Is the reaction between $CH_3C(O)O_2$ and NO_3 important in the night-time troposphere?

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A discharge-flow system equipped with a laser-induced fluorescence (LIF) cell to detect NO_2 and a multi-pass absorption cell to detect NO₃ has been used to study the reaction

$$CH_3C(O)O_2 + NO_3 \rightarrow CH_3C(O)O + NO_2 + O_2$$
(1)

at T = 403-443 K and P = 2-2.4 Torr. The rate constant was found to be independent of temperature with a value of $k_1 =$ $(4 \pm 1) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. The likely mechanism for the reaction is discussed. The atmospheric implications of reaction (1) are investigated using a range of models and several case studies are presented, comparing model results with actual field measurements. It is concluded that reaction (1) participates in a cycle which can generate OH at night. This reaction cycle (see text) can operate throughout the continental boundary layer, but may even occur in remote regions.

We present a kinetic and product study of the reaction between the acetyl peroxyl radical and the nitrate radical

$$CH_3C(O)O_2 + NO_3 \rightarrow CH_3C(O)O + NO_2 + O_2 \qquad (1)$$

Acetyl peroxyl radicals are generated in the atmosphere via a number of reactions, e.g. the sequence of reactions

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O$$
 (2)

$$CH_3CO + O_2 + M \rightarrow CH_3C(O)O_2 + M$$
 (3)

Once formed, acetyl peroxyl radicals can react¹ with NO

$$CH_3C(O)O_2 + NO \rightarrow CH_3C(O)O + NO_2$$
 (4)

or be sequestered by NO₂ to form PAN (peroxyacetylnitrate)¹

$$CH_3C(O)O_2 + NO_2 + M \rightarrow CH_3C(O)O_2NO_2 + M \quad (5)$$

In less polluted areas, reaction with HO₂ becomes an important loss process¹

$$CH_3C(O)O_2 + HO_2 \rightarrow products$$
 (6)

PAN has been identified as an important reservoir species for NO_x (NO and NO_2) in the troposphere.² Although it has a short lifetime at the surface, where it is thermally unstable, once in the cooler free troposphere, PAN can be transported from regions of high NO, to remote areas.^{3,4} In the planetary boundary layer, PAN can still act as a temporary NO_x reservoir; during the day PAN is formed from the oxidation of hydrocarbons⁵ and will decompose thermally throughout the day and into the night. At night, the nitrate radical can intercept the acetyl peroxyl radicals released from the thermal decomposition of PAN, and OH can be generated in the sequence of reactions

$$CH_3C(O)O_2 + NO_3 \rightarrow CH_3C(O)O + NO_2 + O_2 \qquad (1)$$

$$CH_3C(O)O \rightarrow CH_3 + CO_2 \tag{7}$$

(8)

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CH_3O_2 + NO_3 \rightarrow CH_3O + NO_2 + O_2$$
(8)
(9)

$$CH O + O \rightarrow HO + HCHO$$
(10)

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \tag{10}$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{11}$$

There has been one previous study of reaction (1), which was a preliminary investigation by some of us.^{6,7} A more complete investigation of the reaction is presented here. A dischargeflow technique was employed in which thermal decomposition of PAN furnished the acetyl peroxyl radicals. While this source of radicals is a clean one, it necessarily restricts the temperature range (403-443 K) available for experiments to that in which the decomposition of PAN proceeds at a suitable rate.

The atmospheric implications of the reaction between $CH_3C(O)O_2$ radicals and NO_3 are discussed.

Experimental

A conventional discharge-flow system with six static injectors was used (Fig. 1); of these injectors, only the five nearest the observation region were used in quantitative measurements, because the sixth injector was not within the isothermal region of the flow tube. The flow tube was coupled to a metal fluorescence cell which was blackened inside, and had short baffle arms (30 cm) with Brewster angle windows. An optical multi-path absorption cell (12 passes, base path 13 cm) was incorporated downstream of the LIF cell. The flow tube was made of Pyrex and was approximately 1 m in length with an internal diameter of 38 mm. Experiments were performed at T = 403-443 K and between 2 and 2.4 Torr. The flow tube was heated by a Hotfoil tape, the power to which was regulated by an electronic controller in conjunction with a type-T thermocouple attached to the outer surface of the flow tube.

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Fig. 1 Experimental arrangement of the flow tube and detection systems

Throughout the experiments, helium was used as a carrier gas. Nitrate radicals were prepared by the reaction of fluorine atoms with dry nitric acid

$$F + HNO_3 \rightarrow NO_3 + HF$$
 (12)

and detected by optical absorption at $\lambda = 662 \text{ nm.}^8 \text{ An effec$ $tive absorption cross-section } [\sigma = (1.4 \pm 0.2) \times 10^{-17} \text{ cm}^2 \text{ molecule}]$ was determined experimentally for NO₃ via the titration of NO₃ with NO

$$NO_3 + NO \rightarrow 2NO_2$$
 (13)

from which the absolute concentrations of NO₃ could be assigned. The minimum detectable [NO₃] for a signal-to-noise ratio of unity with a 10 s integration time was *ca.* 10^{11} molecule cm⁻³.

Acetyl peroxyl radicals were produced by the thermal decomposition of PAN

$$CH_3C(O)O_2NO_2 + M \rightarrow CH_3C(O)O_2 + NO_2 + M \quad (-5)$$

PAN was introduced into the flow tube via the static injectors by bubbing molecular oxygen through a PAN-*n*-tridecane mixture. Before entering the flow tube, the flow of PANmolecular oxygen was sampled into an IR cell and subsequently transferred to a Perkin-Elmer FTIR spectrometer (series 2000) and a spectrum recorded. Typically, 64 interferograms were recorded at 1 cm⁻¹ resolution. The FTIR analysis served two purposes; first, it provided an indication of the purity of the synthesised PAN and secondly, using the literature values of the absorption cross-sections,⁹ it allowed determination of the concentrations of PAN introduced into the flow tube.

The NO₂ produced in reactions such as reaction (-5) was monitored by LIF. The excitation was provided by an argonion laser (Coherent Innova 70) operating at $\lambda = 488$ nm with a typical power of 1W. The laser radiation was directed through a rotating chopper (chopping frequency 130 Hz). The fluorescence radiation was collected orthogonally to the probe beam; radiation was focused by a Pyrex lens through an interference filter ($\lambda = 550$ nm, FWHM = 3 nm) onto a photocathode of a cooled (223 K) photomultiplier (Thorn EMI 9757QB), operated at 1.5 kV. The output from the photomultiplier was processed by a lock-in amplifier. The response of the detection system was placed on an absolute scale by calibration against known NO₂ concentrations. The minimum detectable [NO₂] was 5 × 10⁹ molecule cm⁻³ for a signal-tonoise ratio of unity and with a 5 s time constant.

Three types of experiments were carried out. First, the PAN-O₂ mixture was introduced into the heated flow tube via the static injectors, a large excess of NO (ca. 5×10^{15} molecule cm⁻³) was added upstream, and the production of NO₂ was monitored as a function of contact time. Second, the PAN-O₂ mixture was added to the heated flow tube in the absence of NO, and the NO₂ formed was measured as a function of contact time. Third, to study the reaction of acetyl

peroxyl radicals with NO₃, the NO₃ was added upstream of the injection of PAN into the flow tube. The decrease of NO₃ concentration caused by the addition of PAN was monitored by optical absorption, and the simultaneous growth of NO₂ was determined by LIF. The possible reaction of *n*-tridecane with NO₃ was checked at every temperature used in this study by bubbling O₂ through a pure sample of tridecane and examining the effect on the NO₃ signal; in no case was any change in the NO₃ signal observed.

The production of NO₂ from the decomposition of PAN was measured in both the presence and the absence of NO in each run immediately before NO₃ was introduced into the flow. In this way, a realistic assessment of the [PAN]₀ (the concentration of PAN at zero contact time) was obtained for each run in which the reaction of NO₃ with acetyl peroxyl radicals was studied. Typical experimental conditions used were: [PAN]₀ = $0.2-2 \times 10^{13}$ molecule cm⁻³; [NO₃]₀ = $0.1-4 \times 10^{13}$ molecule cm⁻³; [NO]₀ $\geq 4 \times 10^{15}$ molecule cm⁻³; [O₂] = 8 $\times 10^{15}$ molecule cm⁻³; pressure = 2-2.4 Torr; temperature = 403-443 K.

Materials

Nitric acid (BDH, 99.9%) was dehydrated by sulfuric acid (BDH, 99.5%) in a 1:2 volume-to-volume mixture and held at *ca.* 258 K. Helium (BOC) was passed through an OXISORB cartridge (Messer Griesheim) to remove any oxygen and a drying tube containing anhydrous phosphorus pentaoxide and a trap held at 77 K containing molecular sieve 4A (BDH) to remove water. Nitrogen dioxide was purified by repeated freeze-pump-thaw cycles at 77 K, and corrections were made for the N_2O_4 - NO_2 equilibrium when calculating the NO_2 concentration in the system from its flow rate. Nitric oxide (Messer Griesheim, >99%) was passed through a trap at 196 K, then purified by repeated freeze-pump-thaw cycles at 77 K. Fluorine (BOC, 5% in helium) was used as supplied.

PAN was prepared by the nitration of peracetic acid in an *n*-tridecane solution by the procedure outlined by Gaffney *et al.*⁹ For this preparation, nitric acid (BDH, 99.9%), sulfuric acid (BDH, 99.9%), *n*-tridecane (Fluka, >97%, (peracetic acid (Aldrich, 40% in dilute acetic acid) and anhydrous magnesium sulfate (BDH) were used as supplied.

Results

The thermal decomposition of PAN was studied by following the formation of NO_2 in the presence of oxygen, and in the presence of both NO and oxygen. An extended mechanism was used to analyse the experimental concentration-time profiles of NO_2

 $CH_3C(O)O_2NO_2 + M \rightarrow CH_3C(O)O_2 + NO_2 + M \quad (-5)$

$$CH_3C(O)O_2 + NO_2 + M \rightarrow CH_3C(O)O_2NO_2 + M \quad (5)$$

$$CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow 2CH_3C(O)O + O_2$$
(14)

$$CH_3C(O)O \rightarrow CH_3 + CO_2$$
 (7)

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CH_3C(O)O_2 + CH_3O_2 \rightarrow CH_3C(O)O + O_2 + CH_3O$$

(15)

(8)

 $CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$ (16a)

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + CH_2O + O_2 \quad (16b)$$

$$CH_3O + O_2 \rightarrow HO_2 + CH_2O \tag{10}$$

$$CH_3C(O)O_2 + HO_2 \rightarrow products$$
 (6)

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$$
(17)

$$CH_3C(O)O_2 + NO \rightarrow CH_3C(O)O + NO_2$$

$$CH_{3}O_{2} + NO \rightarrow CH_{3}O + NO_{2}$$
(18)
$$CH_{3}O + NO + M \rightarrow CH_{3}ONO + M$$
(19a)

(4)

$$CH_3O + NO \rightarrow CH_3O + HNO$$
 (19b)

$$CH_3 + NO + M \rightarrow CH_3NO + M$$
 (20)

$$HO_2 + NO \rightarrow OH + NO_2$$
 (21)

$$OH + NO + M \rightarrow HNO_2 + M$$
 (22)

$$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$$
(23)

$$CH_{3}O + NO_{2} + M \rightarrow CH_{3}ONO_{2} + M$$
(24)

$$CH_3 + NO_2 \rightarrow CH_3O + NO$$
 (25)

When NO is added in sufficient excess, it can be assumed that all of the $CH_3C(O)O_2$ and CH_3 radicals react immediately with NO, so that the kinetic scheme can be simplified to only four reactions

$$CH_3C(O)O_2NO_2 \rightarrow CH_3C(O)O_2 + NO_2$$
 (-5)

$$CH_{3}C(O)O_{2} + NO \rightarrow CH_{3}C(O)O + NO_{2}$$
(4)

$$CH_{3}C(O)O \rightarrow CH_{3} + CO_{2}$$
(7)

$$CH_3 + NO + M \rightarrow CH_3NO + M$$
 (20)

The rate of formation of NO₂ is then

$$\frac{d[NO_2]}{dt} = k_{-5}[PAN] + k_4[NO][CH_3C(O)O_2]$$
(I)

and the rate of formation of CH₃C(O)O₂ radicals is

$$\frac{\mathrm{d}[\mathrm{CH}_{3}\mathrm{C}(\mathrm{O})\mathrm{O}_{2}]}{\mathrm{d}t} = k_{-5}[\mathrm{PAN}] - k_{4}[\mathrm{NO}][\mathrm{CH}_{3}\mathrm{C}(\mathrm{O})\mathrm{O}_{2}]$$
(II)

For the concentrations of NO used, it can be assumed that the $CH_3C(O)O_2$ radicals are at their steady-state concentrations and that, for each molecule of PAN consumed, two molecules of NO₂ are formed. It follows that

$$[NO_2]_t = 2[PAN]_0[1 - exp(-k_{-5}t)]$$
(III)

An equation of this form allows the growth of $[NO_2]$ with contact time to be fitted using a simple nonlinear least-squares fit. Fig. 2 shows a typical fit for the experimental NO₂ growth against contact time using eqn. (III). Table 1 summarises the



Fig. 2 Sample fit between experimental points and the predictions of the simplified kinetic approach. T = 413 K; P = 2.14 Torr; $[PAN]_0 = 8.3 \times 10^{12}$ molecule cm⁻³; $[NO]_0 \approx 4 \times 10^{15}$ molecule cm⁻³; $k_{-5} = 14.3$ s⁻¹. (**II**) Experimental points; (----) profile given by fitting eqn. (III).

 Table 1
 Rate constants for thermal decomposition of PAN obtained in this study

T/K	k_{-5}/s^{-1}
403	11.0
	9.5
	10.7
	9.7
	11.0
413	14.0
	15.5
	14.7
	14.0
	15.7
423	25.1
	20.6
	22.8
	23.6
	22.1
433	37.5
	40.1
	45.1
	38.9
	34.2
443	47.3
	40.9
	48.7
	46.4

rate constants obtained for the thermal decomposition of PAN at the temperatures used, and Fig. 3 shows an Arrhenius plot for the combined data over the temperature range studied. The plot gives the value of $\ln(A/s^{-1})$ to be (20 ± 1) and an activation energy of (59.2 ± 4.6) kJ mol⁻¹; the quoted errors are 95% statistical confidence limits. These data refer, of course, to the restricted temperature range and fixed pressures of our experiments, and should not be regarded as constituting a new generalised Arrhenius expression. Rather, they provide a useful parametrisation for use in the modelling of our laboratory kinetic runs.

The fitting procedure also yields a value for $[PAN]_0$. As explained earlier, the concentration of PAN in the supply flow was determined by FTIR analysis and used to calculate the concentration in the flow tube from the known flow rates. Fig. 4 shows that there is good agreement between both calculated and modelled $[PAN]_0$, which gives confidence in our method and demonstrates that there are no additional sources of NO₂ (*e.g.* from CH₃O₂ formed in a side reaction of CH₃ with O₂) present in the system.

The parameters determined using eqn. (III) depend only on NO being in sufficient excess to give a stoichiometry that is



Fig. 3 Arrhenius plot for the thermal decomposition of PAN in our experiments



Fig. 4 Comparison of the values of initial PAN concentrations ([PAN]₀) given by the simplified kinetic approach with that of FTIR analysis

independent of contact time and with $\Delta[NO_2] = 2\Delta[PAN]$. For the analysis of the experiments with NO₃ present, it is necessary to use the more complex mechanism in a full kinetic model. Table 2 summarises the values of the rate constants employed. As the rate coefficients given in the literature have some uncertainty, especially with regards to their temperature dependence, a step-by-step approach was used to determine which reactions are of greatest importance. The steps were (a) kinetic modelling of the NO₂ concentration-time profiles in the absence and presence of NO; (b) kinetic modelling of the NO₂ and NO₃ concentration-time profiles in the presence of NO₃; and (c) sensitivity analysis of the kinetic model.

(a) $[NO_2]$ -time profiles in the absence of NO_3

Experiments on the thermal decomposition of PAN were carried out both in the presence of a large excess of NO and in the absence of NO. The parameters ([PAN]₀ and k_{-5}) given by the simple kinetic approach can then be used in a full kinetic model of the experimental data. Fig. 5 shows a typical fit of the modelled NO₂ concentration-time profiles. The agreement between the calculated and experimental points is excellent and is to be expected in the PAN-NO system, if the assumptions used to derive eqn. (III) are correct. However,



Fig. 5 Typical growth of NO₂ concentration against contact time for the PAN-NO-O₂ (upper line) system and the PAN-O₂ (lower line) system. T = 413 K; P = 2.14 Torr; $[PAN]_0 = 8.3 \times 10^{12}$ molecule cm⁻³; $[NO]_0 \approx 4 \times 10^{15}$ molecule cm⁻³ (upper line); $[NO]_0 = 0$ (lower line); $k_{-5} = 14.3$ s⁻¹. Experimental points: (\blacksquare) in the absence of NO, (\triangle) in the presence of NO, (---) model without NO, (----) model with NO.

there is one feature used in obtaining the modelled curves for the system containing PAN alone that should be pointed out. The reactions of NO₂ with CH_3O_2 and $CH_3C(O)O_2$

$$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$$
(23)

$$CH_3C(O)O_2 + NO_2 + M \rightarrow CH_3C(O)O_2NO_2 + M$$
 (5)

are not expected, on the basis of the published rate data, to contribute significantly. On the other hand, reactions of NO_2 with CH_3O and CH_3

$$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$$
 (24)

$$CH_3 + NO_2 \rightarrow CH_3O + NO$$
 (25)

have to be assigned much lower rate coefficients than currently accepted in order to achieve the match shown in Fig. 5. The main fate of CH_3O and CH_3 will be reaction with oxygen. The small rate coefficients needed for reactions (24) and (25) indicate that, for our experimental conditions, either the reactions with oxygen are much more important than we expect from the first estimate of the rate coefficients, based on available literature data, or there are other losses for CH_3 and

Table 2 Rate constants used in analysing the thermal decomposition of PAN and the reaction of $CH_3C(O)O_2$ radicals with NO_3

reaction	rate constant/cm ³ molecule ^{-1} s ^{-1}
$CH_{3}O_{2} + NO$	$4.2 \times 10^{-12} \exp(+180/T)$
$CH_{3}O + NO$	2×10^{-12}
$CH_3 + NO$	1×10^{-12}
$HO_2 + NO$	$3.7 \times 10^{-12} \exp(+250/T)$
$CH_{3}O_{2} + HO_{2}$	$3.8 \times 10^{-13} \exp(+800/T)$
$CH_3C(O)O_2 + NO_3$	4×10^{-12} a
$CH_3O + NO_3$	2.4×10^{-12} b
$CH_3O_2 + NO_3$	1×10^{-12} b
$NO_3 + HO_2$	3.5×10^{-12}
$HO_2 + HO_2$	$2.3 \times 10^{-13} \exp(+600/T)$
$CH_3C(O)O_2 + NO$	2.4×10^{-11}
$HO_2 + OH$	$4.8 \times 10^{-11} \exp(+250/T)$
$CH_3C(O)O_2NO_2 \rightarrow CH_3C(O)O_2 + NO_2$	$4.8 \times 10^8 \exp(-7100/T)$ (units of s ⁻¹) ^a
$CH_3C(O)O_2 + NO_2$	$9.7 \times 10^{-29} (T/300)^{-5.6} \times [M]$
$CH_3C(O)O_2 + CH_3C(O)O_2$	$2.5 \times 10^{-12} \exp(+550/T)$
$CH_3 + O_2$	$4.5 \times 10^{-31} (T/300)^{-3} \times [M]$
$CH_3C(O)O_2 + CH_3O_2$	1.4×10^{-11}
$CH_3O + O_2$	$3.9 \times 10^{-14} \exp(-900/T)$
$CH_3C(O)O_2 + HO_2$	$4.5 \times 10^{-13} \exp(+1000/T)$

All data taken from ref. 10 and references therein, except a this work, and b ref. 11. Where no explicit temperature dependence is quoted, the rate coefficients are taken to be the same for all temperatures employed; the values are our best estimates for the temperatures (and, where applicable, the pressures) of our experiments.

 CH_3O (e.g. wall loss). Whatever the true explanation, the observations can be applied to the model for study of the reaction of acetyl peroxyl radicals with NO_3 .

(b) [NO₂]-time and [NO₃]-time curves in the presence of NO₃

For the study of the reaction of NO₃ with $CH_3C(O)O_2$ radicals, the following reactions have to be added to the basic PAN-O₂ mechanism outlined in the study of the thermal decomposition of PAN

$$CH_3C(O)O_2 + NO_3 \rightarrow CH_3C(O)O + NO_2 + O_2 \qquad (1)$$

$$CH_3O + NO_3 \rightarrow CH_3O_2 + NO_2$$
 (26)

$$CH_3O_2 + NO_3 \rightarrow CH_3O + NO_2 + O_2 \tag{9}$$

$$NO_3 + HO_2 \rightarrow NO_2 + OH + O_2$$
 (27)

$$NO_3 + OH \rightarrow NO_2 + HO_2$$
 (28)

$$HO_{2} + HO_{2} \rightarrow H_{2}O_{2} + O_{2}$$
(29)

$$HO_2 + OH \rightarrow H_2O + O_2 \tag{30}$$

The choice of products of reaction (1) is based on the corresponding reaction¹⁰ with NO, reaction (4), and on the reactions of CH_3O_2 and $C_2H_5O_2$ with NO_3 (see Discussion). Previous work carried out in this laboratory^{11,12} established that CH₃O and C₂H₅O are the most significant channels in the reaction of CH_3O_2 and $C_2H_5O_2$ with NO₃, emphasising the parallel reactivity of NO and NO₃ towards peroxyl radicals. Experiments with NO3 were carried out immediately after the thermal decomposition experiments, so that, as stated earlier, the initial PAN concentration evaluated from eqn. (III) could be used in the reaction scheme for the evaluation of the rate coefficient for the reaction of $CH_3C(O)O_2$ with NO₃. Fig. 6 shows typical fits of the kinetic model with experimental points. Table 3 shows the input data used in the modelling and the values of k_1 obtained. Over the temperature range studied, no obvious temperature dependence of the rate coefficient for the reaction of $CH_3C(O)O_2$ radicals with NO₃ was observed; and the mean rate constant obtained from this work for the reaction of $CH_3C(O)O_2$ radicals with NO₃ was $(4 \pm 1) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹; the quoted errors are one standard deviation.

(c) Sensitivity analysis

The rate coefficients used in the kinetic model can be varied



Fig. 6 Sample modelled fit for the concentration-time profiles of NO₂ production and NO₃ consumption for the reaction of acetyl peroxyl radicals with NO₃. (\blacksquare) experimental NO₃, (\blacklozenge) experimental NO₂, (\frown) NO₂ model, (--) NO₃ model

			[PAN] ₀	$[NO_2]_0$	[NO ₃] ₀	1	h (10 = 12 3
	T/K	P/Torr	/1013	molecule	cm ⁻³	$\frac{k_{-5}}{s^{-1}}$	$\frac{k_{10}}{10} = cm^2$
(a)	443	2.22	1.6	2.2	3.7	43.2	5
(b)	423	2.22	1.1	1.8	2.8	22.5	4.5
(c)	403	2.22	0.78	2.1	3.7	10.0	3

Table 3 Numerical modelling of the reaction of NO_3 with $CH_3C(O)O_2$

flow tube temperature/K	flow tube pressure/Torr	$[PAN]_0/10^{12}$ molecule cm ⁻³	k_{-5}/s^{-1}	$[NO_2]_0/10^{12}$ molecule cm ⁻³	$[NO_3]_0/10^{12}$ molecule cm ⁻³	recovered $k_1/10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹
403	2.22	7.8	10.0	21	37	3
403	2.22	6.8	10.0	22	36	2.5
403	2.22	5.4	10.0	15	30	4
403	2.22	4.7	10.0	13	27	1.5
413	2.14	12.6	14.3	9.9	20	5
413	2.14	8.3	14.3	1.5	23	5
413	2.14	8.3	14.3	1.1	32	5
413	2.14	5.5	14.3	1.5	17	5
423	2.22	18.5	22.8	22	60	4
423	2.22	15.6	22.8	19	33	3
423	2.22	11.4	22.5	18	28	4.5
423	2.22	9.4	22.8	20	24	5
433	2.22	13.0	33.7	29	43	5
433	2.22	12.4	33.7	14	22	3
433	2.22	11.3	33.7	22	32	5.5
433	2.22	10.5	33.7	19	31	3
443	2.22	16.4	43.2	22	37	5
443	2.22	10.9	43.2	19	33	3
443	2.22	6.7	43.2	11	31	3

The concentrations of PAN, NO₂ and NO₃ are measured at 298 K. The concentration of molecular oxygen was kept constant at 8×10^{15} molecule cm⁻³.

by a factor of ten without affecting the final value of k_1 , with the notable exceptions of those for the reactions

$$CH_3C(O)O_2 + HO_2 \rightarrow products$$
 (6)

$$CH_3O_2 + NO_3 \rightarrow CH_3O + NO_2 + O_2$$
 (9)

$$CH_{3}C(O)O_{2} + CH_{3}C(O)O_{2} \rightarrow 2CH_{3}C(O)O + O_{2}$$
(14)

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$$
(17)

$$HO_2 + NO_3 \rightarrow NO_2 + OH + O_2 \qquad (27)$$

Reactions (6), (14) and (17) have all been studied by Moortgat et al.,¹³⁻¹⁵ and varying the rate coefficients for these reactions, within the experimental errors quoted in these papers, has no effect on the recovered rate constant for the reaction of NO₃ with PA. Reaction (27) has been studied by many workers¹⁶⁻¹⁹ and the rate of reaction is well defined at 298 K, with a rate constant of 3.5×10^{-12} cm³ molecule⁻¹ s⁻¹. However, little is known about the temperature dependence of this reaction. If one assumes that the rate constant for reaction (27) has a similar temperature dependence to that of the analogous reaction of HO₂ with NO ($E_a = 250 \pm 80 \text{ J mol}^{-1}$),¹⁰ and extrapolates the value of the rate constant to the temperatures used, no effect on the modelled concentration-time profiles of NO₂ and NO₃ is observed. Reaction (9) has been studied by Biggs *et al.*,¹¹ Crowley *et al.*,²⁰ and Daële,²¹ and these workers obtained values for the rate coefficient of $(1.0 \pm 0.6) \times 10^{-12}$, $(1.3 \pm 0.3) \times 10^{-12}$ and $(1.2 \pm 0.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, respectively. Although the values of this rate constant seem to be in good agreement, the value that is used in the kinetic model has a great effect on the modelled NO₃ and NO₂ concentration-time profiles. Table 4 shows the variation of the final rate coefficient obtained for the reaction of $CH_3C(O)O_2$ with NO₃. We now believe that the errors in k_9 quoted in our paper¹¹ have been overestimated, and that k_9 has a value of $(1.0-1.4) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹; the rate constant obtained from this work for the reaction of $CH_3C(O)O_2$ radicals with NO_3 will then be in the range of $(3-5) \times 10^{-12}$ cm³ molecule⁻¹ s⁻

Discussion

The rate of the thermal decomposition of PAN has been studied by many other research groups.²²⁻²⁷ Fig. 7 shows the results reported earlier together with the values obtained in



Fig. 7 Comparison of present data on k_{-5} with values reported in the literature. (**II**) (A) This work, (B) ref. 22 (at 2 Torr), (C) ref. 24, (D) ref. 26, (E) ref. 23, (F) ref. 22 (G) ref. 25 and (H) ref. 27).

this study. For the purposes of comparison, we have calculated the rate constants at 2 Torr between 300 and 460 K (solid line), using the Troe equation and the corresponding parameters given by Bridier *et al.*²² It is evident from Fig. 7 that our results support the thermochemical parameters given by Bridier *et al.*²²

Table 5 shows the rate coefficients for the reactions of NO_3 with some RO_2 radicals and compares them with those for the reactions of RO_2 with NO. The table suggests that, for the organic radicals, the reactions of RO_2 with NO_3 follow the same trends in reactivity as the analogous reactions of RO_2 with NO. The products of the reactions of NO_3 with peroxyl radicals also seem to be the same^{11,12,28} as those of the reactions with NO, *i.e.* an alkoxyl radical and NO_2 ; it is therefore reasonable to assume that the products of reaction (1) are the acyloxyl radical and NO_2 .

The reaction of $CH_3C(O)O_2$ with NO₃ has been the subject of only one previous study,^{6,7} which was carried out in this laboratory. This work was exploratory and the research presented here is a continuation of it. Biggs *et al.*^{6,7} also employed a heated flow tube with detection of NO₃ using a pressure of *ca.* 3 Torr. However, no direct measurement of NO₂ was performed, so that it was impossible to have an independent evaluation of the extent of thermal decomposi-

Table 4 Dependence of the retrieved rate constant obtained for the reaction of NO_3 with $CH_3C(O)O_2$ on the value of the rate coefficient for reaction of CH_3O_2 with NO_3

rate constant used for the	rate constant obtained from the kinetic model for the reaction of $CH_3C(O)O_2$ with NO ₃ $/10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹				
$/10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹	T = 433 K	T = 423 K	T = 413 K		
0.4 0.6 1.0 1.4 1.6	30 15 5 3 3	22 10 4 3 3	25 16 5 4 4		

Table 5 Rate constants for reactions of RO₂ with NO₃ compared to those of RO₂ with NO

RO ₂	rate constant for RO ₂ with NO $/cm^3$ molecule ⁻¹ s ⁻¹	rate constant for RO_2 with NO_3 /cm ³ molecule ⁻¹ s ⁻¹		
HO₂ CH O	7.8×10^{-12} 7.0 × 10^{-12}	3.5×10^{-12}		
$C_2H_5O_2$	$\frac{7.9 \times 10}{8.9 \times 10^{-12}}$	1.0×10^{-12} 2.5×10^{-12} b		
$CH_3C(O)O_2$	2.0×10^{-11}	4.0×10^{-12} c		

All data from ref. 1 except for " ref. 28, b ref. 10 and c this work.

Atmospheric implications

Three cycles can be envisaged that could be involved in production and loss of OH in the night-time troposphere.

cycle I

$$CH_3C(O)O_2NO_2 + M \rightarrow CH_3C(O)O_2 + NO_2 + M \quad (-5)$$

$$CH_3C(O)O_2 + NO_3 \rightarrow CH_3C(O)O + NO_2 + O_2 \qquad (1)$$

$$CH_3C(O)O \to CH_3 + CO_2 \tag{7}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{8}$$

$$CH_3O_2 + NO_3 \rightarrow CH_3O + NO_2 + O_2 \tag{9}$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \tag{10}$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{11}$$

$$2 \times (\mathrm{NO}_2 + \mathrm{O}_3 \to \mathrm{NO}_3 + \mathrm{O}_2)$$
(31)

net: $CH_3C(O)O_2NO_2 + 3O_3 \rightarrow$

$$HCHO + OH + CO_2 + NO_2 + 4O_2$$

cycle II

$$OH + CH_4 + O_2 + M \rightarrow CH_3O_2 + H_2O + M$$
 (32)

$$CH_3O_2 + NO_3 \rightarrow CH_3O + NO_2 + O_2 \qquad (9)$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO$$
 (10)

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{11}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{31}$$

 $\mathsf{net} \colon \mathsf{CH}_4 + 2\mathsf{O}_3 \to \mathsf{H}_2\mathsf{O} + \mathsf{HCHO} + 2\mathsf{O}_2$

cycle III

$$OH + CO + O_2 + M \rightarrow HO_2 + CO_2 + M$$
(33)

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{11}$$

net: $CO + O_3 \rightarrow CO_2 + O_2$

We have used a box model approach to investigate the potential role played by cycle I in generating OH in the night-time troposphere. The OH radicals produced in cycle I can then participate in cycles II and III. The reactions and the rate parameters used in this basic box model (model A) are summarised in Table 6 and include all the reactions incorporated in cycles I, II and III. Box models using the basic reaction scheme have been initialised with concentration fields taken from the Cambridge 2-D model^{29,30} and run at a variety of latitudes (60°N to 60°S) and altitudes (0 to 12 km) as a function of season. These box model runs have allowed us to define those regions in the troposphere where cycle I is likely to be important. We have then looked at particular case studies, notably two continental summer measurement campaigns, the ROSE (Rural Oxidants in the Summer Environment) experiment³¹ and measurements at Schauinsland,³² and one remote environment study, MLOPEX (Mauna Loa Observatory Photochemistry Experiment),³³ in order to investigate in more detail the potential role played by

cycle I, and in particular to see the effect of adding nonmethane hydrocarbons to the basic scheme.

Box model results (model A)

Several points of note should be made about the box model studies using model A. First, unless stated, no deposition processes or emissions are included. Second, models are run for the duration of the night, and initialised using the concentration fields derived from the Cambridge 2-D tropospheric model. Third, since the initial fields are derived from a 2-D model we are tacitly assuming a zonal average for concentrations of chemical species (*i.e.* they are averaged around lines of latitude).

As one might expect, no one single factor determines the efficiency of cycle I; however, by far the most important is temperature. Cycle I becomes more efficient as temperature is raised. The reason is straightforward; first, PAN decomposition is enhanced and second, the rates of both reaction (31) which generates NO_3 and reaction (11) which converts HO_2 into OH increase with temperature, markedly so in the case of reaction (31). It is not therefore surprising to find that cycle I is less efficient in the free troposphere, where temperatures are lower than at the surface. However, temperature is not the only important factor; concentrations of PAN, O₃ and NO₂ also clearly affect the efficiency of cycle I. The results of the basic box model runs can thus be summarised as follows. In general, cycle I is not an efficient source of OH at night in the free troposphere. The inefficiency is a result of lower temperatures, the increased stability of PAN towards thermal decomposition and the generally smaller concentrations of NO_x encountered in the free troposphere compared with those inside the planetary boundary layer.^{29,30} In the planetary boundary layer, as a generalisation, cycle I is more efficient in the northern hemisphere than in the southern hemisphere, quite simply because of the difference in levels of NO_x between the two hemispheres (higher in the northern hemisphere). In the northern hemisphere between 40°N and the equator, model runs suggest that 10^4-10^5 molecule cm⁻³ of OH can be produced at night as a direct result of cycle I throughout the year. It is not surprising to find that at high latitudes (e.g. 60°N), cycle I is only of importance in late spring and summer. However, here too OH concentrations can reach 10^4 molecule cm⁻³ at night. The possibility that PAN, stored at high latitudes during the winter and early spring, can act as a source of NO_x in late spring and summer has been noted previously,³⁴⁻³⁶ but the role played by reaction (1) has not.

Cycle I appears to be most important in spring at midlatitudes. During the winter, NO_x levels can accumulate over continental regions,³⁷ and in spring, when photochemical activity increases, a PAN maximum is observed both in field measurements^{38,39} and in model studies.^{29,30} This combination of high PAN and NO_x is responsible for the enhanced efficiency of cycle I. Fig. 8 shows the production of OH at night in spring at 30°N in the boundary layer and in the free troposphere (6 km). The initial concentrations of the key constituents are summarised in Table 7.

Apart from the reactions included in cycle I, two other reactions can be important in initiating night-time production of OH

$$CH_{3}C(O)O_{2} + CH_{3}O_{2} \rightarrow CH_{3}C(O)O + CH_{3}O + O_{2}$$

(15)

$$HO_2 + NO_3 \rightarrow OH + O_2 + NO_2$$
 (27)

In the absence of NO_3 , reaction (15) can initiate OH production through steps (7), (8) and (10), which may have implications for remote regions where NO_x levels are low. However, in most model runs, the loss of acetyl peroxyl rad-

Table 6	Reactions and	rate parameters	used in model A
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reaction	rate constant/cm ³ molecule ⁻¹ s ⁻¹
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.20 \times 10^{-13} \exp(600/T)$
$HO_2 + CH_3C(O)O_2 \rightarrow CH_3CO_3H + O_2$	$1.30 \times 10^{-13} \exp(1040/T)$
$HO_2 + CH_3COO_2 \rightarrow CH_3CO_2H + O_3$	$3.00 \times 10^{-13} \exp(1040/T)$
$HO_2 + CH_3O_2 \rightarrow CH_3O_2H + O_2$	$3.80 \times 10^{-13} \exp(780/T)$
$HO_2 + NO \rightarrow OH + NO_2$	$3.70 \times 10^{-12} \exp(240/T)$
$HO_2 + NO_3 \rightarrow OH + NO_2 + O_2$	3.00×10^{-12}
$HO_2 + O_3 \rightarrow OH + O_2 + O_2$	$3.00 \times 10^{-12} \exp(-600/T)$
$CH_3(U)O_2 + NO \rightarrow CH_3O_2 + NO_2 + CO_2$	$2.00 \times 10^{-14} \operatorname{avm}(-1080/T)$
$CH_{3}O + O_{2} \rightarrow RCHO + RO_{2}$ $CH_{2}O(O)O + CH_{1}O \rightarrow CH_{1}O + CH_{1}O + CO$	$7.20 \times 10^{-12} \exp(-1080/1)$
$CH_3C(0)O_2 + CH_3O_2 \rightarrow CH_3O_2 + CH_3O + CO_2$ $CH_3C(0)O_2 + CH_3O_2 \rightarrow CH_3O_2 + CH_3O + CO_2$	5.50×10^{-12}
$CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow products$	$2.80 \times 10^{-12} \exp(530/T)$
$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2$	$3.30 \times 10^{-14} \exp(365/T)$
$CH_{3}O_{2} + CH_{3}O_{2} \rightarrow CH_{3}OH + HCHO + O_{2}$	$6.60 \times 10^{-14} \exp(365/T)$
$CH_3O_2 + CH_3O_2 \rightarrow CH_3OOCH_3 + O_2$	$1.10 \times 10^{-14} \exp(365/T)$
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	$4.20 \times 10^{-12} \exp(180/T)$
$NO + NO_3 \rightarrow NO_2 + NO_2$	$1.80 \times 10^{-11} \exp(110/T)$
$NO + O_3 \rightarrow NO_2 + O_2$	$1.80 \times 10^{-12} \exp(-1370/T)$
$NO_2 + O_3 \rightarrow NO_3 + O_2$ NO + HCHO + HNO + HO + CO	$1.20 \times 10^{-16} \exp(-2430/T)$
$NO_3 + HCHO \rightarrow HNO_3 + HO_2 + CO$	$3.00 \times 10^{-12} \text{ avp}(-1885/T)$
$OH + CO_4 + O_2 \rightarrow CO_3 + O_2 + O_2$	5.50×10^{-13} $exp(-1885/1)$
$OH + H_2O_2 \rightarrow HO_2 + H_2O_2$	$2.90 \times 10^{-12} \exp(-160/T)$
$OH + HCHO \rightarrow H_2O + HO_2 + CO$	$8.80 \times 10^{-12} \exp(25/T)$
$OH + HO_2 \rightarrow O_2 + H_2O$	$4.80 \times 10^{-11} \exp(250/T)$
$OH + HO_2NO_2 \rightarrow H_2O + NO_2 + OH$	$1.50 \times 10^{-12} \exp(360/T)$
$OH + HONO \rightarrow NO_2 + H_2O$	$1.80 \times 10^{-11} \exp(-390/T)$
$OH + HNO_3 \rightarrow H_2O + NO_3$	1.50×10^{-13}
$OH + CH_3O_2H \rightarrow H_2O + HCHO + OH$	$1.00 \times 10^{-12} \exp(190/T)$ 1.00 × 10 ⁻¹² cm ⁻ (100/T)
$OH + OH_3O_2H \rightarrow H_2O + CH_3O_2$ $OH + NO_1 \rightarrow HO_1 + NO_2$	$1.90 \times 10^{-1} \exp(190/T)$ 2.30 $\times 10^{-11}$
$OH + O_3 \rightarrow HO_2 + O_2$ $OH + O_3 \rightarrow HO_2 + O_3$	$1.90 \times 10^{-12} \exp(-1000/T)$
$OH + PAN \rightarrow HCHO + H_2O + NO_2 + CO_2$	$9.50 \times 10^{-13} \exp(650/T)$
$OH + H_2 + O_2 \rightarrow H_2O + HO_2$	$7.70 \times 10^{-12} \exp(-2100/T)$
$NO_3 + CH_3O_2 \rightarrow CH_3O + NO_2 + O_2$	1.00×10^{-12}
$NO_3 + CH_3C(O)O_2 \rightarrow CH_3O_2 + NO_2 + CO_2$	5.00×10^{-12}
$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2M$	$k_0 = 1.90 \times 10^{-33} \exp(980/T)$
$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$	$F_c = 0.6$
	$k_0 = 1.80 \times 10^{-12} (1/300)^{-12}$
$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	$\kappa_{\infty} = 4.70 \times 10$ F = 0.60
	$k_0 = 5.00 \times 10^{-6} \exp(-10000/T)$
	$k_m = 2.60 \times 10^{15} \exp((-10900/T))$
$CH_3C(O)O_2 + NO_2 + M \rightarrow PAN + M$	$\tilde{F_c} = 0.30$
	$k_0 = 2.70 \times 10^{-28} (T/300)^{-7.1}$
	$k_{\infty} = 1.20 \times 10^{-11} (T/300)^{-0.90}$
$PAN + M \rightarrow CH_3C(O)O_2 + NO_2 + M$	$F_{\rm c} = 0.30$
	$k_0 = 4.90 \times 10^{-5} \exp(-12100/T)$ $k_0 = 4.00 \times 10^{16} \exp(-12600/T)$
$OH + NO + M \rightarrow HONO + M$	$\kappa_{\infty} = 4.00 \times 10^{-1} \exp(-13000/1)$ $F_{-} = \exp(-T/1300)$
	$k_{\rm c} = 7.40 \times 10^{-31} (T/300)^{-2.4}$
	$k_{\rm m} = 3.20 \times 10^{-11}$
$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	$\ddot{F_c} = \exp(-T/250) + \exp(-1050/T)$
	$k_0 = 2.20 \times 10^{-3} (T/300)^{-4.4} \exp(-11080/T)$
	$k_{\infty} = 9.70 \times 10^{14} (T/300)^{0.1} \exp(-11080/T)$
$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	$F_{\rm c} = \exp(-T/250) + \exp(-1050/T)$
	$k_0 = 2.70 \times 10^{-30} (T/300)^{-3.4}$
$OH \pm NO \pm M \rightarrow HNO \pm M$	$\kappa_{\infty} = 2.00 \times 10^{-12} (T/300)^{0.2}$
$OII + IO_2 + IVI - IIIO_3 + IVI$	$r_c = 0.45$ $k_c = 2.60 \times 10^{-30} (T/200)^{-2.9}$
	$k_{\rm o} = 6.00 \times 10^{-11}$
$OH + OH + M \rightarrow H_2O_2 + M$	$F_c = 0.5$
	$k_0 = 8.00 \times 10^{-31} (T/300)^{-0.8}$
	$k_{\infty} = 3.00 \times 10^{-11}$

Table 7 Initial concentrations used in the spring simulations as shown in Fig. 8 $\,$

height/km	0	6
pressure/mb	1000	486
temperature/K	293	266
O ₃ /ppb	80	100
NO ₂ /ppt	500	80
CO/ppb	200	100
PAN/ppt	50	90

icals via reaction (15) is an order of magnitude slower than via reaction (1). With very high NO₃ concentrations (typically greater than 20 ppt), reaction (27) competes with reaction (11) (the reaction of HO₂ with O₃).

These simplified model runs have allowed us to show that reaction (1) is important in the planetary boundary layer, especially in the northern hemisphere. However, because of the nature of the 2-D model, we are unable to determine whether this importance is restricted to continental environments, or whether cycle I can operate efficiently in remote

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Fig. 8 Night-time OH concentrations derived from the box model A; the upper curve shows a simulation for the planetary boundary layer and the lower curve is for 6 km at 30°N in spring (March 31st)

regions. In addition, allowance is not made here for loss processes for NO_3 such as heterogeneous uptake on aerosols. Clearly, adding non-methane hydrocarbons, especially fastreacting ones, will tend to suppress night-time OH concentrations. It is thus instructive to compare both the basic model (model A) and one containing several non-methane hydrocarbons (model B) with field measurements. The non-methane hydrocarbons considered in model B include ethane, propane, *n*-butane, 2-methylpropane (isobutane), ethene, propene, but-1-ene and ethyne and their degradation products.

ROSE July 11 1990

The ROSE experiment is described in detail in the paper of Cantrell et al.³¹ The essential feature of the ROSE experiment is that many species were measured simultaneously. The species include O₃ and NO_r and, most importantly, peroxyl radicals, which were monitored by the chemical amplification technique throughout the measurement period. The first point of note is that the RO₂ concentration is non-zero after dusk. Inspection of Fig. 2 of Cantrell's paper suggests that a reasonable estimate of [RO₂] is 10 ppt, though there are clearly large fluctuations above and below this value. We have run models A and B from dusk on July 11 to dawn July 12. The initial conditions applied are summarised in Table 8. Note that PAN was not measured on July 11 but was measured on other days. Fig. 8 of Cantrell's paper suggests that a PAN concentration of 200 ppt is a reasonable estimate. In Fig. 9 and 10, we present the model results for the OH concentrations and total RO_2 (*i.e.* total alkyl peroxyl and HO_2) for the two models. As anticipated, OH concentrations from model A reach higher levels (ca. 2×10^5 molecule cm⁻³) than in model

 Table 8
 Initial conditions used in the case studies

	ROSE	Schauinsland	MLOPEX
height/km	0	1.15	3.4
pressure/mb	1000	880	660
temperature/K	297	293	281
O ₃ /ppb	35	83	40
NO ₂ /ppt	1400	800	38
CO/ppb	135	240	143
PAN/ppt	200	100	21
C ₂ H ₆ /ppb	2	1.30	
C ₃ H ₈ /ppb	2.18	0.06	
$n-C_4H_{10}$	0.73	0.34	
iso-C ₄ H ₁₀	0.45	0.10	
HCHO/ppb	4.00	1.00	
CH ₃ CHO/ppb	0.64	0.68	
C ₂ H ₄ /ppb	0.31	0.11	
C ₃ H ₆ /ppb	0.15	0.06	



Fig. 9 Night-time OH concentrations derived from simulations of the ROSE experiment. The upper line is for the box model A run and the lower shows the reduction in OH on adding non-methane hydrocarbons (model B).



Fig. 10 Night-time total RO_2 derived for simulations of the ROSE experiment. The lower line is for the box model A run and the upper line shows the marked increase in RO_2 upon addition of non-methane hydrocarbon chemistry (model B).

B $(9 \times 10^4 \text{ molecule cm}^{-3})$. However, the total $[\text{RO}_2]$ is smaller in model A (*ca.* 3 ppt) than in model B (*ca.* 7 ppt). This latter value of $[\text{RO}_2]$ is close to the average value for total $[\text{RO}_2]$ measured during the night. Some chemistry is still missing from the second model, such as that of isoprene, but it is encouraging to see that this model, is nevertheless, in reasonable agreement with observations. One would envisage that isoprene chemistry would increase $[\text{RO}_2]$ further, while suppressing [OH].

Schauinsland August 24 1990

Mihelcic *et al.*³² were the first to measure $[RO_2]$ and $[NO_3]$ simultaneously. These workers used the matrix-isolation EPR (MIEPR) technique. Several species were measured, but unfortunately no measurements are available for PAN at the time of the experiment because of instrument failure (A. Volz-Thomas, personal communication). However, we have run a series of simulations using model B, with initial concentrations of PAN in the range 0–2.5 ppb. There are several interesting features of the Schauinsland measurements that should be addressed. First, given the very high levels of O₃ (*ca.* 800 ppt) and the high temperatures (293 K), $[NO_3]$, which only reached 10 ppt, is very low. Second, for the early part of the night (9 pm to midnight), $[NO_2]$ and $[RO_2]$ appear to be correlated, but after midnight $[NO_3]$ drops and

Table 9 Summary of the model simulations for the Schauinsland measurements

	NO ₂ /ppb			NO ₃ /ppt		HO ₂ /ppt			$\sum \mathbf{RO}_2/\mathbf{ppt}$			
time	a	b	с	а	b	с	а	b	с	a	b	с
21.30	0.82	0.52	0.70	5.0	21.0	19.2	< 5	1.8	2.3	< 5	2.6	10.1
22.30	0.68	0.46	0.65	5.2	17.8	18.4	10	1.7	2.2	5	2.7	11.0
23.30	0.82	0.36	0.62	8.0	15.0	17.5	< 5	1.6	2.1	11	2.7	11.0
00.30	0.71	0.31	0.60	5.2	12.6	16.6	< 5	1.5	2.1	5	2.9	11.0
01.45	0.78	0.26	0.57	7.7	10.1	15.9	< 5	1.4	2.0	< 5	3.0	11.0
02.45	0.66	0.22	0.55	< 3	9.0	15.3	5	1.3	1.9	33	3.1	11.0
03.45	0.65	0.18	0.53	9.5	7.7	14.7	<5	1.2	1.9	<5	3.1	11.0

Column a for each species are the actual measurements by Mihelcic *et al.*³² Column b is the model run with heterogeneous removal of NO₃ but no initial PAN and column c is the model run with an initial concentration of 2.5 ppb.

[RO₂] rises to very high levels (33 ppt). Third, [NO₂] remains fairly constant throughout the night, tailing off only slowly.

Mihelcic *et al.* suggest that heterogeneous loss of NO_3 on aerosols is mainly responsible for the low $[NO_3]$ encountered. Table 9 summarises the results of the selected model runs; although many simulations have been made, we show results from two extreme cases. The first simulation (column b in Table 9) has no initial [PAN], but does include heterogeneous loss of NO₃ as suggested by Mihelcic *et al.*³² However, inspection of the results from the simulation shows that, even with this loss included, $[NO_3]$ is still some 10–15 ppt too high during the first part of the night.

Mihelcic *et al.*³² suggest that the sudden drop in $[NO_3]$ and increase in $[RO_2]$ after midnight could be due to a flux of highly reactive species such as terpenes, which react rapidly with NO₃ liberating RO₂ radicals. The correlation between $[NO_3]$ and $[RO_2]$ before midnight might be thought to be in keeping with cycle I, where an increase in $[NO_3]$ would result in increased RO₂ production. However, it must be recognised that cycle I does not alone control RO₂ production under the conditions encountered by Mihelcic *et al.*

The slow fall-off of $[NO_2]$ was the most important feature of the measurements. The model simulation (column b in Table 9) shows that $[NO_2]$ drops off rapidly and in turn affects $[NO_3]$. There are a number of reasons why $[NO_2]$ might decline slowly. The first is advection of air rich in NO₂ reaching the measurement site. However, one can add an advection term to the model (*i.e.* a positive flux of NO₂) to sustain NO₂, but $[NO_3]$ then rises to some 20 ppt above measured values even with the highest heterogeneous loss rate suggested by Mihelcic *et al.* Another possibility is that some emission of NO rapidly converts NO₃ to NO₂ via the reaction.

$$NO + NO_3 \rightarrow 2NO_2$$
 (13)

However, this reaction alone cannot sustain the required [NO₂], even with a large NO flux. The third and strongest candidate is PAN decomposition. Thermal decomposition of PAN provides a source of NO_2 and, unlike a simple advection of NO₂, the product $CH_3C(O)O_2$ radicals also suppress [NO₃]. Hence, in the second simulation shown in Table 9 (column c) where the initial [PAN] is 2.5 ppb, [NO₂] are in much better agreement with observations, and [NO₃] are certainly no worse. It is possible to obtain quite close agreement between model and measurements for NO₂, NO₃ and RO₂ for the early part of the night by including PAN and some positive flux of either NO_2 or NO or both. One suspects that all three processes are contributing to [NO₂] and, without further measurements, it is difficult to be more precise. However, modelling strongly suggests that cycle I may explain why [NO₃] was so low and why [NO₂] remains fairly constant. In addition, the observation that $[RO_2]$ and $[NO_3]$ are correlated, at least for the early part of the night, is perfectly consistent with the operation of cycle I.

MLOPEX May 1-June 4 1988

During the MLOPEX campaign, the concentrations of many chemical species were measured, but not those of NO3 or RO₂! However, this site is a remote one, at 600 mbar (approximate altitude of 3.5 km), where levels of NO_x are low, and it is therefore a good indicator as to how much cycle I may contribute to OH production in remote regions. We have run model A using the initial concentrations given by Ridley and Robinson,³³ which are summarised in Table 8. The modelled OH-concentration profile is shown in Fig. 11. It is clear from Fig. 11 that OH levels remain fairly constant at *ca*. 1×10^4 molecule cm⁻³. Tanner and Eisele⁴⁰ have published measurements of OH during the MLOPEX II campaign, conducted in 1992. They use an ion-assisted OH measurement technique which allows measurements of OH concentrations of the order of 10^4 molecule cm⁻³. These results predate the main body of measurements, so that it is impossible to carry out a comparative model run. However, Tanner and Eisele measure OH concentrations into the night. In one example (August 1-2 1992, Fig. 5 in the paper), the OH concentration is virtually constant at 3×10^4 molecule cm⁻³ for the early part of the night, dipping as O₃ increases at midnight. In a second example (May 15-16 1992, Fig. 6 in the paper), OH levels are even higher at night, but drop steadily towards the detection limit. Tanner and Eisele could not explain these measurements with any certainty, but we believe that cycle I can go some way to providing a satisfactory solution.

Summary of model results and thoughts on NO₃ chemistry

The production of OH at night via NO_3 chemistry has been proposed previously by Platt *et al.*⁴¹ These workers investigated the impact of a number of reactions of NO_3 with hydrocarbons and concluded that biogenic species such as isoprene



Fig. 11 Night-time OH concentrations derived from simulations of the MLOPEX campaign

and dimethyl sulfide (DMS) from the sea gave the highest production rates for RO_2 and, by implication, for OH. This suggestion rather restricts the role of NO_3 to forested and coastal areas. Platt *et al.*⁴¹ also highlighted the rapid reaction of NO_3 with alkenes, but noted that the products of the reaction were not well defined. It is interesting to look at an example, the reaction of NO_3 with but-2-ene. The initial reaction sequence will be the addition of NO_3 to the alkene, followed by the addition of oxygen to form a peroxyl radical

$$CH_{3}CH = CHCH_{3} + NO_{3} + M \rightarrow$$

$$CH_3CH(ONO_2)CHCH_3 + M$$
 (34)

 $CH_3CH(ONO_2)CHCH_3 + O_2 + M \rightarrow$

$$CH_3CH(ONO_2)CH(O_2)CH_3 + M$$
 (35)

Hjorth *et al.*⁴² have made an indirect measurement of the rate constant for the reaction of the 2,3-dimethyl-2-nitroxy-3-peroxybutyl radical with NO₃, of *ca.* 5×10^{-12} molecule cm⁻³ s⁻¹. Since the peroxyl radical formed in reaction (35) is very similar in structure, it is not unwarranted to assume a similar rate constant for reaction with NO₃. Hjorth *et al.* were also able to infer that the products of the reaction of the peroxyl radical with NO₃ were the alkoxyl radical and NO₂, analogous to those of the reactions of other RO₂ with NO₃.^{11,12,28} Hence, one might expect that the peroxyl radical in our example will react with NO₃

 $CH_3CH(ONO_2)CH(O_2)CH_3 + NO_3 \rightarrow$

$$CH_3CH(ONO_2)CH(O)CH_3 + NO_2 + O_2$$
 (36)

There are two possibilities for further reaction of the alkoxyl radical: reaction with O_2 or thermal decomposition

$$CH_{3}CH(ONO_{2})CH(O)CH_{3} + O_{2} \rightarrow$$

$$CH_{3}CH(ONO_{2})C(O)CH_{3} + HO_{2} \quad (37a)$$

$$CH_{3}CH(ONO_{2})CH(O)CH_{3} \rightarrow 2CH_{3}CHO + NO_{2} \quad (37b)$$

Channel (37*a*) produces HO₂, but NO_x is tied up as a difunctional organic nitrate; channel (37*b*) releases NO₂ to allow the reformation of NO₃, but no RO₂ radicals are generated. Evidence from the work of Barnes *et al.*⁴³ suggests that channel (37*b*) probably dominates. Thus, in many cases, reaction of NO₃ with alkenes may not lead to significant OH production at night.

In contrast, cycle I releases NO₂ (to rebuild NO₃) and produces RO₂. Cycle I, as we have shown, can occur throughout the year, and comparison with field studies has added weight to the assertion that reaction (1) is an important night-time reaction in the troposphere. Further modelling studies are warranted, and plans are under way to investigate the role played by reaction (1) using a 3-D tropospheric model currently being developed in Cambridge. Although cycle I produces OH concentrations at night that are between 15–1% of the day-time values, we anticipate that the OH formed will have a significant effect on model predictions. Note that the reaction of NO₃ with aldehydes can be an important source of acyl peroxyl radicals RC(O)O₂ at night, and will therefore also contribute to OH production at night.

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