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Rates of Reaction between the Nitrate Radical and some Aliphatic Esters

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Rate coefficients for the reaction of NO_3 with methyl formate, methyl acetate, methyl propionate, methyl butyrate, ethyl formate, ethyl acetate, ethyl propionate, propyl formate, propyl acetate and *n*-hexane have been determined at 296 ± 2 K. The rate coefficients, which should strictly be interpreted as upper limits, were found to be 0.36 ± 0.08, 0.7 ± 0.2, 3.3 ± 0.8, 4.8 ± 0.5, 1.7 ± 0.3, 1.3 ± 0.3, 3.3 ± 0.4, 5.4 ± 0.9, 5 ± 2 and 14.7 ± 3.0, respectively (in units of 10^{-17} cm^3 $molecule^{-1}$ s^{-1}). The activation energy for the reaction between ethyl acetate and NO_3 was determined to be 23 ± 8 kJ mol^{-1} between 273 and 373 K. The rate coefficients for aliphatic esters may be predicted from available group reactivity factors for alkanes provided that formate carbonyl hydrogen atoms are treated as primary hydrogen atoms.

There is little doubt about the key role of the nitrate radical in night-time tropospheric chemistry. Much work has been performed to investigate the nature of the nitrate radical itself and its reaction with many groups of organic and inorganic compounds.[1,2] Unsaturated hydrocarbons react readily with the nitrate radical through double-bond addition and this reaction is an important night-time sink for such compounds. Saturated organic substances and their derivatives have received less attention because of their low reactivity. In this case, the nitrate radical attack proceeds by hydrogen-atom abstraction. This is a slow process that cannot often contribute significantly to the nocturnal destruction of such hydrocarbons. Saturated hydrocarbons, including compounds containing various functional groups may, however, constitute a major night-time source of nitric acid.[3,4] In this context it is important to know reaction rates and their temperature dependences for the compounds under consideration, *e.g.* in order to assess the contribution to acid deposition. When direct information is lacking, rate coefficients may be estimated from available correlations. For alkanes, the group reactivity approach of Bagley *et al.*[3] is expected to give fairly accurate values. Organic compounds, reacting by hydrogen abstraction, exhibit an approximately linear relation between the logarithm of the NO_3 rate coefficient and the corresponding logarithm of the OH rate coefficient as well as with the first ionisation potential of the compound.[1] For oxygenates in general and esters in particular, a comprehensive test of the applicability of the predictive tools has been prevented by the lack of experimental data.

In this paper, rate coefficients are reported for reaction of the NO_3 radical with methyl formate, methyl acetate, methyl propionate, methyl butyrate, ethyl formate, ethyl acetate, ethyl propionate, propyl formate, propyl acetate and *n*-hexane at 296 K. The temperature dependence and rate in the presence of molecular oxygen for the reaction between NO_3 radicals and ethyl acetate is also presented.

Experimental

The conventional fast flow-discharge technique was used. This particular experimental set-up, shown in Fig. 1, has not been described before and some details are given below.

The apparatus is made from borosilicate glass except for minor components. The 100 cm long flow tube has an inner diameter of 30.0 mm and its temperature may be controlled between 258 and 383 ± 1.5 K. Nitrate radicals are generated by reaction of fluorine atoms from a microwave discharge with nitric acid according to the reaction

$$HNO_3 + F \rightarrow NO_3 + HF \qquad (1)$$

Nitric acid vapour was obtained from a bubbler containing anhydrous nitric acid at 273 K and using helium as carrier. The anhydrous nitric acid was prepared by low-pressure distillation of a 2 : 1 mixture of concentrated sulfuric and nitric

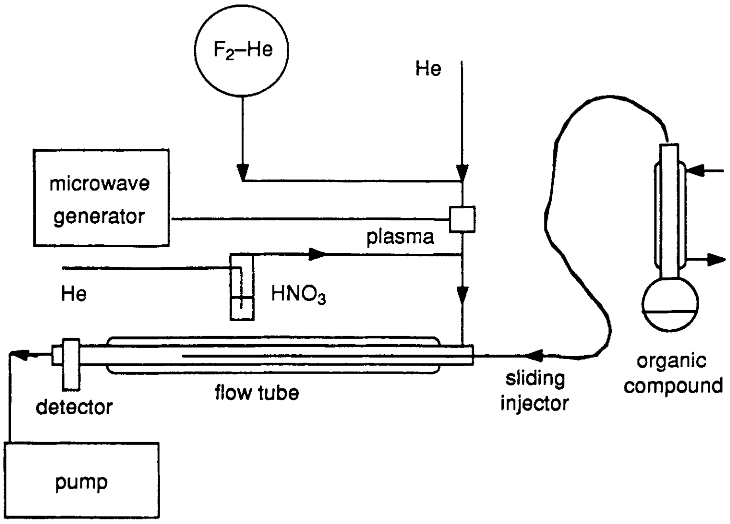

Fig. 1 Schematic picture of the experimental set-up

Table 1 Experimental conditions and upper-limit rate constants for the reaction of NO_3 with *n*-hexane and aliphatic esters at 296 ± 2 K

compound	p(total)/mbar	[org]/10^{16} molecule cm^{-3}	no. of expts.	v/cm s^{-1}	$k/10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}
n-hexane	11.1–13.9	0.18–1.57	6	223–272	(28 ± 3) (14 ± 2) see text
methyl formate M	26.1–33.2	3.99–10.1	4	66– 83	0.3 ± 0.1
methyl formate F	23.3–32.1	1.75–8.85	6	86–107	0.41 ± 0.06
methyl acetate M	22.5–28.0	1.28–4.89	6	90–107	0.7 ± 0.2
methyl acetate F	6.5–21.5	0.14–7.01	11	93–302	7.2 ± 0.4
methyl propionate M	22.5–26.9	1.09–2.79	5	100–123	3.3 ± 0.8
methyl butyrate M	11.9–12.8	0.28–0.93	5	130–174	4.8 ± 0.5
ethyl formate M	21.3–27.8	0.52–4.56	13	89–109	1.7 ± 0.3
ethyl formate F	20.2–30.5	0.50–7.20	6	86–118	2.2 ± 0.4
ethyl acetate M	22.4–30.8	0.58–5.24	12	80–103	1.4 ± 0.3
ethyl acetate F	22.2–28.3	0.47–3.52	6	95–118	1.1 ± 0.2
ethyl propionate M	13.3–15.4	0.28–1.10	10	70–123	3.3 ± 0.4
ethyl propionate F	11.5–13.8	0.18–1.28	6	118–150	3.8 ± 0.1
propyl formate M	20.8–23.5	0.32–1.88	6	99–113	5.4 ± 0.9
propyl acetate M	5.8–13.5	0.26–1.02	6	149–235	5 ± 2

$[NO_3]_0 \leqslant 1.5 \times 10^{13}$ molecule cm^{-3}. M = Compound supplied by Merck, Darmstadt, Germany, F = Compound supplied by Fluka, Buchs, Switzerland. p is the range of experimental pressures, [org] is the range of organic compound concentration, v is the range of linear flow velocities in the flow tube and k is the mean of the observed rate coefficients for the compound. Errors are 95% confidence limits.

acid (PA quality). The anhydrous acid was found to contain small amounts of dissolved NO_2 immediately after distillation. The NO_2 could be reduced to a level that did not interfere with the experiments by purging with helium for 30 min before use. Helium of a stated purity of 99.9995%, passed through a 4 Å molecular sieve trap kept at 77 K, was used as bath gas in the experiments. The flow in the system is induced by a two-stage rotary vane pump capable of maintaining a linear flow velocity of just over 1100 cm s^{-1} in the flow tube at pressures between 1 and 100 mbar. The flow in the system is set up and controlled by rotameters and needle valves but the actual flow rate through the tube during experiments is measured by a precision wet gas meter, placed after the pump and connected to a timing device. This arrangement also permits a simple test for leaks in the system. The flow tube pressure is measured by capacitance gauges (Barocel 600-1000T, 600-10T). The flow may be throttled by a tap downstream of the detector, to reduce the linear flow velocity and/or increase the pressure in the flow tube.

The set-up is equipped to detect nitrate radicals by optical absorption at 662 nm. It has a conventional double beam arrangement and a cuvette with an optical path of 45.0 mm, coupled to external White optics. The cuvette has a rectangular cross-section of the same area as the flow tube. In this investigation 16 passes were used giving a total pathlength of 72 cm. Light from a 12 V, 100 W tungsten halogen lamp is collimated and focused in the plane of the White nesting mirror, repeatedly passed through the cuvette and thereafter focused in the rotation plane of a chopper and further on to the entrance slit of a Beckman DU-2 prism monochromator of 0.5 m focal length. The monochromator was operated at a slit width that gave a 0.45 nm half-intensity bandwidth. The light leaving the monochromator is passed to a photomultiplier tube and pre-amplifier unit. The reference beam from the lamp is taken directly, *via* an iris diaphragm, and focused in the chopper plane. A beam splitter is used to bring the two beams onto a common axis before entering the monochromator and the arrangement is such that the photomultiplier measures either the reference or the analytical beam. The signal from the photomultiplier pre-amplifier is passed on to a lock-in amplifier together with a reference signal from the chopper. With this arrangement, a fractional change in light intensity of 5×10^{-4} can be measured with an integration time of 30 s.

Because of the slow reactions under investigation, several steps had to be taken in order to have measurable changes in NO_3 concentration. By throttling, the flow rate was decreased to between 0.5 and 2 m s^{-1} and the pressure was kept between 10 and 30 mbar to increase the contact time and the concentration of organic compound, respectively. The flow tube is preceded by a vacuum line with bulbs for preparation and supply of reactant mixtures for the flow tube. In this case, however, a slightly different approach was used to obtain high concentrations of organic compound. The pure compound was allowed to boil at reduced pressure in a conventional distillation set-up and the vapour was passed on to the flow tube without adding helium. The pressure in the delivery system was controlled by the condenser temperature which was kept slightly below room temperature by circulating liquid from a thermostat. The organic compound was delivered to the flow tube through a movable injector *via* a rotameter and needle valve. The contact time between nitrate radicals and the organic compound can be varied by sliding the injector along the axis of the flow tube. One practical limit for this delivery system is set by the vapour pressure of the organic compound. When its pressure at just below room temperature is less than twice the pressure in the flow tube then the flow through the needle valve becomes sub-critical and the flow depends not only on the constant pressure upstream of the valve but also on the downstream pressure. The flow rate is measured by directing the vapour from after the needle valve to a calibrated volume connected to a mercury differential manometer. If the flow through the needle valve is sub-critical then the changing pressure in the calibrated volume during a flow measurement affects the flow and it becomes difficult to determine the flow rate accurately. When the organic compound was not added to the flow tube through the injector then the flow was bypassed in order to maintain steady state conditions in the distillation set-up.

The objective of the experiments was to determine the rate of reaction (2) as defined by eqn. (I).

$$\text{ester} + NO_3 \rightarrow \text{products} \qquad (2)$$

$$d[NO_3]/dt = -k[NO_3][\text{ester}] \qquad (I)$$

The change in signal without and with NO_3 addition, Δ_{NO_3}, and the corresponding change in signal when both NO_3 and the organic substance was added, Δ_{ester}, as a function of injector position, *i.e.* reaction time, was measured. All experiments were performed under pseudo-first-order conditions. For pseudo-first-order conditions and small absorbances, it can be shown that eqn. (II) holds.

$$\ln(\Delta_{NO_3}/\Delta_{ester}) = k't \qquad \text{(II)}$$

The first-order rate coefficients $k' = k[\text{ester}]$ were obtained from least-squares straight lines [eqn. (II)] and the desired rate coefficients k from similar fits of k' *vs.* [ester]. The influence of flow dynamics and diffusion on the observed rate coefficients was estimated by calculating correction factors according to Keyser.[5] In no case did the correction factor change the rate coefficient by more than 1% and no corrections were applied to the rate coefficients. The pressure drop over the flow tube was insignificant because of the low linear flow rates employed.

The chemicals used in the experiments are listed in Table 1 together with some experimental details. All compounds had a stated purity of better than 98% and most were claimed to be better than 99%. Gas-chromatographic analysis with a detection limit of around 0.1% was performed on a Perkin-Elmer 990 GC analyser using N_2 as carrier gas. The instrument was equipped with a 6 m long, 2 mm i.d. packed column with a medium-polarity stationary phase and a FID detector. The analysis showed no trace of impurities in the esters except for methyl formate (M) (3% formic acid), ethyl formate (F) (0.8% ethanol, 0.3% ethyl acetate) and propyl formate (M) (3% propan-1-ol). (M = Merck, Darmstadt, Germany, F = Fluka, Buchs, Switzerland). The distillation which is used to deliver the organic compounds in this investigation serves to purify the substances. The first fraction was always discarded as was the last half of the liquid charged in the distillation flask.

Results and Discussion

Effect of Impurities

The possible presence of reactive impurities presents a limitation to the determination of rate coefficients for slowly reacting substances. The effect of such impurities could be to increase the observed rate of NO_3 disappearance. To be certain of a reasonably good determination of the main constituent rate coefficient then less than 10% of the loss of NO_3 should be caused by the impurity. If only one reactive impurity is present, if its maximum concentration is at the detection limit of the GC analysis (0.1%) and if this concentration is directly reflected in the gas phase then the fraction of main component is 0.999 and that of impurity is 0.001 of total organic added. The required relation between main and impurity rate coefficient is expressed by eqn. (III)

$$0.999k_m > 10 \times 0.001 \times k_i \qquad \text{(III)}$$

Indexes m and i denote main constituent and impurity rate coefficient, respectively. With k_m values for the reaction between nitrate radicals and saturated esters of the order of 1×10^{-17} cm^3 molecule^{-1} s^{-1} it follows that $k_i < 10^{-15}$ cm^3 molecule^{-1} s^{-1} in order not to influence the determination. With decreasing concentration of the impurity or a greater main constituent rate coefficient, correspondingly higher impurity reactivities may be tolerated. Alkenes and di-alkenes with about the same molecular weight and thus a boiling point similar to those of the main constituents investigated here would be expected to have k values in the range 10^{-13}–10^{-11} cm^3 molecule^{-1} s^{-1}.[1] Thus, it is evident that impurities at levels far below the detection limit of most analytical techniques have the potential to affect the experiments severely. To obtain circumstantial evidence that the value determined for a particular compound is not influenced by impurities, experiments were often made on the same substance obtained from different sources. To be fully accepted, k values identical within the limits of error should be determined from the different experiments. If the values differ, as in the case of methyl acetate (*cf.* Table 1), the lowest one was taken as an estimate of the rate coefficient, as were values that were determined using only one preparation. In the case of propyl acetate, three preparations were tried. Two of these gave high and irreproducible values, indicating the presence of a reactive impurity. The third preparation gave rate coefficients which changed with compound storage time. The value presented in Table 1 is the lowest of all determinations and was obtained with substance from a fresh bottle. Because of the possible presence of impurities in the investigated compounds, the coefficients given in Table 1 are, in principle, upper-limit estimates. In practice, however, there are indications that the experimentally determined numbers reflect the desired quantities, as will be discussed below.

Test of the Experimental Set-up with *n*-Hexane

The rate coefficient for the reaction of nitrate radicals with *n*-hexane was determined as a test of the suitability of the present apparatus for studying slow reactions. Table 1 presents some experimental information and Fig. 2 shows the second-order plot. This coefficient has been determined by Atkinson by relative rate experiments.[2] The value may also be calculated from the group reactivity factors determined by Bagley *et al.*[3] in a study of alkane reactions with NO_3. The observed value is $(2.8 \pm 0.3) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. The rate coefficient predicted by the group reactivity approach[3] is $(1.0 \pm 0.6) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. Bagley *et al.*[3] presented arguments for two NO_3 radicals being consumed for each alkane molecule according to reactions (3) and (4).

$$RH + NO_3 \rightarrow R + HNO_3 \qquad (3)$$

$$R + NO_3 \rightarrow \text{products} \qquad (4)$$

The first step (3), alkyl radical formation, is followed by the rapid reaction (4) to form stable products. The fact that two NO_3 radicals disappeared for every reacted alkane molecule was taken into account when the correlation was developed.[3] Similar secondary reactions must take place also in our *n*-hexane experiments and when our measured value is divided by a factor of two, a good agreement with the calculated value is found. The relative rate coefficient[2] is

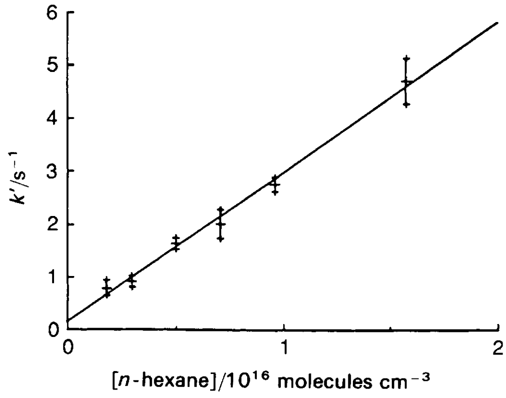

Fig. 2 Plot of pseudo-first-order rate coefficients *vs.* concentration of *n*-hexane

$(1.05 \pm 0.26) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} and was determined relative to the value of *n*-heptane which, in turn, originates from another relative rate measurement. In relative rate investigations the concentration of organic compound rather than NO_3 concentration is followed which makes such experiments insensitive to the stoichiometric factors discussed above. The agreement between the relative rate determination and our corrected value is fair. This appears to confirm the assumption of a 2 : 1 stoichiometry for NO_3 and *n*-hexane also in our case. The result obtained for *n*-hexane indicates that the present apparatus and technique may be used for the study of slow reactions.

Possible Reactions Causing too Slow a Rate to be Observed

The hydrogen atom at the carbonyl carbon in formates is formally similar to an aldehyde hydrogen if only its next-neighbour atom is taken into account. Aldehydes, however, are considerably more reactive than any of the formates investigated here. To ensure that the formate hydrogen atom was not behaving like an aldehyde hydrogen, the possibility of measuring experimental rates that are too low was considered. While there are a number of possible reasons for observing erroneously high rates in a kinetic experiment, there are few causes for measuring rates that are too low. One such cause would be if a fraction of the nitrate radicals consumed in the first reaction step is regenerated from one of the subsequent organic intermediates. No such reaction sequence has been reported in the literature. Another possibility which may lead to rates that are too low is formation and subsequent decay of N_2O_5 according to equilibrium (5).

$$NO_2 + NO_3 \rightleftharpoons N_2O_5 \qquad (5)$$

If the NO_2 concentration in the flow tube is high enough, *e.g.* through decomposition of nitric acid in the bubbler, then N_2O_5 would form in significant concentrations. This would lead to a rapid initial loss of NO_3. If reactions (5) came close to equilibrium before the organic compound was added then loss of NO_3 through reaction with the organic compound would induce decomposition of N_2O_5 and thus partial replenishment of NO_3. Model calculations using the FACSIMILE[6] computer program, including reactions (2) and (5) and with representative pressures, rates and concentrations show that for an initial $[NO_2] : [NO_3]$ ratio of 1, nearly all NO_3 would be lost on the timescale of our experiments, making measurements impractical. For decreasing ratios, the influence of reaction (5) would decrease. At a ratio of 0.5, the error in the observed rate coefficient, as compared to the case without any NO_2 present, would be 5%. Some results from the calculations are presented in Table 2. The calculations also show that the combined effect of reactions (5) is always a net loss of NO_3 under our experimental conditions. The conclusion is that the low rates observed are not caused by equilibrium (5). Another indication that NO_2 in the nitric acid is not influencing the experiments is the insensitivity of the NO_3 concentration to changes in excess HNO_3 concentration. If the HNO_3 had carried a fixed and significant fraction of NO_2 along, then the NO_3 would have changed accordingly.

Reaction with Esters

The rate coefficients presented in this work are the first determinations for reactions between NO_3 radicals and esters. Some experimental information is summarised in Table 1 and Fig. 3 shows an example of experimental data. The observed rate coefficients together with values calculated from available correlations[1,3] are given in Table 3. The experimentally obtained rate coefficients are lower than those calculated with the NO_3/OH correlation represented by equation (IV)[1] as can be seen in Fig. 4. The ester k_{OH} values were taken from ref. (7).

$$\log(k_{NO_3}) = (-5.1 \pm 0.7) + (0.95 \pm 0.06)\log k_{OH} \qquad (IV)$$

The difference is in most cases not significant but the systematic bias indicate that the NO_3/OH correlation[1] tend to overestimate rate coefficients for esters. If an experimentally determined rate coefficient was severely influenced by the presence of reactive impurities, it would be expected to fall above the line describing the correlation. This is not the case for any of the determinations and this is taken as an indication that the experimental values are fair measurements of

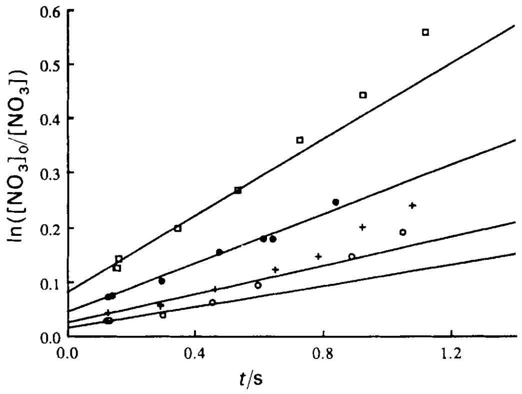

Fig. 3 Example of experimental data. Pseudo-first-order plots for different concentrations of methyl formate. ○, 2.34×10^{16}; +, 3.08×10^{16}; ●, 5.05×10^{16}; □, 8.85×10^{16} (in molecules cm^{-3})

Table 2 Computer simulation of reactions in the flow tube with respect to the possible presence of NO_2

$[NO_2]^a/10^{13}$	$[NO_3]^a/10^{13}$	$[org]^a/10^{16}$	p/mbar	T/K	$k_5{}^b/10^{-13}$	$k_{-5}{}^b/10^{-2}$	$k_2{}^b/10^{-17}$	$k_{2calc}{}^b/10^{-17}$	comment
2	2	1	25	296	3.77	1.08	1.00	1.26	accel.
2	2	1	100	296	7.14	2.00	1.00	1.28	accel.
2	2	1	2	296	0.52	0.19	1.00	1.06	
2	2	10	25	296	3.77	1.08	1.00	1.25	accel.
0.5	2	1	25	296	3.77	1.08	1.00	1.02	
1	2	1	25	296	3.77	1.08	1.00	1.05	
10	2	1	25	296	3.77	1.08	1.00	1.28	accel.
2	2	1	25	296	3.77	1.08	10.00	12.60	accel.
2	2	1	25	296	3.77	1.08	100.00	561.00	ret.

Rate coefficients for reaction (5) were taken from ref. 1, k_2 is the actual rate coefficient for the NO_3–ester reaction put into the calculation and k_{2calc} is the rate coefficient that would be obtained from an NO_3 first-order plot under the given conditions. The comments 'accel.' and 'ret.' indicate that the first-order plots show a deviation from linearity and have an accelerating or retarding tendency at long reaction times, respectively. [a] Units: molecule cm^{-3}. [b] Units: cm^3 molecule^{-1} s^{-1}.

Table 3 Measured and calculated rate constants for the gas-phase reaction of NO_3 with aliphatic esters and *n*-hexane at 296 ± 2 K

reactant	OH/NO_3 k	E_i k	group reactivity k_{min}	k	k_{max}	k_{exp}
n-hexane	16.30	34.7	4.85	8.79	15.53	14.7 ± 2.0 see text
methyl formate	0.74	28.1	0.01	0.13	0.74	0.36 ± 0.08
methyl acetate	1.14	112	0.02	0.20	1.12	0.7 ± 0.2
methyl propionate	3.25	100	1.22	2.35	4.72	3.3 ± 0.8
methyl butyrate	9.10	141	2.43	4.50	8.32	4.8 ± 0.5
ethyl formate	3.23	49.0	1.22	2.28	4.35	1.7 ± 0.3
ethyl acetate	4.68	251	1.23	2.35	4.72	1.3 ± 0.3
ethyl propionate	6.52	[a]	2.43	4.50	8.32	3.3 ± 0.4
propyl formate	7.21	63.1	2.43	4.43	7.95	5.4 ± 0.9
propyl acetate	10.26	240	2.43	4.50	8.32	5 ± 2

The OH/NO_3 values were calculated from the correlation between $\log(k_{OH})$ and $\log(k_{NO_3})$ and the E_i values originate from the correlation between ionization potential and $\log(k_{NO_3})$, both given by ref. 1. The k_{OH} values were taken from ref. 7, while the ionisation potentials for esters were taken from ref. 9. The values listed under 'group reactivity' were calculated using the group reactivity factors by Bagley *et al.*[3] and k_{min} and k_{max} enclose the 95% confidence interval. k_{exp} are observed rate coefficients from this work. [a] The value of E_v is not available. All rate constants are in units of 10^{-17} cm³ molecule⁻¹ s⁻¹.

the desired rate coefficients. The NO_3/*n*-hexane rate coefficient is well described by eqn. (IV) when combined with the k_{OH} value of Atkinson *et al.*[8]

Calculation of k_{ester} values according to eqn. (V),[1] using first ionisation potential (E_v) values from Benoit and Harrison[9] give values which are between one and two orders of magnitude too high, compared with the experimental data.

$$\log(k_{NO_3}) = (-4.7 \pm 1.1) - (1.0 \pm 0.1)E_v \qquad \text{(V)}$$

This discrepancy is possibly explained by the presence of oxygen in the compounds investigated. The ionisation is expected to take place at an oxygen lone-pair orbital while the abstraction of a hydrogen atom takes place at some distance from such a site. Thus, in the case of esters, the ionisation potential has little to tell about hydrogen-atom reactivity.

If hydrogen-atom abstraction is the main reaction path for esters then rate coefficients would be expected to show a dependence on the number and type of hydrogen atoms in the compounds under study. This suggests that an estimate of nitrate radical reactivities with esters could be made by applying the group reactivity factors for alkanes described by Bagley *et al.*[3] The values in the column labelled 'group reactivity' of Table 3 were calculated by treating the esters as hypothetical alkanes with the same type and number of CH bonds as the ester under consideration. It is seen that the group reactivity approach, in all cases, predicts the experimental value to within the 95% confidence limit. The hydrogen atom on the carboxyl carbon atom in formates was included as a primary hydrogen in the calculations. This atom shows a formal similarity to an aldehyde hydrogen. However, an aldehyde hydrogen atom would be expected to, by itself, give rate coefficients between 5×10^{-15} and 5×10^{-16} cm³ molecule⁻¹ s⁻¹.[1] This is much larger than any of the observed rate coefficients for formates in this investigation. Thus, the carbonyl hydrogen atom in formates has a considerably lower reactivity than an aldehyde hydrogen on an ordinary carboxyl group. It is also suggested that the alkoxy residue influences the reactivity of the formate hydrogen. For the methyl esters there is a significant increase in reactivity with increasing acid residue chain length. This is not the case for ethyl and propyl esters when going from formates to acetates and this may be interpreted as an activation of the formate hydrogen by an increased alcohol residue chain length.

The reaction of NO_3 with ethyl acetate was studied at temperatures between 273 and 373 K in order to verify the assumed mechanism. Fig. 5 shows the resulting Arrhenius plot and Table 4 gives the experimental conditions together with the individual rate coefficients. The regression gave an activation energy of 23 ± 8 kJ mol⁻¹. The plot is linear within the error limits over the investigated temperature range, except for the point at the highest temperature. The activation energy determined is close to that for reaction of

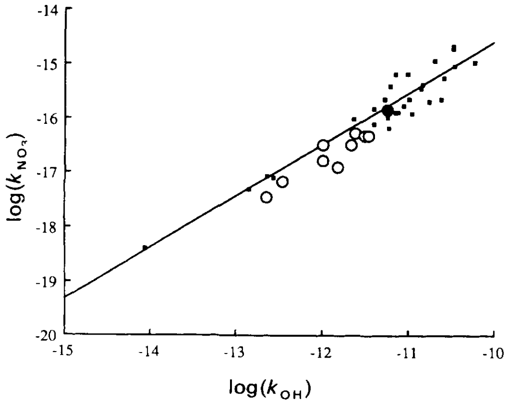

Fig. 4 Logarithm of the rate constant for the reaction of NO_3 *vs.* logarithm of the rate constant for the reaction of OH with the same compound. ■, Data pairs constituting the basis for the abstraction reaction correlation;[1] (——) best fit to these points; ○, data pairs for esters from this work. The ester k_{OH} values were taken from ref. 7; ●, data for *n*-hexane from this work and using k_{OH} from ref. 8

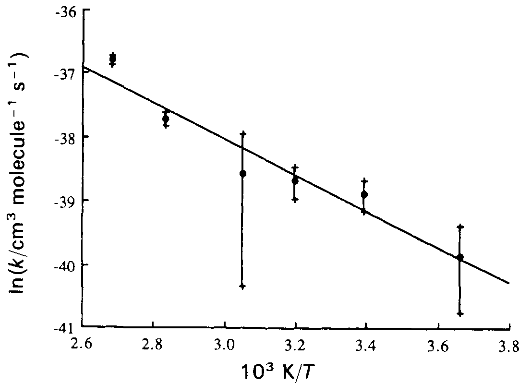

Fig. 5 Arrhenius plot for the reaction of NO_3 radical with ethyl acetate; $\ln k = -29.645 - 2795.4/T$

Table 4 Experimental conditions and rate coefficients for the gas-phase reaction of NO_3 with ethyl acetate at different temperatures

T/K	p(total)/mbar	[EtAc]/10^{16} molecule cm^{-3}	no. of expts.	v/cm s^{-1}	$k/10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}
273	21.8–29.5	0.60–5.08	6	90–118	(0.5 ± 0.3)
295	22.2–30.8	0.47–5.24	12	80–118	(1.3 ± 0.3)
313	21.9–29.4	0.51–4.24	5	105–134	(1.6 ± 0.4)
328	22.3–29.3	0.56–3.73	5	107–134	(1.8 ± 1.5)
353	22.4–29.5	0.48–3.52	5	115–146	(4.2 ± 0.4)
373	21.8–28.2	0.29–2.61	6	127–150	(10.5 ± 0.7)

$[NO_3] \leqslant 1.5 \times 10^{13}$ molecule cm^{-3}.

secondary CH bonds with NO_3 radicals in alkanes[3] of 27 ± 1 kJ mol^{-1}, which supports the hypothesis that the reaction proceeds mainly by secondary hydrogen atom abstraction. The deviating point may be an indication that also primary hydrogen atoms start to contribute to the observed rate coefficient at elevated temperature.

Secondary Reactions

The possiblity of secondary reactions between NO_3 radicals and organic intermediates which could affect the determinations has to be considered. For many of the compounds, systematically curved first-order plots were obtained, an example of which is shown in Fig. 3. The plots show a loss of NO_3 radicals at long reaction times which is greater than expected from first-order kinetics. This indicates that new reaction channels open on the timescale of the experiment. One possibility for such reactions is when unknown products or intermediaries of suitable reactivity has accumulated enough to affect the NO_3 concentration. The intermediaries should be of alkyl radical character, but their actual chemical behaviour is not known at present. In some cases, the rate of NO_3 loss was approximately doubled at long reaction times compared to the initial rate. For such first-order plots, only the initial part of the curves were used for the rate coefficient determination.

Some experiments were made where the reaction of NO_3 with ethyl acetate was studied in the presence of molecular oxygen and the results are given in Table 5. As can be seen, no significant change in the observed rate coefficient results from the addition of oxygen. This is in contrast to isobutane which gives observed rate coefficients about twice as large in the presence of molecular oxygen than in its absence.[3] Bagley *et al.* offer an explanation involving a secondary chain reaction between nitrate, alkylperoxy and alkoxy radicals. Not observing this phenomenon in the present case may be taken as an indication of fairly stable intermediaries. Another indication that our determinations are not affected unduly by secondary reactions is the good agreement between our experimental values and those calculated from Bagley *et al.*,[3] which were already corrected for secondary reactions.

The first-order plots were, in several cases, seen to have non-zero y-axis intercepts (*cf.* Fig. 3). The intercept value increases with increasing concentration of organic compound. This has been explained earlier in terms of the presence of small amounts of rapidly reacting impurities in the organic substances.[3] Another possible explanation in our case is that the formation efficiency of F atoms and NO_3 radicals change somewhat with pressure in the system. Significant increases in pressure occurred when the organic compound was added in high concentration. A third plausible reason for the non-zero intercepts is dilution of NO_3 by the relatively large amounts of ester added. None of these effects will affect the slope of the first-order plots as long as the pressure change and the dilution are constant for all data points in an experiment.

Atmospheric Implications

The principal esters utilised in industry are butyl and ethyl acetate.[10,11] In 1989 the Swedish use of butyl acetate, mainly as solvent in rapid-drying industrial paint, was about 7400 tonnes. Ethyl acetate is used in the manufacturing of printing ink, paint and glue with a national consumption of 3500 tonnes in 1989. The greater part of these solvents will end up to the atmosphere since only a small number of large industrial installations have any restrictions regarding solvent emissions at present. The presence of esters in the atmosphere has been demonstrated *e.g.* by Helmig *et al.*[12]

A possible environmental disturbance from reaction between NO_3 and esters is local, night-time formation of nitric acid close to strong point sources of esters. An estimate of the upper limits for such formation was made. Nitrogen dioxide and ozone, both at 1.23×10^{12} molecules cm^{-3} (50 ppb) reacted at 290 K according to reactions (5) and (6) to produce NO_3 and N_2O_5.

$$O_3 + NO_2 \rightarrow O_2 + NO_3 \qquad (6)$$

After 1 h reaction, the concentration of NO_3, buffered by N_2O_5, was 2.6×10^9 molecules cm^{-3}. This represents an upper limit on NO_3 concentration at these conditions since no loss of N_2O_5 by reaction with water[13] or any other NO_3-consuming reaction, *e.g.* with more reactive hydrocarbons, were included. The calculated NO_3 concentration may be compared with a value of 1×10^9 molecules cm^{-3} used in the literature for lifetime calculations of alkanes[3] in polluted atmosphere. Ambient NO_3 concentrations of 0.9×10^9 and 7×10^9 molecules cm^{-3} have been observed for conditions similar to, and more polluted than those described above, respectively.[14,15] The rates for reaction (5) and (6) were taken from ref. 1 and 16. Then, a point source of 50 : 50 mixture of ethyl and butyl acetate, injecting at 13.9 g s^{-1} (50 kg h^{-1}) was introduced. This source could be a large paint shop using rapid drying paint or a printing works. The mean temporal and spatial ester concentration over 1 h in the plume was

Table 5 Experimental conditions and rate coefficients for the gas-phase reaction of NO_3 with ethyl acetate in presence of molecular oxygen

$[O_2]$(%)	p(total)/mbar	[EtAc]/10^{16} molecule cm^{-3}	no. of expts.	v/cm s^{-1}	$k/10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}
0.6	20.7–27.7	0.35–4.05	6	110–140	1.2 ± 0.4
6.0	22.1–26.7	0.64–3.02	5	105–123	1.4 ± 0.4

$[NO_3]_0 \leqslant 1.5 \times 10^{13}$ molecule cm^{-3}.

calculated by a Gaussian dispersion model and was found to be 2.1×10^{12} molecules cm^{-3}, assuming a wind speed of 2 m s^{-1}. The dispersion parameters used for the Gaussian plume calculations were $\sigma_y = 0.31x^{0.71}$ and $\sigma_z = 0.06x^{0.71}$, where x is the distance (m) from the source. These parameters are representative for stable conditions during night time.[17] At the same time reaction (2) was included with a k value of 3.5×10^{-17} cm^3 $molecule^{-1}$ s^{-1} at 290 K. The temperature dependence for reaction (2) was that determined above for ethyl acetate.

The mean, upper limit HNO_3 formation rates in the plume, at 285, 290 and 295 K were found to be 0.012, 0.029 and 0.066 ppb h^{-1}, respectively. Taking into account the simplifications made above it is likely that the formation rate under real conditions is somewhat lower than the upper limit. The predicted HNO_3 formation rate from the nocturnal reaction between alkanes and NO_3 in polluted air is 0.09 ppb h^{-1}.[3] The other possible night-time source of nitric acid is the reaction of N_2O_5 with water vapour or wet aerosols. Tuazon *et al.*[18] calculated an HNO_3 formation rate of 0.3 ppb h^{-1} at polluted conditions through these reactions. Apparently, the HNO_3 formation from reaction between esters and NO_3, under the conditions described above, is not expected to be dominant but could be significant when compared with other night-time sources. The contribution from the title reactions to the atmospheric destruction of esters is negligible and $<0.1\%$ h^{-1} of the organic compound was transformed at 290 K. The main route for breakdown of esters in the atmosphere is expected to be day-time reaction with hydroxy radicals.[7]

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