THE KINETICS AND MECHANISM OF THE PHOTO-OXIDATION OF PROPIONALDEHYDE UNDER SIMULATED ATMOSPHERIC CONDITIONS

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Summary

The photolysis of dilute mixtures of HONO in synthetic air containing NO, NO_2 and C_2H_5CHO has been carried out at room temperature and atmospheric pressure. Hydroxyl radicals from the photolysis of HONO initiate a short-chain reaction in which NO is oxidized to NO_2 in reactions of the type $RO_2 + NO \rightarrow RO + NO_2$ ($R \equiv C_2H_5CO$, C_2H_5, CH_3 or H). When R is C_2H_5CO, reaction with NO_2 to form peroxypropionyl nitrate (PPN) competes with NO oxidation:

$$C_2H_5COO_2 + NO \xrightarrow{k_7} CH_3 + CO_2 + NO_2$$

$$C_2H_5COO_2 + NO_2 \xrightarrow{k_8} C_2H_5COO_2NO_2$$
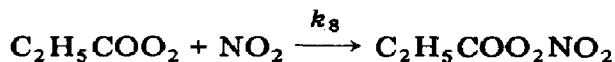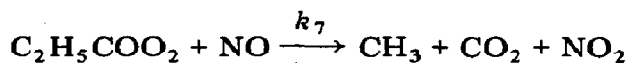
From measurements of the rates of formation of NO, NO_2 and PPN in a flow system with short contact times, kinetic information has been derived for the reactions which occur following the attack of HO on propionaldehyde:

$$HO + C_2H_5CHO \xrightarrow{k_5} H_2O + C_2H_5CO$$
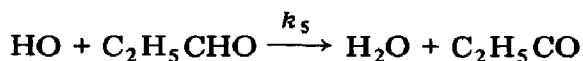
A kinetic analysis of the results yielded the ratio $k_7/k_8 = 1.9$ and $k_5 \leqslant 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} based on the value $k_{HO+HONO} = 6.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

1. Introduction

Aldehydes are recognized as playing an important role in the chemistry of the polluted troposphere. They are emitted as primary pollutants from the partial combustion of hydrocarbon fuels in internal combustion engines and they arise as secondary pollutants from the atmospheric photo-oxidation of hydrocarbons. A recent conference on *Chemical Kinetic Data Needs for Modeling the Lower Troposphere* [1] devoted an entire session to the kinetics and photochemistry of aldehydes.

The photo-oxidation of formaldehyde and acetaldehyde has been studied in smog chamber experiments [2] and the analytical data have been computer simulated on the basis of proposed kinetic mechanisms [3, 4]. In the case of acetaldehyde several important steps in the mechanism have been characterized from kinetic studies under atmospheric conditions based on end-product analyses [5]. These studies involved room temperature photolyses of dilute mixtures of HONO, NO, NO_2 and CH_3CHO in synthetic air at atmospheric pressure. Hydroxyl radicals are generated in this system from the photolysis of HONO. From measurements of the rates of formation of NO, NO_2, peroxyacetyl nitrate (PAN) and methyl nitrate in a flow system with short photolysis times, kinetic information was derived for the reactions which occur following the initial attack of HO on acetaldehyde:

$$HO + CH_3CHO \longrightarrow H_2O + CH_3CO$$
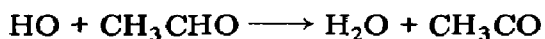
Thus it was established that a short-chain reaction was involved in which NO is oxidized to NO_2 by peroxy radical reactions of the type

$$RO_2 + NO \longrightarrow RO + NO_2 \qquad (R \equiv CH_3CO, CH_3, H)$$
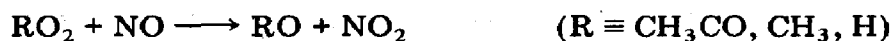
When R is CH_3CO, reaction with NO_2 to form PAN competes with NO oxidation:

$$CH_3CO_3 + NO \longrightarrow CH_3 + CO_2 + NO_2$$

$$CH_3CO_3 + NO_2 \longrightarrow CH_3COO_2NO_2$$
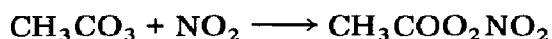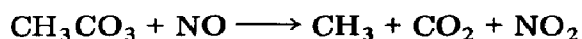
The first quantitative measurements of the ratio of the rate constants of these two reactions were made in the work reported in ref. 5.

In the present paper we report an extension of these studies to the photo-oxidation of propionaldehyde studied under simulated atmospheric conditions.

2. Experimental details

The photolysis of $HONO-NO-NO_2-C_2H_5CHO$ mixtures was carried out in a flow system of the type described previously [5 - 8]. Hydroxyl radicals were produced from the photolysis of gaseous nitrous acid. Gas mixtures containing nitrous acid and propionaldehyde in synthetic air were prepared in large Teflon or Tedlar bags. The reactants were drawn through the photolysis cell via the internal pump of a chemiluminescent analyser for NO and via an auxiliary pump. The changes in the concentrations of the reactants and the products were monitored by chemiluminescence analysis or by gas chromatography.

2.1. Preparation of gas mixtures

Mixtures of gaseous HONO in synthetic air ($[N_2]:[O_2] = 4:1$) were stored in a 240 dm^3 Teflon bag sealed with heat sealing tape and provided with Teflon inlet and sampling ports. This reservoir was suspended about

1.2 m above the laboratory bench and was shielded from natural sunlight and laboratory lighting by aluminium foil and a black-out cloth. HONO was generated by the action of H_2SO_4 on $NaNO_2$ [9] and was swept into the Teflon bag in a stream of nitrogen of which the flow rate was monitored with a rotameter. The concentration of HONO in the reservoir was typically about 5 ppm (1 ppm = 2.43×10^{13} molecules cm^{-3} at 296 K and 760 Torr) with about 0.5 ppm each of NO and NO_2 which are formed as byproducts.

In one series of experiments mixtures of 1 - 10 ppm propionaldehyde in nitrogen were made up in a separate Tedlar bag (about 200 dm^3). In a second series of experiments the propionaldehyde (7.5 ppm) was added to the HONO mixture in the first Teflon bag, to which the oxygen was added last to reduce the possibility of propionaldehyde being oxidized in the reservoir.

2.2. Procedure for a run

Gas mixtures were drawn at a controlled flow rate through a 39.5 cm^3 cylindrical Pyrex cell fitted with quartz end windows, and irradiated with UV light (330 - 380 nm) from a filtered high pressure mercury arc. The light intensity was monitored with a photocell placed directly behind the cell following a mirrored disc with a pinhole at its centre.

The flow of reactant gases was provided by the internal pump of a chemiluminescent analyser together with an auxiliary diaphragm pump (Charles Austin, Capex Mk II). The flow rate, which was controlled with needle valves and monitored downstream of the photolysis cell with Rotameters, was typically 11 cm^3 s^{-1}. A supplementary flow of nitrogen (BOC white-spot) from a high pressure cylinder was adjusted with a mass flow control meter (Pye) and a needle valve to maintain a constant pressure in the photolysis cell. The pressure in the flow system was measured using a Baratron pressure gauge (MKS Inc.). To minimize any losses of NO_x species by adsorption all sampling lines were constructed of Teflon tubing and fittings.

The rates of change in the concentrations of NO, NO_2 and peroxy-propionyl nitrate (PPN) were measured from the changes in concentration of these species on photolysis for a few seconds. For each series of experiments with added propionaldehyde, the photodissociation rate ϕk_a of HONO was determined from measurements of NO and NO_2 formation rates in the absence of the aldehyde. All rates were corrected for the small changes in concentrations of NO and NO_2 arising from the photolysis of NO_2 in the mixtures.

In the experiments to determine the effect of varying the $[NO_2]/[NO]$ ratio, either (i) a mixture of about 10 ppm NO_2 in nitrogen was prepared in the Tedlar reservoir and metered into the flow system as above or (ii) a mixture consisting of 106 ppm NO in nitrogen from a high pressure cylinder was added to the gas stream and the concentration of NO was varied by altering the flow rate of NO in nitrogen and the nitrogen ballast flow rate.

All experiments were carried out at room temperature (302 ± 3 K) and atmospheric pressure (about 730 Torr).

2.3. Analytical procedures

NO, NO_2 and HONO were analysed by means of the ozone chemiluminescence technique using a TECO model 12A NO_x analyser as previously described [10, 11]. The instrument was calibrated regularly with a standard mixture of NO (106 ppm) in nitrogen (Air Products Ltd.). Briefly, the system consists of measuring NO directly by its chemiluminescent reaction with ozone. NO_2 and HONO are converted to NO either via catalytic conversion in the analyser or by reduction with $FeSO_4$ crystals. HONO is removed from the gas stream by passage through an alkali scrubber. The three components NO, NO_2 and HONO are then determined by difference from the three types of NO readings. Small correction factors were applied for (i) the quenching of the NO_2 fluorescence signal by the water vapour carried over from the alkali scrubber, (ii) loss of NO_x species on the walls of the catalytic converter and (iii) absorption of NO_2 in the alkali scrubber. This system cannot distinguish between organic nitrites, organic nitrates and NO_2 or between peroxyacyl nitrates and HONO. Since, however, the organic nitrites and nitrates and peroxyacyl nitrates were produced in very small quantities this does not introduce a significant error in the analytical data for NO_2 or HONO.

The analysis of propionaldehyde in the gas mixtures was carried out by gas chromatography with flame ionization detection. The separation was achieved on a 1 m column packed with Chromosorb W-HP (Phase Separations Ltd.) containing 10% poly(ethylene glycol) (PEG 200) and operated at room temperature. A gas sample from the photolysis cell was drawn into a 7.5 cm^3 stainless steel sample loop using the auxiliary pump and was injected into the gas chromatograph. Calibrations for propionaldehyde were made by preparing mixtures containing up to 10 ppm of propionaldehyde gas in nitrogen in a Tedlar reservoir. Aliquots were then injected either via the sample loop or from an air-tight gas syringe with further dilution of the propionaldehyde–nitrogen mixture with additional white-spot nitrogen.

An attempt was made to analyse PPN by gas chromatography with electron capture detection in the manner used for PAN [5]. The analytical data derived were extremely erratic, probably owing to adsorption of the PPN on the walls of the injection loop and possible decomposition of the PPN on the analytical column. To circumvent this problem the PPN was converted to ethyl propionate by reaction with basic ethanol solution [11]. About 20 dm^3 of the gaseous reaction mixture was passed through a trap immersed in liquid air downstream of the photolysis cell. 0.2 cm^3 of a saturated solution of sodium ethoxide in ethanol was then added to the trap from a 10 cm^3 burette fitted with a syringe needle. The mixture was slowly warmed to 273 K allowing the sodium ethoxide to react with the trapped PPN. About 1 μl of the ester–ethanol mixture was injected into the gas chromatographic system operated under the same conditions as for the pro-

pionaldehyde analysis. The ratio of the peak area for the ester to that for the ethanol was normalized for the volume of reactant mixture collected from the photolysis cell. The PPN calibration was achieved by preparing a sample of PPN in one of the large plastic reservoirs by the photolysis of methyl nitrite with sun lamps in the presence of propionaldehyde. The concentration of PPN formed in the reservoir was determined by drawing a sample through a series of traps immersed in liquid air. Sodium ethoxide was added to the traps as in the experimental runs. The ratio of the peak areas for the samples from each trap were compared with that of standard solutions of ethyl propionate. Thus, with a knowledge of the total volume of gas passed through the traps, the concentration of PPN in the reservoir was derived. More than 80% of the total PPN observed appeared in the first trap and less than 1% of the total PPN appeared in the third trap.

This method of PPN analysis appears to be highly selective, as under the basic reaction conditions propionaldehyde does not react with ethanol to form ethyl propionate and the only source of the ester is from the hydrolysis of PPN. Samples collected when the cell was not irradiated did not produce any ester.

3. Results

3.1. Propionaldehyde dependence of the rates of formation of NO and NO_2

The effect of increasing the concentration of propionaldehyde on the rates of formation of NO and NO_2 in the photolysis of HONO was examined with a range of mixtures containing total $[NO_x]$ = [HONO] + [NO] + $[NO_2]$ from 3.4 to 7.1 ppm. The experimental conditions are summarized in Table 1. Figure 1 illustrates how the rates of formation of NO, NO_2 and NO + NO_2, each divided by the initial concentration of HONO, vary as a function of increasing aldehyde concentration (data given in Table 2). R_{NO} decreased and became negative while R_{NO_2} increased and $R_{NO + NO_2}$ decreased, all with increasing aldehyde concentration. These results indicate that, following the initial attack of hydroxyl radicals on the aldehydes, there is a chain sequence oxidizing NO to NO_2. At high aldehyde concentrations this

TABLE 1

Summary of the experimental conditions for the propionaldehyde dependence of R_{NO}

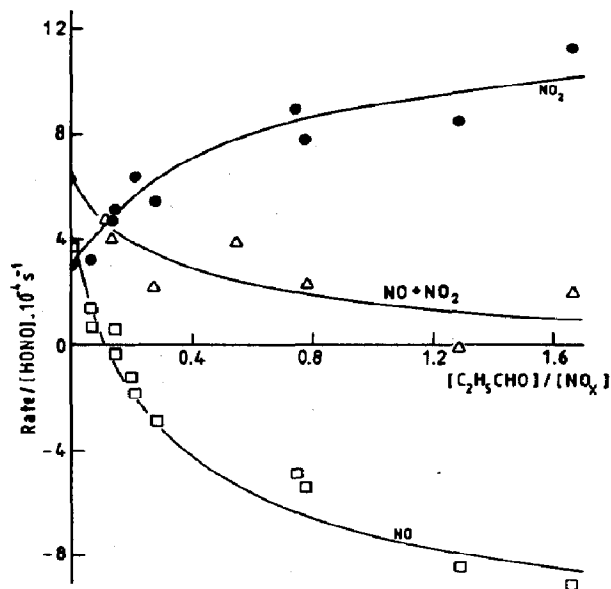| Experiment	Photolysis time (s)	ϕk_a ($\times 10^{-4}$ s^{-1})	[NO] (ppm)	$[NO_2]$ (ppm)	[HONO] (ppm)	$[C_2H_5CHO]$ (ppm)
1	3.8	3.465	0.3598	0.3991	3.234	0.19 - 6.31
2	3.5	4.507	0.4814	0.2852	3.404	0.90 - 7.02
3	3.5	4.186	0.5593	0.2095	3.949	0.29 - 1.40
4	3.6	2.503	0.4177	0.2366	4.867	0.24 - 4.96

Fig. 1. Rates of formation of NO, NO_2 and $(NO + NO_2)$ (each divided by [HONO]) as a function of $[C_2H_5CHO]$. Data from Table 2.

chain process is inhibited by one or more of the reaction components. The variation in the rates of formation at low $[C_2H_5CHO]/[NO_x]$ ratios is believed to be due to variation in the light intensity and in the NO_x concentration coupled with inaccuracies in determining small amounts of propionaldehyde.

TABLE 2

Effect of the propionaldehyde concentration on product formation rates

Experiment[a]	$\dfrac{[C_2H_5CHO]}{[NO_x]}$	R_{NO} $(\times 10^{-4}\,s^{-1})$	R_{NO_2} $(\times 10^{-4}\,s^{-1})$	$R_{NO} + R_{NO_2}$ $(\times 10^{-4}\,s^{-1})$	R_{PPN} $(\times 10^{-4}\,s^{-1})$	ΔR_{NO} $(\times 10^{-4}\,s^{-1})$
1.1	1.292	−8.540	8.374	−0.166	3.460	11.757
1.2	0.786	−5.429	7.752	2.301	2.791	8.666
1.3	0.148	−0.372	5.160	4.788	1.177	3.587
1.4	0.054	1.719	7.036	8.755	0.724	1.496
2.1	1.673	−9.275	11.254	1.979	3.625	13.307
2.2	0.217	−1.818	6.349	4.531	0.926	5.850
3.1	0.285	−2.937	4.641	1.704	2.122	6.672
3.2	0.142	0.587	3.449	4.036	1.746	3.147
3.3	0.065	1.435	3.267	4.702	0.998	2.299
4.1	0.750	−4.894	8.963	4.069	1.502	7.223
4.2	0.199	−1.205	3.422	2.217	1.089	3.535
4.3	0.279	−3.261	5.440	2.179	0.592	5.591
4.4	0.069	0.614	1.266	1.880	0.699	1.879
4.5	0.140	−1.502	4.697	3.195	5.668	3.832

[a]Experimental conditions as given in Table 1.

3.2. *The formation of peroxypropionyl nitrate in the photolysis of HONO + CH₃CH₂CHO mixtures*

The effect of increasing the propionaldehyde concentration on the rate of formation of PPN was investigated. The rate of formation of PPN increased with increasing concentration of propionaldehyde as shown in Table 2 and illustrated in Fig. 2. The corresponding reduction in the rate of formation ΔR_{NO} of NO is also shown in Fig. 2. The increase in the rate of formation of PPN corresponds to about a quarter of the increase in the rate of NO oxidation over the propionaldehyde range investigated. This type of behaviour is analogous to that observed in the photo-oxidation of acetaldehyde [5] and is consistent with the formation of PPN by combination of the peroxyacyl radical with NO_2:

$$C_2H_5COO_2 + NO_2 \longrightarrow C_2H_5COO_2NO_2$$
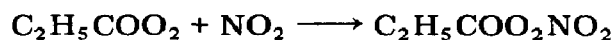
which competes with the $NO \rightarrow NO_2$ conversion reaction
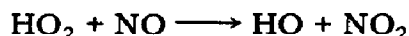
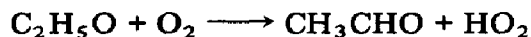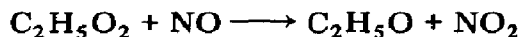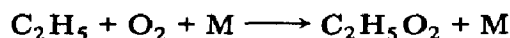$$C_2H_5COO_2 + NO \longrightarrow C_2H_5 + CO_2 + NO_2$$
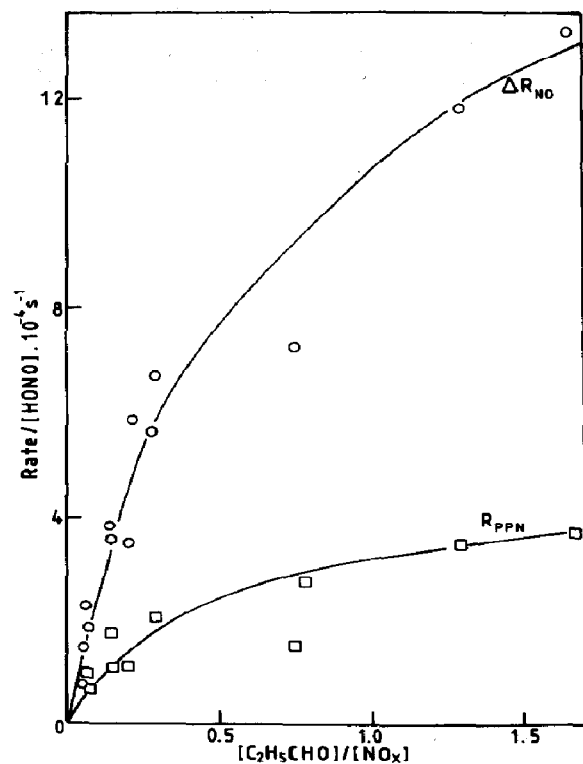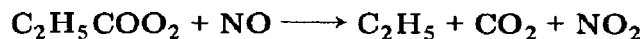
Fig. 2. Rate of formation of PPN and the rate of reduction in the rate of formation of NO as a function of $[C_2H_5CHO]$.

3.3. The effect of NO and NO_2 on the product formation

Experiments were carried out to test the effect of the concentration ratio $[NO_2]/[NO]$ upon the rates of formation of NO, NO_2 and PPN. The ratio $[NO_2]/[NO]$ was altered by adding NO or NO_2 to the gas stream flowing through the photolysis cell, while the concentrations of HONO and C_2H_5CHO were kept essentially constant. The data are listed in Table 3 and plotted in Fig. 3. The rate of formation of NO increased, *i.e.* became less negative, and the rate of formation of NO_2 decreased as the concentration ratio $[NO_2]/[NO]$ was increased. This indicates that there is a competition between the radicals reacting with NO_2 (resulting in chain termination) and reacting with NO (promoting the chain sequence and regeneration of hydroxyl radicals). The reaction sequence is thus the reactions given above followed by

$$C_2H_5 + O_2 + M \longrightarrow C_2H_5O_2 + M$$

$$C_2H_5O_2 + NO \longrightarrow C_2H_5O + NO_2$$

$$C_2H_5O + O_2 \longrightarrow CH_3CHO + HO_2$$

$$HO_2 + NO \longrightarrow HO + NO_2$$

At high NO_2 concentrations the oxidation of NO to NO_2 is inhibited, whereas the rate of formation of NO reaches a limiting value which is less than the rate of photolysis of HONO. Thus NO_2 does not completely suppress the oxidation of NO. This is probably due to the decomposition of PPN and subsequent reactions of the peroxy radicals with NO to promote the oxidation chain
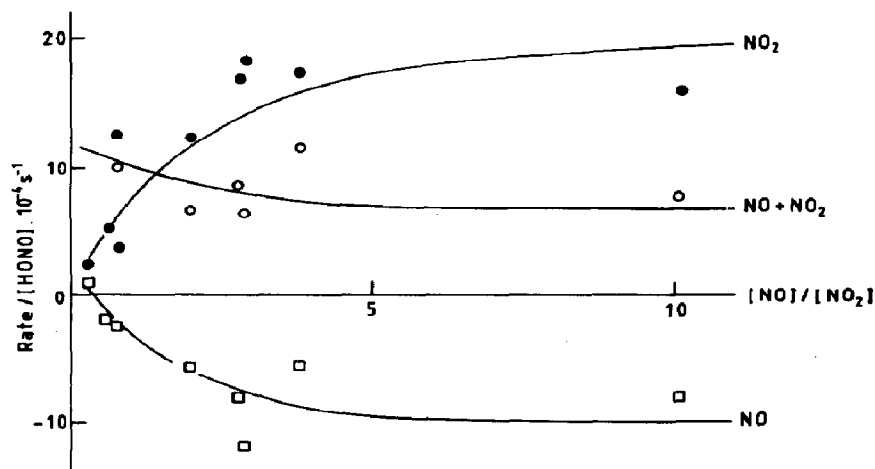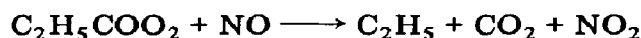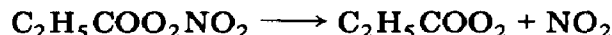
$$C_2H_5COO_2NO_2 \longrightarrow C_2H_5COO_2 + NO_2$$

$$C_2H_5COO_2 + NO \longrightarrow C_2H_5 + CO_2 + NO_2$$

Fig. 3. Rates of formation of NO, NO_2 and (NO + NO_2) as a function of $[NO]/[NO_2]$.

TABLE 3

Effect of NO and NO_2 concentrations on product formation rates

Experiment	[NO] (ppm)	[NO_2] (ppm)	R_{NO} ($\times 10^{-4}$ s^{-1})	R_{NO_2} ($\times 10^{-4}$ s^{-1})	$R_{NO} + R_{NO_2}$ ($\times 10^{-4}$ s^{-1})	R_{PPN} ($\times 10^{-4}$ s^{-1})	ΔR_{NO} ($\times 10^{-4}$ s^{-1})
5.1	0.5325	0.1876	−8.166	16.766	8.600	0.868	12.470
5.2	0.5563	0.1879	−11.888	18.180	6.292	2.428	16.192
5.3	0.5530	1.7167	−1.231	3.108	1.877	4.880	10.055
5.4	0.6567	1.0389	−2.267	5.073	2.805	6.482	11.587
5.5	0.2125	0.2696	−2.466	3.524	1.058	1.965	11.786
5.6	0.4629	0.1227	−5.604	17.214	11.550	0.61	16.095
5.7	0.4786	0.2391	−5.656	12.256	6.600	0.983	16.087
5.8	0.4879	0.6589	−2.440	12.576	9.919	2.302	12.871
5.9	0.6872	0.0681	−8.067	15.851	7.784	0.287	18.494

Mean concentrations: [C_2H_5CHO] = 1.74 ppm; [HONO] = 3.04 ppm.
Photolysis time, 3.8 s.
$\phi k_a = 1.1 \times 10^{-3}$ s^{-1}.

4. Kinetic treatment of the results

The following reaction scheme is proposed for the photolysis of HONO in the presence of C_2H_5CHO in a synthetic air mixture containing NO and NO_2:

$$HONO + h\nu \longrightarrow HO + NO \qquad\qquad \phi k_a \qquad\qquad (1)$$

$$HO + NO + M \longrightarrow HONO + M \qquad k_2 = 6.1 \times 10^{-12} \ [12] \qquad (2)$$

$$HO + NO_2 + M \longrightarrow HONO_2 + M \qquad k_3 = 1.1 \times 10^{-11} \ [12] \qquad (3)$$

$$HO + HONO \longrightarrow H_2O + NO_2 \qquad k_4 = 6.6 \times 10^{-12} \ [13] \qquad (4)$$

$$HO + C_2H_5CHO \longrightarrow H_2O + C_2H_5CO \qquad \text{(see text)} \qquad (5)$$

$$C_2H_5CO + O_2 \longrightarrow C_2H_5COO_2 \qquad k_6 = 5 \times 10^{-12} \ [14] \qquad (6)$$

$$C_2H_5COO_2 + NO \longrightarrow C_2H_5 + CO_2 + NO_2 \qquad\qquad\qquad (7)$$

$$C_2H_5COO_2 + NO_2 \longrightarrow C_2H_5COO_2NO_2 \qquad \text{(see text)} \qquad (8)$$

$$\longrightarrow \text{radicals} \qquad\qquad\qquad\qquad (9)$$

$$C_2H_5 + O_2 + M \longrightarrow C_2H_5O_2 + M \qquad k_{10} = 4.8 \times 10^{-12} \ [14] \qquad (10)$$

$$C_2H_5O_2 + NO \longrightarrow C_2H_5O + NO_2 \qquad k_{11} = 7.1 \times 10^{-12} \ [14] \qquad (11)$$

$$C_2H_5O + NO_2 \longrightarrow C_2H_5ONO_2 \qquad k_{12} = 1.2 \times 10^{-11} \ [14] \qquad (12)$$

$$C_2H_5O + O_2 \longrightarrow CH_3CHO + HO_2 \qquad k_{13} = 8 \times 10^{-15} \ [14] \qquad (13)$$

$$C_2H_5O \longrightarrow HCHO + CH_3 \qquad k_{14} = 2 \times 10^{-5} \ s^{-1} \ [13] \qquad (14)$$

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M \qquad k_{15} = 1.8 \times 10^{-12} \ [14] \qquad (15)$$

$$CH_3O_2 + NO \longrightarrow CH_3O + NO_2 \qquad k_{16} = 7.6 \times 10^{-12} \ [14] \qquad (16)$$

$$CH_3O + O_2 \longrightarrow HCHO + HO_2 \qquad k_{17} = 1.3 \times 10^{-15} \ [14] \qquad (17)$$

$$CH_3O + NO_2 \longrightarrow CH_3ONO_2 \qquad k_{18} = 1.2 \times 10^{-11} \ [14] \qquad (18)$$

$$HO_2 + NO \longrightarrow HO + NO_2 \qquad k_{19} = 8.3 \times 10^{-12} \ [14] \qquad (19)$$

The rate constants for a temperature of 298 K are in units of centimetres cubed per molecule per second and for third-order reactions refer to an air pressure of 1 atm. This mechanism is directly analogous to that proposed for a similar study of the $HONO-CH_3CHO-NO-NO_2$ system [5]. It is clearly possible to extend the reaction scheme by including additional reactions, but these are not required under the present experimental conditions. The values of the rate constants are taken from recent data evaluations [12 - 14].

As for the CH_3CHO system [5] it is necessary to include reactions of NO_2 with the peroxypropionyl radicals (reaction (9)) yielding radicals which allow the chain oxidation of NO to continue at higher $[NO_2]/[NO]$ ratios to explain the present observations.

4.1. The NO and NO₂ dependence of R_{PPN} and ΔR_{NO}

A rigorous kinetic analysis of the results is not justified on the basis of the above simplified mechanism since the detailed nature of the radical-chain-carrying reactions of the acylperoxy radicals is uncertain. It is possible, however, to obtain information on the relative importance of reactions (7) - (9) from the observed dependence of R_{PPN} on the ratio $[NO_2]/[NO]$.

The steady state concentration of propionylperoxy radicals is given by

$$[C_2H_5COO_2] = \frac{k_5[HO][C_2H_5CHO]}{k_7[NO]} f_1$$

where

$$f_1 = \frac{k_7[NO]}{k_7[NO] + (k_9 + k_8)[NO_2]}$$

is the fraction of $C_2H_5COO_2$ radicals which react with NO. The rate of formation of PPN, normalized to [HONO], is then given by the expression

$$R_{PPN} = \frac{k_8[NO_2]}{[HONO]} \frac{k_5[HO][C_2H_5CHO]f_1}{k_7[NO]} \tag{I}$$

If we assume that the difference between the rates of removal of NO in reaction (2) in the absence and presence of C_2H_5CHO is negligible the reduction in R_{NO} in the presence of C_2H_5CHO is given by

$$\Delta R_{NO} = \frac{k_5[HO][C_2H_5CHO]f_1}{[HONO]} \left(1 + \frac{f_2}{f_1}A\right) \tag{II}$$

in which

$$f_2 = \frac{k_9[NO_2] + k_7[NO]}{k_7[NO] + (k_8 + k_9)[NO_2]}$$

is the fraction of $C_2H_5COO_2$ radicals which react with NO and NO_2 to produce radicals. A is a stoichiometric factor giving the effective number of NO molecules oxidized by these radicals before HO is regenerated. Combination of eqns. (I) and (II) yields

$$\frac{\Delta R_{NO}}{R_{PPN}} = \frac{k_7[NO]}{k_8[NO_2]} \left(1 + \frac{f_2}{f_1}A\right)$$

and substituting for f_2/f_1 leads to

$$\frac{\Delta R_{NO}}{R_{PPN}} = (1 + A)\frac{k_7[NO_2]}{k_8[NO]} + \frac{k_9}{k_8}A \tag{III}$$

As in the case of the CH_3CHO photo-oxidation study, the quantity A should not vary greatly for $[NO]/[NO_2] > 0.5$ and therefore a plot of $\Delta R_{NO}/R_{PPN}$ versus $[NO]/[NO_2]$ should be linear with a slope corresponding to $(k_7/k_8)(1 + A)$ and an intercept corresponding to $(k_9/k_8)A$. Figure 4 shows
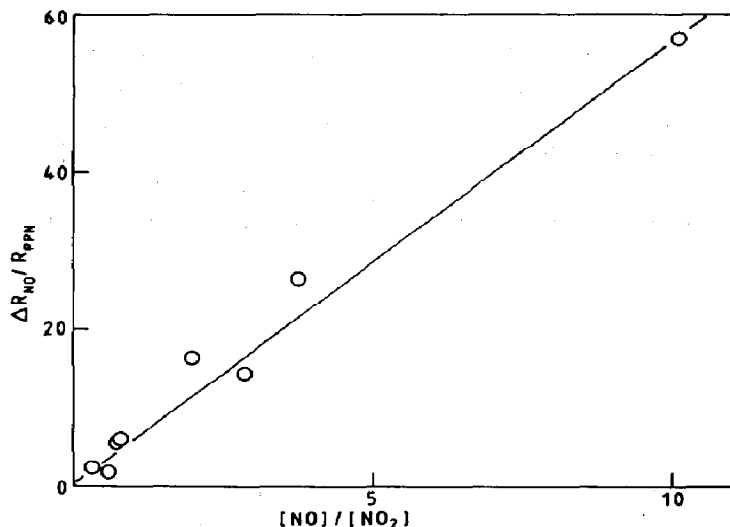
Fig. 4. A plot of $\Delta R_{NO}/R_{PPN}$ vs. $[NO]/[NO_2]$ (data from Table 3).

a plot of the data from Table 3 according to eqn. (III). A least-mean-squares treatment yields a slope of 5.6 ± 0.6 and an intercept of 0.168 ± 2.2. Thus from a mean value of $A = 1.995$, calculated from the proposed mechanism and the listed recommended rate constants, it follows that $k_7/k_8 = 1.87 \pm 0.2$ and $k_9/k_8 = 0.084 \pm 1.1$. The positive intercept on Fig. 4 is consistent with the occurrence of reaction (9), although this is a minor pathway for $C_2H_5COO_2$ radicals.

4.2. The effect of changing $[C_2H_5CHO]$ on R_{NO}

The steady state concentrations of HO in the presence of C_2H_5CHO can be shown to be given by

$$[HO] = \frac{\phi k_a[HONO]}{k_x[NO_x] + k_5[C_2H_5CHO](1 - f_3)} \qquad (IV)$$

where f_3 is the fraction of HO radicals which are generated in the chain sequence following their attack on C_2H_5CHO and

$$k_x[NO_x] = k_2[NO] + k_3[NO_2] + k_4[HONO]$$

From eqns. (II) and (IV) it follows that

$$\frac{\phi k_a}{\Delta R_{NO}} = \frac{1 - f_3}{f_1\{1 + (f_2/f_1)A\}} + \frac{1}{f_1\{1 + (f_2/f_1)A\}} \frac{k_x[NO_x]}{k_5[C_2H_5CHO]}$$

where $f_1\{1 + (f_2/f_1)A\}$ is the number of NO molecules oxidized for each $C_2H_5COO_2$ radical produced by attack of HO on C_2H_5CHO and can be evaluated for a given $[NO_2]/[NO]$ ratio from the rate constant ratios derived in the previous section.

Plots of $\phi k_a/\Delta R_{NO}$ versus $[NO_x]/[C_2H_5CHO]$ are shown in Fig. 5 for various initial conditions of $[NO_2]/[NO]$. These plots correspond to an
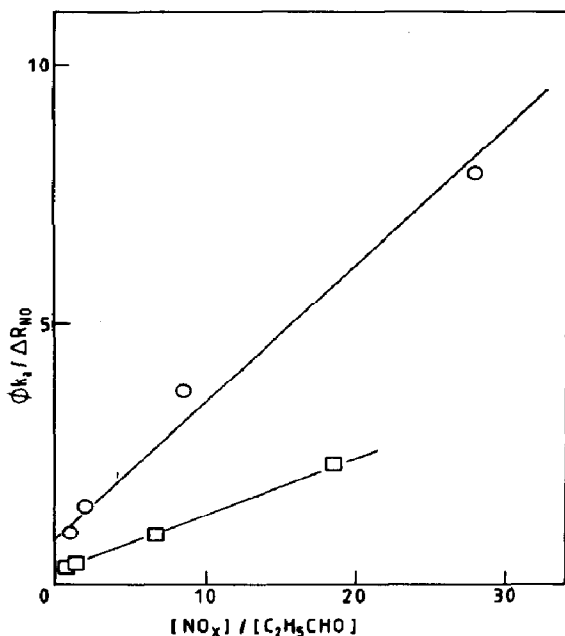
Fig. 5. $\phi k_a/\Delta R_{NO}$ vs. $[NO_x]/[C_2H_5CHO]$: $\bigcirc$, $[NO]/[NO_2] = 0.1956$; $\square$, $[NO]/[NO_2] = 1.8385$.

average value of $k_x/k_5 = 0.27 \pm 0.08$ based on a stoichiometric factor of $f_1\{1 + (f_2/f_1)A\} = 1.898$. It follows from the average value of $k_x/k_4 = 1.07 \pm 0.03$ that $k_4/k_5 = 0.25 \pm 0.07$ which corresponds to the average over all runs.

The intercept at infinite concentration of propionaldehyde when all the hydroxyl radicals produced are reacting exclusively with propionaldehyde corresponds to the fraction of the hydroxyl radicals lost following reaction (4), i.e. $1 - f_3$. If no radicals are lost in the reaction chain the limiting rate ΔR_{NO} would be infinite and the intercept zero, whereas if all the radicals produced were lost the intercept would be unity.

The value of the intercept is dependent on the concentration ratio $[NO]/[NO_2]$. This arises from the competition between reactions (7) and (8), i.e. the reactions of the peroxypropionyl radical with NO and NO_2 respectively.

The values of $1 - f_3$ obtained from the intercept are less than those calculated from the recommended rate constants and concentrations of NO, NO_2 and O_2 present. This discrepancy is probably due to a decrease in f_1 and f_2 as the ratio $[NO_x]/[C_2H_5CHO]$ decreases arising from an increase in the mean effective ratio $[NO_2]/[NO]$. It is therefore probable that the ratio k_4/k_5 calculated from the gradient is a lower limit owing to the decrease in the stoichiometry factor as the ratio $[NO_x]/[C_2H_5CHO]$ decreases, leading to an upper limit determination of k_5.

5. Discussion

From our experimental ratio of rate constants $k_4/k_5 \geqslant 0.25$ it follows from the recommended value of $k_4 = 6.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K [13] that k_5 is 2.6×10^{-11} cm^3 molecule^{-1} s^{-1} or less at room temperature. This result for the rate constant of the HO attack on C_2H_5CHO can be compared with the literature results of 2.1×10^{-11} cm^3 molecule^{-1} s^{-1} [15], 1.8×10^{-11} cm^3 molecule^{-1} s^{-1} [16] and 1.7×10^{-11} cm^3 molecule^{-1} s^{-1} [17] obtained in relative rate studies and of 3.1×10^{-11} cm^3 molecule^{-1} s^{-1} [18] and 1.7×10^{-11} cm^3 molecule^{-1} s^{-1} [19] derived in absolute rate studies. Since our present result represents an upper limit the level of agreement is satisfactory.

The rate constant ratio $k_7/k_8 = 1.9$ for the reactions of the $C_2H_5COO_2$ radical with NO and NO$_2$ is in line with the ratio $k_{20}/k_{21} = 1.7$ for the analogous reactions

$$CH_3COO_2 + NO \longrightarrow CH_3 + CO_2 + NO_2 \tag{20}$$

$$CH_3COO_2 + NO_2 \longrightarrow CH_3COO_2NO_2 \tag{21}$$
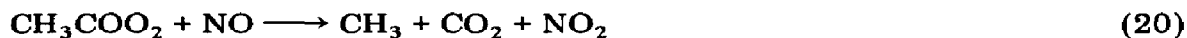
which was determined using a similar experimental technique [5]. The ratio k_{20}/k_{21} has also been measured in experiments involving the thermal decomposition of PAN in the presence of NO. Thus Cox and Roffey [20] report $k_{20}/k_{21} = 1.58 \pm 0.61$ at 295 K while Hendry and Kenley [21] found $k_{20}/k_{21} = 3.5 \pm 0.5$ independent of temperature over the range 298 - 318 K. To the best of our knowledge there has been no previous experimental determination of the ratio k_7/k_8.

The general features of the photo-oxidation of propionaldehyde initiated by the photolysis of HONO in air containing NO and NO$_2$ follow the pattern of results observed under similar experimental conditions for acetaldehyde. The mechanism of these flow system studies consists of a short-chain reaction in which NO is oxidized to NO$_2$ by the peroxy radicals, HO$_2$, CH$_3$O$_2$, $C_2H_5O_2$ and $C_2H_5COO_2$. In the case of the $C_2H_5COO_2$ radical the NO reaction is in competition with the NO$_2$ reaction which forms PPN.

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