Anala-R®) was dried before use by preparing a 1 : 2 mixture (by volume) of nitric and sulfuric acid (BDH, Aristar®) at *ca.* 258 K. Helium was passed through an 'Oxisorb' cartridge (Messer Griesheim) to remove oxygen, a column containing phosphorus pentoxide to remove water, and two molecular sieves (BDH 13X and 4A) held at 77 K, to remove hydrocarbons, water and CO_2 respectively. Fluorine (5% in helium, BOC) was used as supplied.

Results

Relative-rate studies

If it is assumed that the loss of the substrate and reference compound are due solely to reaction with NO_3, then it can be shown that:

$$\ln \frac{[\text{substrate}]_{t=0}}{[\text{substrate}]_t} - D_t = \frac{k_s}{k_r} \left(\ln \frac{[\text{reference}]_{t=0}}{[\text{reference}]_t} - D_t \right) \quad (I)$$

where k_s is the rate coefficient for the reaction of NO_3 with the substrate, k_r is the rate coefficient for the reaction of NO_3 with the reference compound and D_t is the dilution term, given by the equation:

$$D_t = \ln \left(\frac{[I]_{t=0}}{[I]_t} \right) \quad (II)$$

where I represents an internal standard, a compound which does not react with NO_3 on the time-scale and conditions of the experiment so that it can be used to allow for the dilution that occurs when the NO_3 radical precursor, N_2O_5, is added to the reaction vessel.
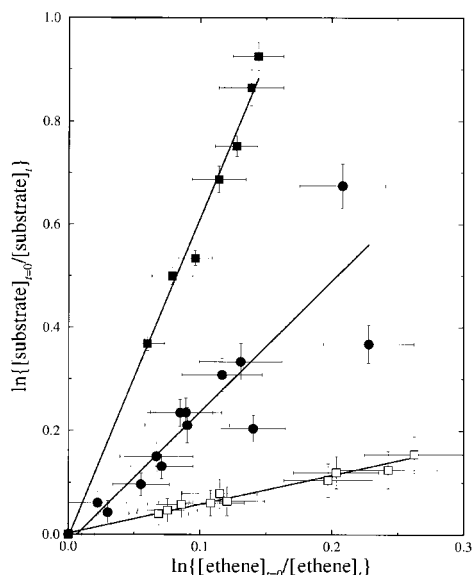
Fig. 1 Relative-rate plots for the reaction of the NO_3 radical with methyl vinyl ketone, acrolein and methyl acrylate (reference compound: ethene). ■ = Acrolein, ● = methyl vinyl ketone, □ = methyl acrylate.

The data plotted in the form of eqn. (I) are displayed in Fig. 1 and 2, and the values of k_s/k_r are summarised in Table 1. A weighted least-squares regression, which takes into account the errors in the measured concentrations of both the substrate and the reference compounds, was used to obtain the gradient of the best straight line.[10] The errors in the measured concentrations were estimated by repeatedly sampling the same mixture. The errors given for the values of k_1–k_5 determined by the relative-rate technique incorporate both the 95% confidence limits from the slopes and the quoted error in the value of the rate coefficient for the reference compound.

The values of the rate constants used for reactions of NO_3 with the reference compounds propene and ethene were taken as $(9.3 \pm 1.9) \times 10^{-15}$ and $(1.85 \times 0.24) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, respectively.[11,12]
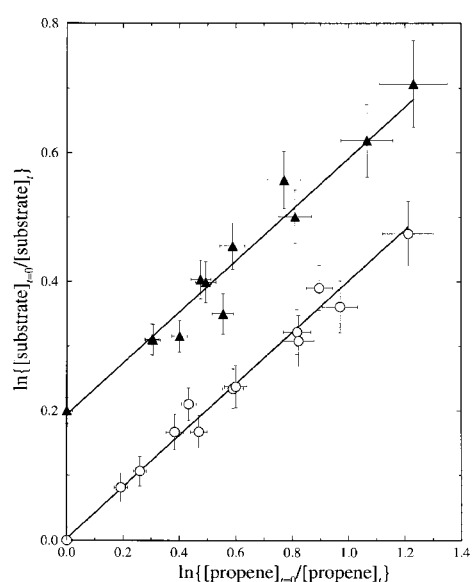

Fig. 2 Relative-rate plots for the reaction of the NO_3 radical with methacrolein and methyl methacrylate (reference compound: propene). Data for methyl methacrylate are displaced by 0.2 units on the ordinate. ▲ = Methyl methacrylate, ○ = methacrolein.
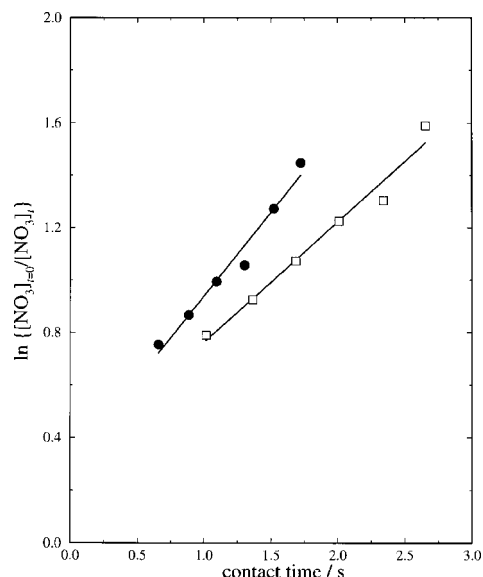

Fig. 3 First-order plots obtained in flow-tube experiments on the reactions of NO_3 with methyl vinyl ketone and methyl acrylate. Data for methyl vinyl ketone are displaced by 0.2 units on the ordinate. ● = Methyl vinyl ketone, □ = methyl acrylate.

Products observed at atmospheric pressure

The products of reactions (1) and (2) were investigated; the experimental conditions were exactly the same as for the relative-rate experiments, except that O_2 was used as the bath gas instead of N_2. Two distinct gas-chromatographic product peaks were observed in each case, the retention times of the two peaks being the same when either methyl vinyl ketone or methacrolein was the starting compound. The retention time of one of the peaks is identical to that of methyl glyoxal on two different columns (Alltech, Chromosorb 102 and Porapak Q). Attempts were made to identify the second product, but all proved unsuccessful. An FTIR-spectroscopic investigation of the products of reactions (1) and (2) revealed the presence of CO (presumably arising from decomposition of methyl glyoxal) along with MPAN (peroxymethacryloyl nitrate) for reaction (2) only.[13] No other products could be unambiguously identified in this investigation.
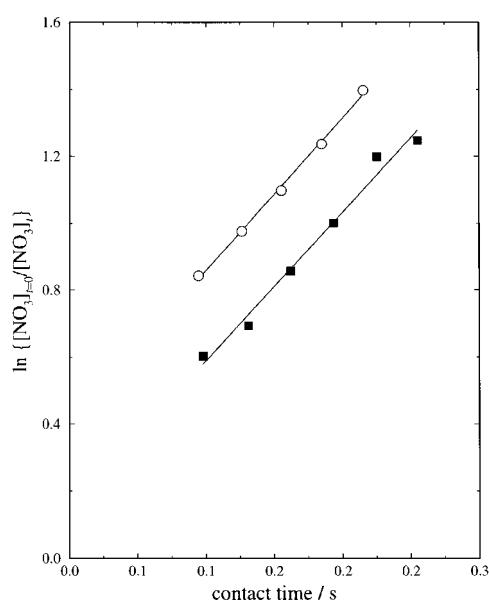

Fig. 4 First-order plots obtained in flow-tube experiments on the reactions of NO_3 with methacrolein and acrolein. ○ = Methacrolein, ■ = acrolein.
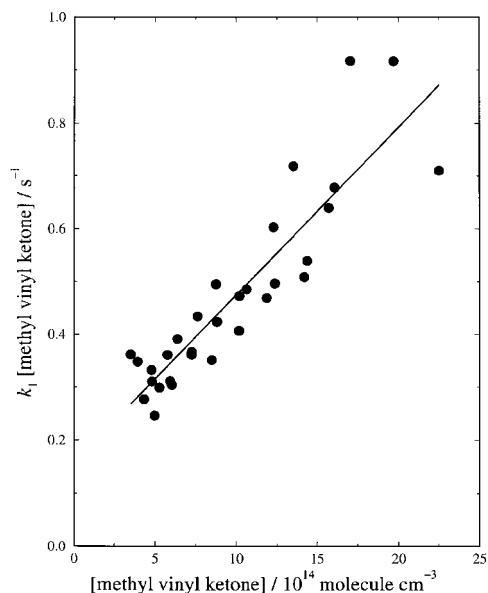
Fig. 5 Second-order plot obtained for reaction of NO_3 with methyl vinyl ketone.

Discharge-flow (absolute) studies

Pseudo-first order rate constants, k', for reactions (1)–(4) were obtained from the gradients of $\ln\{[NO_3]_{t=0}/[NO_3]_t\}$ plotted as a function of time. Typical first-order plots obtained for
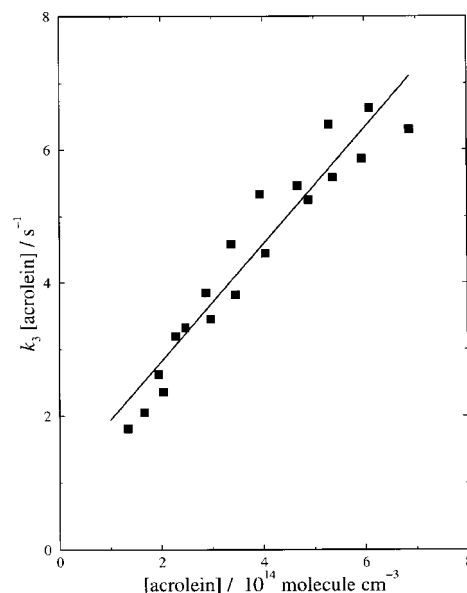

Fig. 7 Second-order plot obtained for reaction of NO_3 with acrolein.

each substrate are shown in Fig. 3 and 4. Second-order rate coefficients were obtained from the slope of a plot of k' as a function of concentration of organic reagent. The second-order plots are shown in Fig. 5–8. Table 2 summarises the rate coefficient data obtained, the errors quoted being the 95%
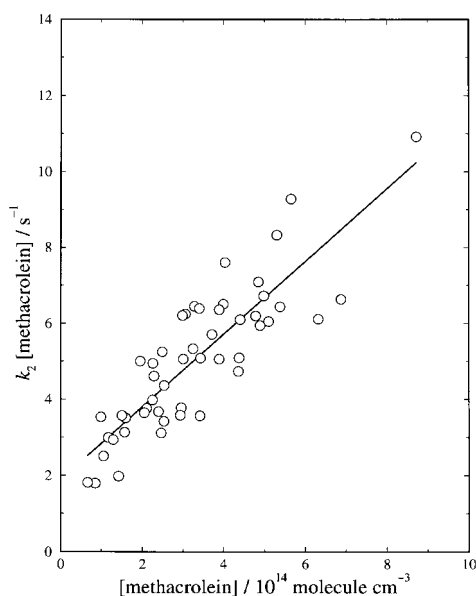

Fig. 6 Second-order plot obtained for reaction of NO_3 with methacrolein.
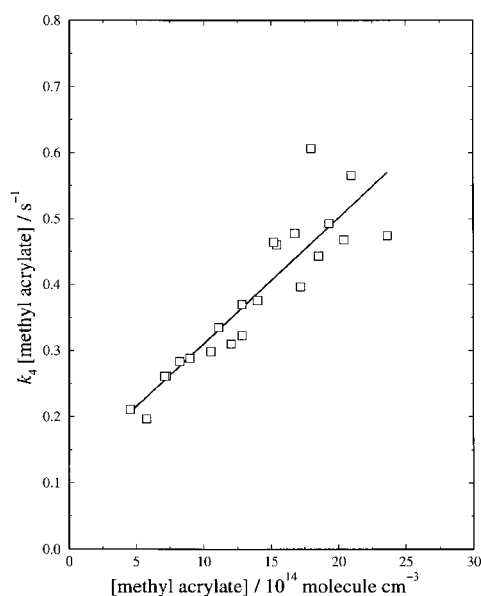

Fig. 8 Second-order plot obtained for reaction of NO_3 with methyl acrylate.

Table 2 Summary of rate coefficients obtained from the discharge-flow experiments

Substrate	Pressure/ Torr	Temperature/K	k/cm^3 molecule^{-1} s^{-1}
Methyl vinyl ketone	6.6 ± 0.6	296 ± 1	$(3.2 \pm 0.6) \times 10^{-16}$
Methacrolein	2.5 ± 0.3	300 ± 7	$(9.6 \pm 2.0) \times 10^{-15}$
Acrolein	2.4 ± 0.1	293 ± 2	$(8.9 \pm 2.8) \times 10^{-15}$
Methyl acrylate	9.0 ± 0.4	295 ± 2	$(1.9 \pm 0.4) \times 10^{-16}$

Table 3 Values of $\Delta[NO_2]/-\Delta[NO_3]$ obtained from the discharge-flow system (all experiments were performed at 297 ± 1 K)
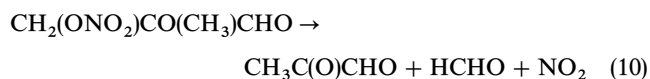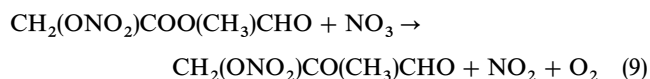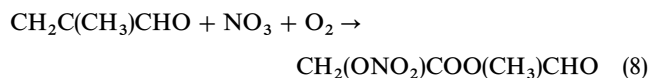
Substrate	[Substrate]/[NO_3]	Pressure/Torr	$\Delta[NO_2]/-\Delta[NO_3]$
Methyl vinyl ketone	10–50	1.4	0.45 ± 0.06
Methacrolein	100–1000	2.3 ± 0.3	0.95 ± 0.30
Acrolein	10–50	2.5	0.54 ± 0.02

confidence limits of the slopes. In an attempt to determine the overall reaction stoicheiometry, we measured, in a separate series of experiments, the yield of NO_2 as well as the loss of NO_3 (see later for explanation). Table 3 gives the values of the ratio of $[NO_2]$ observed to $[NO_3]$ consumed.
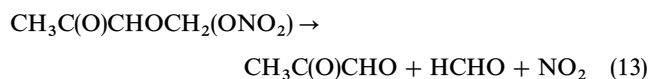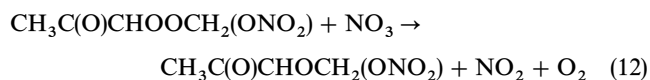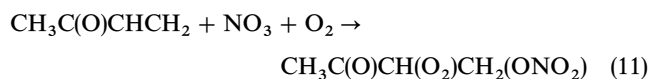
Discussion

Products and the yield of NO_2

Kwok *et al.*[14] have suggested that the abstraction pathway dominates for the reactions of NO_3 with methacrolein and acrolein, analogous to the behaviour of OH.[15] Methyl glyoxal, $CH_3C(O)CHO$, was observed as a product in our studies for both reactions (1) and (2). It can be shown that, in order to form methyl glyoxal from methacrolein, addition of NO_3 must occur *via* a mechanism such as

$$CH_2C(CH_3)CHO + NO_3 + O_2 \rightarrow$$
$$CH_2(ONO_2)COO(CH_3)CHO \quad (8)$$

$$CH_2(ONO_2)COO(CH_3)CHO + NO_3 \rightarrow$$
$$CH_2(ONO_2)CO(CH_3)CHO + NO_2 + O_2 \quad (9)$$

$$CH_2(ONO_2)CO(CH_3)CHO \rightarrow$$
$$CH_3C(O)CHO + HCHO + NO_2 \quad (10)$$

We also observe MPAN, which must arise from abstraction;[13] hence, both pathways seem to be occuring for methacrolein.

For reaction of NO_3 with methyl vinyl ketone, methyl glyoxal was also observed. In this reaction, we would expect addition to dominate: the reactions of NO_3 with ketones which contain no carbon–carbon unsaturated functionality, and therefore presumably react *via* an abstraction mechanism, are known to be very slow.[16] A route can be envisaged for the formation of methyl glyoxal following the addition of NO_3

$$CH_3C(O)CHCH_2 + NO_3 + O_2 \rightarrow$$
$$CH_3C(O)CH(O_2)CH_2(ONO_2) \quad (11)$$

$$CH_3C(O)CHOOCH_2(ONO_2) + NO_3 \rightarrow$$
$$CH_3C(O)CHOCH_2(ONO_2) + NO_2 + O_2 \quad (12)$$

$$CH_3C(O)CHOCH_2(ONO_2) \rightarrow$$
$$CH_3C(O)CHO + HCHO + NO_2 \quad (13)$$

The yield of NO_2 form the reactions studied in the flow tube provides some further information about the mechanism of reaction. For reactions (1)–(3), NO_2 was observed as a product, indicating, at least *prima facie*, that NO_3 addition to the carbon–carbon double bond had occurred. In each of these experiments, conducted in the absence of O_2, the addition of NO_3 would be expected to be followed by the elimination of NO_2 to leave an epoxide. If the reaction were to proceed wholly by an addition mechanism followed by immediate elimination, we would expect $\Delta[NO_2]/-\Delta[NO_3]$ to be very near to unity. In the case of the reaction of NO_3 with methyl vinyl ketone [reaction (1)], we do not anticipate any abstraction by NO_3. In reality, $\Delta[NO_2]/-\Delta[NO_3]$ is much less than unity. Possible explanations are either that a bifunctional compound (NO_2, NO_3 or NO_3, NO_3) may also be formed, resulting in the consumption of two NO_3 molecules with no NO_2 released, or that the initial adduct does not decompose completely on the timescale of the experiment.

The value of $\Delta[NO_2]/-\Delta[NO_3]$ of roughly 0.5 for the reaction of acrolein suggests that the rate constants for addition and abstraction are roughly equal. Both abstraction and addition must also occur for reaction with methacrolein [reaction (2)], because we observe MPAN (abstraction

channel) and methyl glyoxal (addition channel); a value of $\Delta[NO_2]/-\Delta[NO_3]$ of near to unity thus seems to be somewhat high for this process. We conclude that secondary reactions are taking place and that the concentrations of organic reagent used are insufficiently in excess to suppress the reaction of organic radicals with NO_3. For reaction (4), with methyl acrylate, we suspect that NO_2 is not observed as a direct result of the higher flow tube pressures employed, which would not only cause quenching of the NO_2 fluorescence, but also favour the reaction of NO_2 with NO_3.

Comparison of rate coefficients measured by the two techniques

Rate coefficients measured by relative-rate and flow-tube methods sometimes appear to be different. That turns out to be the case in our study with some, but not all, of the compounds. We shall show that we believe the relative-rate method to give a more reliable (or, at least, more directly applicable) rate constant. However, we present our data for both methods, because such differences as we find shed light on the behaviour of the different compounds. There are several potential reasons for errors arising in flow-tube experiments: (i) fast reactions of the reactant present in lower concentration with products of the primary process; (ii) the reaction of this reactant with impurities present in the excess reactant; and (iii) an increase in the reactivity of the wall upon addition of the excess reactant. We have employed a numerical model of likely secondary chemistry in an attempt to interpret our observations, but wish to emphasize that our modelling activities were not directed at obtaining a rate constant for the primary reaction from the flow-tube data, but rather at understanding better the chemistry that occurs in the flow tube.

In the experiments with methyl vinyl ketone and methyl acrylate, there is a positive intercept in the first-order plots (Fig. 3) which can be attributed to the initial consumption of NO_3 by a rapid reaction with impurities. So long as the impurities react rapidly, the plots will be linear, and their slopes will correctly represent the pseudo-first order rate coefficients. However, the second-order plots, which are reasonably good straight lines, show positive intercepts. We assume that these intercepts originate from an increase in the reactivity of the wall, which is not dependent on the concentration of the carbonyl species in the range of the experiments. For methyl vinyl ketone, there is quite good agreement between the rate coefficients obtained by relative-rate and flow-tube methods without the need to invoke secondary reactions. Methyl acrylate reacts very slowly with NO_3 (this was the slowest reaction of the series that we were able to study in the flow system). As a result, the secondary reaction of NO_3 with the NO_2 formed

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \quad (14)$$

is particularly evident, especially since rather high pressures were used. Invoking this reaction alone is sufficient to reconcile the flow-tube data with the rate constant from the relative-rate study.

The rate constants determined by relative-rate experiments for the α,β-unsaturated aldehydes (acrolein, methacrolein) differ more substantially from those measured using the flow-tube system; the flow-tube experiments give a much higher value for the rate constants (see Tables 1 and 2). According to our analysis of the flow-tube data, all three causes of error, (i), (ii) and (iii), need to be invoked to explain the flow-tube data on the reaction of NO_3 with acrolein and methacrolein. The positive intercepts in Fig. 4 are clearly indicative of the presence of fast-reacting impurities, but secondary chemistry of acyl radicals as well as of NO_2 is also important. A good fit between experimental and modelled data can be obtained

using the rate coefficients from the relative-rate studies, especially if the wall-loss rates of NO_3 in the presence of reactant are incorporated.

Comparison of rate coefficients with those of other studies

Table 4 details the rate constants obtained in this work and some other recently determined values of the rate constants where available. The value of k_1 determined by the relative-rate technique lies between the lower limits obtained by Kwok et al.[14] and Rudich et al.[17] The value obtained for k_2 using the relative-rate technique is less than the upper limit of Rudich et al.,[17] and in excellent agreement with the results of Kwok et al.,[14] as is our value obtained for k_3 using the relative-rate technique.
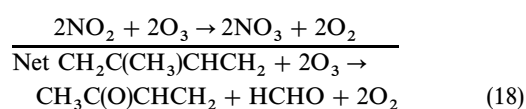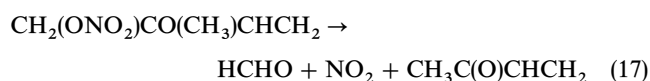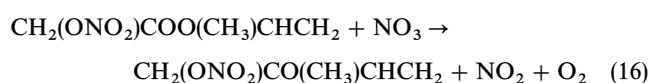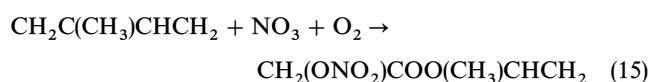
Reactivity and reaction mechanisms

Inspection of Table 1 shows that the reactivity for the species studied lies in the order methacrolein $\simeq$ methyl methacrylate > acrolein > methyl vinyl ketone > methyl acrylate. NO_3 is an electrophilic species and will add most readily to a carbon–carbon double bond which is electron rich,[18,19] but may also abstract a labile hydrogen, such as an aldehydic one. All the species studied possess an α,β-unsaturated carbonyl group but have different substituents attached to it. The ketone (methyl vinyl ketone) and the two esters (methyl acrylate and methyl methacrylate) can react with NO_3 only via the addition mechanism. The presence of electron-withdrawing substituents attached to the carbon–carbon double bond will lower the electron density on the double bond and thus reduce the reactivity; the rate constant for reaction of the NO_3 radical with methyl acrylate is consequently lower than that for reaction with methyl vinyl ketone since the $-OCH_3$ group of the ester has an electron-withdrawing effect, whilst the $-CH_3$ group of methyl vinyl ketone donates electron density to the double bond. A similar effect is observed in comparing the reactivity of methyl acrylate with methyl methacrylate; the electron-donating inductive effect of the methyl group attached to the carbon–carbon double bond in methyl methacrylate increases the electron density on the bond and hence increases the reactivity relative to that of methyl acrylate.

Rationalizing the reactivity of the α,β-unsaturated aldehydes towards the NO_3 radical is less straightforward since the radical may either abstract the aldehydic hydrogen or add to the carbon–carbon double bond. The rate constant for the addition channel ($k_{addition}$) would be expected to be greater in the case of methacrolein than acrolein as the methyl group would have an electron-donating effect on the double bond. The rate constant for abstraction ($k_{abstraction}$) of an aldehydic
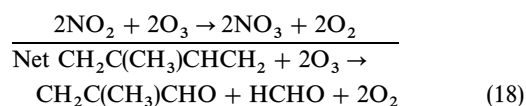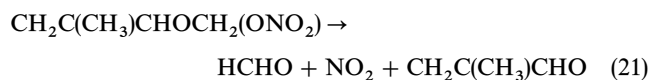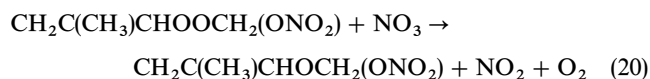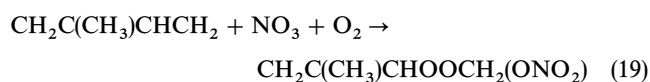
hydrogen by the NO_3 radical is sensitive to substituents on the carbonyl group. This behaviour is exemplified by the reactions of NO_3 with HCHO, CH_3CHO, C_2H_5CHO and C_3H_7CHO, for which the rate constants are[20] 0.058×10^{-14}, 0.29×10^{-14}, 0.57×10^{-14} and 1.09×10^{-14} cm^3 molecule^{-1} s^{-1}, respectively. The rate constant $k_{abstraction}$ for acrolein would therefore be expected to be less than $k_{abstraction}$ for methacrolein. Furthermore, $k_{addition}$ for acrolein is also expected to be less than that for methacrolein, so that the increased reactivity of methacrolein compared with acrolein can be attributed to the operation of both effects.

Atmospheric implications

The reaction of NO_3 with isoprene has been studied by Berndt and Böge.[21] These workers concluded that methyl vinyl ketone and methacrolein were major products of the reaction, with the yield of methyl vinyl ketone being greater than that of methacrolein. A mechanism is proposed for the atmospheric oxidation in which 1–2 addition takes place

$$CH_2C(CH_3)CHCH_2 + NO_3 + O_2 \rightarrow$$
$$CH_2(ONO_2)COO(CH_3)CHCH_2 \quad (15)$$

$$CH_2(ONO_2)COO(CH_3)CHCH_2 + NO_3 \rightarrow$$
$$CH_2(ONO_2)CO(CH_3)CHCH_2 + NO_2 + O_2 \quad (16)$$

$$CH_2(ONO_2)CO(CH_3)CHCH_2 \rightarrow$$
$$HCHO + NO_2 + CH_3C(O)CHCH_2 \quad (17)$$

$$\underline{2NO_2 + 2O_3 \rightarrow 2NO_3 + 2O_2}$$
Net $CH_2C(CH_3)CHCH_2 + 2O_3 \rightarrow$
$$CH_3C(O)CHCH_2 + HCHO + 2O_2 \quad (18)$$

Alternatively, 3–4 addition may occur

$$CH_2C(CH_3)CHCH_2 + NO_3 + O_2 \rightarrow$$
$$CH_2C(CH_3)CHOOCH_2(ONO_2) \quad (19)$$

$$CH_2C(CH_3)CHOOCH_2(ONO_2) + NO_3 \rightarrow$$
$$CH_2C(CH_3)CHOCH_2(ONO_2) + NO_2 + O_2 \quad (20)$$

$$CH_2C(CH_3)CHOCH_2(ONO_2) \rightarrow$$
$$HCHO + NO_2 + CH_2C(CH_3)CHO \quad (21)$$

$$\underline{2NO_2 + 2O_3 \rightarrow 2NO_3 + 2O_2}$$
Net $CH_2C(CH_3)CHCH_2 + 2O_3 \rightarrow$
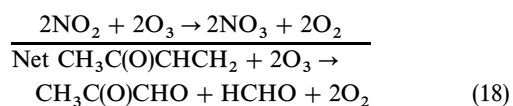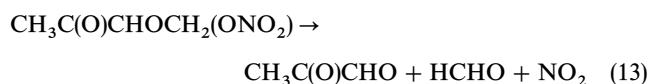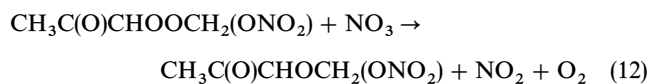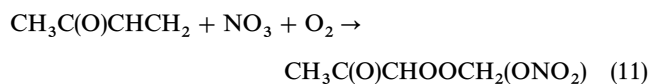$$CH_2C(CH_3)CHO + HCHO + 2O_2 \quad (18)$$

Oxidation of isoprene, a species that may persist into the night, by NO_3 will thus yield methyl vinyl ketone and meth-
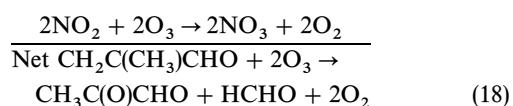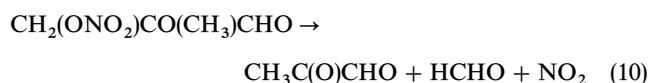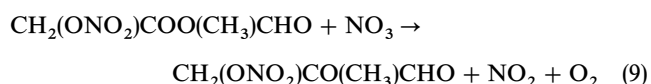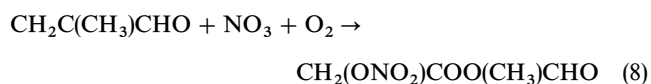
Table 4 Comparison of rate constants determined in this work to other recent determinations

Substrate	$k/10^{-15}$ cm^3 molecule^{-1} s^{-1}	Technique	Ref.
Methyl vinyl	0.32 ± 0.06	Flow tube	This work
ketone	0.47 ± 0.17	Relative rate	This work
	<0.6	Relative rate	14
	<0.12	Flow tube	17
Methacrolein	9.6 ± 2.0	Flow tube	This work
	3.7 ± 1.0	Relative rate	This work
	4.4 ± 1.7	Relative rate	14
	$\leqslant 8.0$	Flow tube	17
Acrolein	8.9 ± 2.8	Flow tube	This work
	1.1 ± 0.4	Relative rate	This work
	1.11 ± 0.17	Relative rate	16
Methyl	0.19 ± 0.04	Flow tube	This work
acrylate	0.10 ± 0.06	Relative rate	This work
Methyl	3.6 ± 1.3	Relative rate	This work
methacrylate			

acrolein. Provided $[O_3]$ is relatively high, NO_3 itself will *not* be removed. The oxidation of methyl vinyl ketone and methacrolein by NO_3 in the atmosphere must therefore now be considered. As we have noted earlier, oxidation of methyl vinyl ketone by NO_3 in the presence of O_2 produces methyl glyoxal,

$$CH_3C(O)CHCH_2 + NO_3 + O_2 \rightarrow$$
$$CH_3C(O)CHOOCH_2(ONO_2) \quad (11)$$

$$CH_3C(O)CHOOCH_2(ONO_2) + NO_3 \rightarrow$$
$$CH_3C(O)CHOCH_2(ONO_2) + NO_2 + O_2 \quad (12)$$

$$CH_3C(O)CHOCH_2(ONO_2) \rightarrow$$
$$CH_3C(O)CHO + HCHO + NO_2 \quad (13)$$

$$\frac{2NO_2 + 2O_3 \rightarrow 2NO_3 + 2O_2}{\text{Net } CH_3C(O)CHCH_2 + 2O_3 \rightarrow}$$
$$CH_3C(O)CHO + HCHO + 2O_2 \quad (18)$$

The addition of NO_3 to methacrolein also yields methyl glyoxal

$$CH_2C(CH_3)CHO + NO_3 + O_2 \rightarrow$$
$$CH_2(ONO_2)COO(CH_3)CHO \quad (8)$$

$$CH_2(ONO_2)COO(CH_3)CHO + NO_3 \rightarrow$$
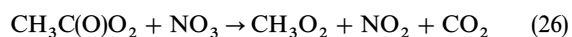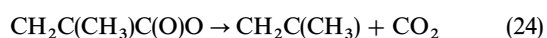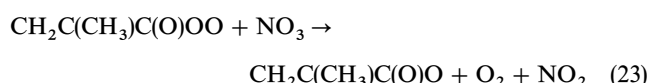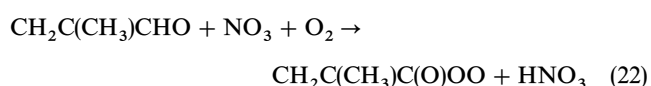$$CH_2(ONO_2)CO(CH_3)CHO + NO_2 + O_2 \quad (9)$$

$$CH_2(ONO_2)CO(CH_3)CHO \rightarrow$$
$$CH_3C(O)CHO + HCHO + NO_2 \quad (10)$$

$$\frac{2NO_2 + 2O_3 \rightarrow 2NO_3 + 2O_2}{\text{Net } CH_2C(CH_3)CHO + 2O_3 \rightarrow}$$
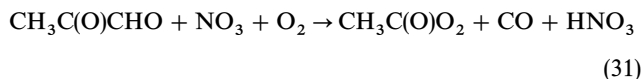$$CH_3C(O)CHO + HCHO + 2O_2 \quad (18)$$

Hence, addition of NO_3 to methyl vinyl ketone and methacrolein yield methyl glyoxal and once more, provided $[O_3]$ is sufficiently high, NO_3 will not be removed. NO_3 also abstracts the aldehydic hydrogen from methacrolein

$$CH_2C(CH_3)CHO + NO_3 + O_2 \rightarrow$$
$$CH_2C(CH_3)C(O)OO + HNO_3 \quad (22)$$

$$CH_2C(CH_3)C(O)OO + NO_3 \rightarrow$$
$$CH_2C(CH_3)C(O)O + O_2 + NO_2 \quad (23)$$

$$CH_2C(CH_3)C(O)O \rightarrow CH_2C(CH_3) + CO_2 \quad (24)$$

$$CH_2C(CH_3) + 2O_2 \rightarrow HCHO + CH_3C(O)O_2 \quad (25)$$

$$CH_3C(O)O_2 + NO_3 \rightarrow CH_3O_2 + NO_2 + CO_2 \quad (26)$$

$$CH_3O_2 + NO_3 \rightarrow CH_3O + NO_2 + O_2 \quad (27)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \quad (28)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad (29)$$

$$\frac{3O_3 + 3NO_2 \rightarrow 3NO_3 + 3O_2}{\text{Net } CH_2C(CH_3)CHO + NO_3 + 4O_3 \rightarrow}$$
$$2CO_2 + 2HCHO + HNO_3 + OH + 3O_2 \quad (18)$$
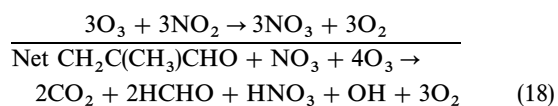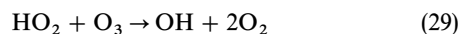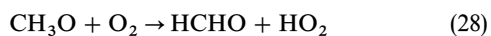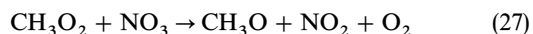
Although one NO_3 radical is consumed, one OH radical is formed in its place. MPAN can also be formed in the reaction

$$CH_2C(CH_3)C(O)OO + NO_2 + M \rightarrow$$
$$CH_2C(CH_3)C(O)ONO_2 + M \quad (30)$$
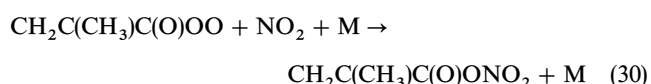
and the oxidation of methyl glyoxal follows a similar pattern

$$CH_3C(O)CHO + NO_3 + O_2 \rightarrow CH_3C(O)O_2 + CO + HNO_3$$
$$(31)$$

followed by reactions (26)–(29) and $2 \times (18)$ leads to the net reaction

$$\text{Net } CH_3C(O)CHO + NO_3 + 3O_3 \rightarrow$$
$$CO + CO_2 + HCHO + OH + HNO_3 + 3O_2$$
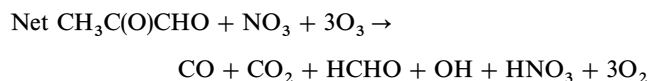
Only one molecule of NO_3 is thus required to oxidise the products of isoprene degradation in the atmosphere, since MPAN formation makes only a minor contribution.[13] At the same time, one OH radical is formed in its place. The implications of the process are that NO_3 concentrations can remain high in the presence of fast-reacting organic species (as a result of NO_3 regeneration), but that one molecule of OH may be produced for every NO_3 consumed. The prerequisite for this mechanism to operate is that O_3 levels must be quite high, typically in excess of 30 ppb. At the very surface of the Earth at night, O_3 is rapidly destroyed either *via* dry deposition or by reaction with NO emitted at night. However, away from the surface, but still in the boundary layer (the so called residual boundary layer), O_3 will not be deposited, and any NO emitted at night will have been converted to NO_2 near the surface. In this residual boundary layer, NO_3 can build to very high levels (100 ppt).[3] Aliwell and Jones[3] have recently reported NO_3 concentrations that are on average 89 ppt in summer over Cambridge UK, and that peak at 450 ppt. A diurnally varying boundary layer model[5] consisting of two levels has been shown to reproduce these very high levels of NO_3 in the residual boundary layer. At the very surface (up to approximately 300 m) in the nocturnal boundary layer, model NO_3 levels are low, typically zero to 20 ppt, because O_3 declines rapidly at night and also because of titration by NO fluxes. In the residual boundary layer, where NO_3 concentrations are high, NO_3 will dominate the night-time oxidation of methacrolein, and reaction with NO_3 can make up a significant fraction of the total overall loss of methacrolein. The daytime ratio of methyl vinyl ketone to methacrolein concentrations is greater than unity, and often around 2–2.5.[22,23] During the day, oxidation of isoprene by OH generates more methyl vinyl ketone than methacrolein, and also OH reacts more quickly with methacrolein than methyl vinyl ketone, driving the partition of these species apart.[23] At night, if we ignore NO_3, ozonolysis of isoprene generates more methacrolein than methyl vinyl ketone, and ozone also reacts more quickly with methyl vinyl ketone than methacrolein. Martin *et al.*[22] observed at a rural site that the ratio of methyl vinyl ketone to methacrolein concentrations is a maximum by day and a minimum by night, consistent with OH oxidation by day and O_3-dominated night-time oxidation. In urban regions, the methyl vinyl ketone to methacrolein concentration ratio remains above unity throughout the day.[22] Biesenthal and Shepson[23] have shown that both methyl vinyl ketone and methacrolein sources have a strong automotive component, which may itself be the cause of the high ratio at night; however, NO_3 will also drive the partitioning of methyl vinyl ketone and methacrolein apart. If isoprene lingers into the night, NO_3 oxidation produces more methyl vinyl ketone than methacrolein, and, as we have seen, NO_3 reacts considerably faster with methacrolein than with methyl vinyl ketone, *i.e.* the behaviour is the exact analogue of OH chemistry during the day. The high ratio of methyl vinyl ketone to methacrolein concentrations in urban regions may be further evidence that NO_3 plays an important role in the planetary boundary layer. Measurements from the Southern Oxidant Study (SOS)[24–27] show how the ratio of methyl vinyl ketone to methacrolein concentrations changes when a forested area

is impacted by urban plumes. One of the conclusions drawn from the SOS study is that NO$_3$ reacts with methacrolein, and that substantial amounts of MPAN are formed at night as a product of this interaction.[24]

Conclusion

Rate coefficients for five structurally similar α,β-unsaturated-carbonyl compounds have been measured by relative and absolute methods. The relative-rate measurements are in good agreement with the results of previous studies where they exist. However, the kinetic data obtained using the absolute method are, in some cases, significantly higher than those from the relative method. Secondary chemistry, together with small amounts of reactive impurities, may be the cause of the discrepancy. Product studies have enabled us to elucidate a mechanism for the oxidation of methyl vinyl ketone and methacrolein by NO$_3$ in the atmosphere. We conclude that NO$_3$ may be an important oxidant for methacrolein in the urban boundary layer and may also be important where urban plumes impact on forested areas.

Acknowledgements

References

1 F. Fehsenfeld, J. Calvert, R. Fall, P. Goldan, A. B. Guenther, C. N. Hewitt, B. Lamb, S. Liu, M. Trainer, H. Westberg and P. Zimmerman, *Global Biogeochem. Cycles*, 1992, **6**, 389.
2 *Scientific Assessment of Ozone Depletion*, 1994 World Meteorological Organization, Global Ozone Research and Monitoring Project—Report No. 37, 1995, Geneva, Switzerland.
3 S. Aliwell and R. L. Jones, *J. Geophys. Res.*, 1998, **103**, 5719.
4 M. E. Jenkin, S. M. Saunders and M. J. Pilling, *Atmos. Environ.*, 1997, **31**, 81.
5 D. J. Fish, D. E. Shallcross and R. L. Jones, *Atmos. Environ.*, 1999, **33**, 687.
6 J. A. Bagley, C. E. Canosa-Mas, M. R. Little, A. D. Parr, S. J. Smith, S. J. Waygood and R. P. Wayne, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 2109.
7 A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne and M. R. Wilson, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2913.
8 C. E. Canosa-Mas, M. D. King, R. Lopez, C. J. Percival, R. P. Wayne, D. E. Shallcross, J. A. Pyle and V. Daele, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 2211.
9 W. B. DeMore, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb and M. J. Molina, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, JPL Publication 97-4, NASA, 1997.
10 T. Brauers and B. J. Finlayson-Pitts, *Int. J. Chem. Kinet.*, 1997, **29**, 665.
11 C. E. Canosa-Mas, S. J. Smith, S. J. Waygood and R. P. Wayne, *J. Chem. Soc., Faraday Trans. II*, 1991, **87**, 3473.
12 C. E. Canosa-Mas, S. J. Smith, S. Toby and R. P. Wayne, *J. Chem. Soc., Faraday Trans. II*, 1988, **84**, 263.
13 C. E. Canosa-Mas, M. D. King, D. E. Shallcross and R. P. Wayne, *Phys. Chem. Chem. Phys.*, 1999, **1**, 2411.
14 E. C. Kwok, S. M. Aschmann, J. Arey and R. Atkinson, *Int. J. Chem. Kinet.*, 1996, **28**, 925.
15 R. Atkinson, *J. Phys. Chem. Ref. Data Monograph No. 1*, 1989.
16 R. Atkinson, *J. Phys. Chem. Ref. Data Monograph No. 2*, 1994.
17 Y. Rudich, R. K. Talukdar, R. W. Fox and A. R. Ravishankara, *J. Phys. Chem.*, 1996, **100**, 5374.
18 R. Atkinson, *J. Phys. Chem. Ref. Data*, 1997, **26**, 215.
19 R. P. Wayne, I. Barnes, P. Biggs, J. P. Burrows, C. E. Canosa-Mas, J. Hjorth, G. Le Bras, G. K. Moortgat, D. Perner, G. Poulet, G. Restelli and H. Sidebottom, *Atmos. Environ.*, 1991, **25A**, 1.
20 B. D'Anna and C. J. Nielsen, *Int. J. Chem. Kinet.*, 1997, **93**, 3479.
21 T. Berndt and O. Böge, *Int. J. Chem. Kinet.*, 1997, **29**, 755.
22 R. Martin, H. Westberg, E. Allwine, L. Ashman, C. Farmer and B. Lamb, *J. Atmos. Chem.*, 1991, **13**, 1.
23 T. A. Biesenthal and P. B. Shepson, *Geophys. Res. Lett.*, 1997, **24**, 1375.
24 T. K. Starn, P. B. Shepson, S. B. Bertman, J. S. White, B. G. Splawn, D. D. Reimer, R. G. Zika and K. Olszyna, *J. Geophys. Res.*, 1998, **103**, 22425.
25 T. K. Starn, P. B. Shepson, S. B. Bertman, D. D. Reimer, R. G. Zika and K. Olszyna, *J. Geophys. Res.*, 1998, **103**, 22437.
26 G. Nouaime, S. B. Bertman, C. Seaver, D. Elyea, H. Huang, P. B. Shepson, T. K. Starn, D. D. Reimer, R. G. Zika and K. Olszyna, *J. Geophys. Res.*, 1998, **103**, 22463.
27 J. M. Roberts, J. Williams, K. Baumann, M. P. Buhr, P. D. Goldan, J. Holloway, G. Hubler, W. C. Kuster. A. A. McKeen, T. B. Ryerson, M. Trainer, E. J. Williams, F. C. Fehsenfeld, S. B. Bertman, G. Nouaime, C. Seaver, G. Grodzinsky, M. Rogers and V. L. Young, *J. Geophys. Res.*, 1998, **103**, 22473.

Paper 9/04613E