J. Chem. Soc., Faraday Trans. 1, 1984, **80**, 617–628

Formation of Organic Nitro-compounds in Flowing $H_2O_2+NO_2+N_2$+Organic Vapour Systems

Part 3.—Effects of O_2 Addition on $H_2O_2+NO_2+N_2$+Alkane Systems

By Donald L. Baulch, Ian M. Campbell* and Jonathan M. Chappel

Department of Physical Chemistry, The University, Leeds LS2 9JT

Received 13th June, 1983

The effects of oxygen on the product distribution from the surface-initiated reactions in flowing mixtures of H_2O_2, NO_2, N_2 and RH, where RH = ethane, propane, n-butane and n-pentane, at 298 K have been studied. In the absence of O_2, the principal products are the corresponding nitroalkane, alkyl nitrite and alkyl nitrate. In the presence of sufficiently large concentrations of O_2, the predominant product is the alkyl nitrate and the only other products of significance, in some cases, are the corresponding carbonyl compounds.

The variation of the product yields with $[O_2]/[NO_2]$ gives values for the rate-constant ratios $k_8/(k_3+k_4)$ for reaction at both primary and secondary radical sites:

$$R+NO_2(+M) \rightarrow RNO_2(+M) \qquad (3)$$

$$R+NO_2(+M) \rightarrow RONO^*(+M) \qquad (4)$$

$$R+O_2(+M) \rightarrow RO_2(+M). \qquad (8)$$

Possible mechanisms by which the products are formed are discussed.

In the preceding papers in this series[1, 2] we showed that the mechanism for formation of nitro-compounds in the system $H_2O_2+NO_2+RH$ (where RH = ethane, propane, n-butane and n-pentane) was as follows:

$$H_2O_2+NO_2 \xrightarrow{\text{wall}} OH+HNO_3 \qquad (1)$$

$$OH+RH \longrightarrow R+H_2O \qquad (2)$$

$$R+NO_2(+M) \longrightarrow RNO_2(+M) \qquad (3)$$

$$R+NO_2(+M) \longrightarrow RONO^*(+M) \qquad (4)$$

$$RONO^*+M \longrightarrow RONO+M \qquad (5)$$

$$RONO^* \longrightarrow RO+NO \qquad (6)$$

$$RO+NO_2(+M) \longrightarrow RONO_2(+M) \qquad (7)$$

where $RONO^*$ is an internally excited species and reaction (1) occurs on the boric-acid-coated walls of the flowtube. In the present work we have investigated the effects of addition of O_2 to these systems.

In the presence of O_2, under the conditions of our experiments, we should expect the combination

$$R+O_2(+M) \rightarrow RO_2(+M) \qquad (8)$$

to compete with steps (3) and (4) in the scheme above. Under the conditions in our systems the RO_2 radicals would be expected to react overwhelmingly with NO_2 to yield the alkyl peroxynitrate

$$RO_2+NO_2(+M) \rightarrow RO_2NO_2(+M).$$

However, such species apparently have a limited stability and so are unlikely to appear as final products. Spicer *et al.*[3] have generated CH_3 radicals in the presence of O_2 and NO_2 by photodissociation of $CH_3N_2CH_3$ at 298 K, when the main product was methyl nitrate. In another study, based on the photolysis of $N_2O+CH_4+O_2+NO_2$ mixtures at 298 K, Simonaitis and Heicklen[4] also found methyl nitrate to be a major product but came to no firm conclusion on how $CH_3O_2NO_2$, the intermediate species, became converted to CH_3ONO_2.

Our main aims were to examine the systems containing ethane, propane, n-butane and n-pentane in turn (i) to identify major products and establish their yields, (ii) from the latter to obtain relative kinetic parameters for the reactions of the alkyl radicals with NO_2 and O_2 and (iii) to gain some insight into the mechanisms leading to the observed products.

EXPERIMENTAL

The flow system has been described in detail before.[5] All experiments were conducted at a temperature of 298 K and at a total pressure of 40.0 kPa. Using the same procedures as described in the preceding papers,[1,2] the flowrates of H_2O_2 vapour and NO_2 into the system were kept constant so that the added concentrations were $[H_2O_2]_0 = 2.8 \times 10^{-6}$ mol dm^{-3} and $[NO_2] = 5.5 \times 10^{-5}$ mol dm^{-3}. Ethane composed the main carrier gas in $H_2O_2+NO_2+O_2+C_2H_6$ systems whereas in the other systems the main carrier gas was N_2 containing 10% of the alkane.

Oxygen was taken from a cylinder (B.O.C. Ltd) and was added through a calibrated capillary flowmeter to produce a range of $[O_2]$ extending up to the equivalent of 35% of the total carrier gas.

Product yields were measured by the procedures described before[2] based upon gas chromatography.

RESULTS

ETHANE SYSTEM

The major products were nitroethane, ethyl nitrate and acetaldehyde. The main trends were a rise in acetaldehyde yield and a fall in nitroethane yield as $[O_2]$ increased, while the apparent yield of ethyl nitrate showed little variation relatively. However, since reactions (3) and (4) are in competition with reaction (8), part of the nitrate yield arises from the reaction sequence (4), (6), (7) and part from the consequence of reaction (8). The part of the yield of ethyl nitrate arising from the occurrence of step (4) initially will be expected to preserve a constant ratio to the nitroethane ($EtNO_2$) yield: this part, denoted as $[EtNO_3'']$, may therefore be calculated from the yield of nitroethane on the basis of the yield ratio $[EtNO_3]/[EtNO_2]$ when $[O_2] = 0$ (see preceding paper). The remainder of the yield of ethyl nitrate [arising from step (8)] is denoted as $[EtNO_3']$. Table 1 shows a representative selection of results, illustrating the trends, while further results for this system appear later in fig. 1.

PROPANE SYSTEM

The major products in this system are 1- and 2-isomers of nitropropane ($PrNO_2$), propyl nitrite (PrONO) and propyl nitrate ($PrNO_3$), together with acetone and traces of propionaldehyde. Table 2 shows a representative selection of the results, illustrating the trends, while further results for this system appear later in fig. 1. As for the ethane

Table 1. Product yields (in μmol dm^{-3}) from $H_2O_2 + NO_2 + C_2H_6 + O_2$ systems at 298 K with $[H_2O_2]_0 = 2.8 \times 10^{-6}$ mol dm^{-3}, $[NO_2] = 5.5 \times 10^{-5}$ mol dm^{-3} and $[C_2H_6] = 1.65 \times 10^{-2}$ mol dm^{-3}

$[O_2]/10^{-3}$ mol dm^{-3}	$[CH_3CHO]$	$[EtNO_2]$	$[EtNO_3']$	$[EtNO_3'']$
0	0	0.494	0	0.442
0.540	0.152	0.226	0.450	0.208
2.28	0.203	0.0816	0.594	0.075
3.44	0.289	0.0544	0.611	0.050
4.93	0.345	0.0449	0.680	0.041
6.53	0.361	0.0296	0.610	0.027

Table 2. Product yields (in μmol dm^{-3}) from $H_2O_2 + NO_2 + N_2 + C_3H_8 + O_2$ systems at 298 K and total pressure of 40 kPa with $[H_2O_2]_0 = 2.8 \times 10^{-6}$, $[NO_2] = 5.5 \times 10^{-5}$ and $[C_3H_8] = 1.7 \times 10^{-3}$ mol dm^{-3}

$[O_2]$ $/10^{-3}$ mol dm^{-3}	$[CH_3COCH_3]$	$[PrNO_2]$		$[PrONO]$		$[PrNO_3']$	
		1-	2-	1-	2-	1-	2-
0	0	0.15	0.50	0.076	0.13	0	0
0.442	0.017	0.085	0.13	0.027	0.043	0.097	0.44
1.47	0.022	0.046	0.055	0.014	0.018	0.17	0.56
3.63	0.018	0.020	0.020	0.006	0.006	0.20	0.60
5.42	0.033	0.017	0.019	[a]	[a]	0.25	0.72
6.38	0.035	0.013	0.014	[a]	[a]	0.21	0.64

[a] Too small for accurate measurement.

system, $[PrNO_3']$ denotes that part of the propyl nitrate yield resulting from reaction of propyl radicals with O_2 in step (8). The yield of $PrNO_3''$ [representing that part originating from reaction of propyl radicals with NO_2 in step (4)] is extremely small under the conditions used here, for reasons discussed in the preceding paper,[2] and is therefore not shown in table 2.

n-BUTANE SYSTEM

The major products in this system are the 1- and 2-isomers of nitro-n-butane ($BuNO_2$), n-butyl nitrite (BuONO) and n-butyl nitrate ($BuNO_3$), with smaller yields of butyraldehyde and butanone. Table 3 shows a representative selection of results and further results for this system are shown later in fig. 2. As very little $BuNO_3$ is produced in the absence of O_2 (see preceding paper), the total yield of $BuNO_3$ is ascribed to a mechanism commencing with reaction of n-butyl radicals with O_2, *i.e.* step (8).

n-PENTANE SYSTEM

The major products expected in this system are the 1-, 2- and 3-isomers of nitro-n-pentane ($PeNO_2$), n-pentyl nitrite (PeONO) and n-pentyl nitrate ($PeNO_3$). The chromatographic analysis produced closely overlapping peaks corresponding to 2- and 3-$PeNO_3$, which were converted to a combined yield of these products on the basis of the combined peak area. The 1-$PeNO_3$ product peak coincided with the peak

Table 3. Product yields (in μmol dm^{-3}) from $H_2O_2+NO_2+N_2+n\text{-}C_4H_{10}+O_2$ systems at 298 K and total pressure of 40 kPa with $[H_2O_2]_0 = 2.8\times10^{-6}$, $[NO_2] = 5.5\times10^{-5}$ and $[n\text{-}C_4H_{10}] = 1.7\times10^{-3}$ mol dm^{-3}

$[O_2]$ /10^{-3} mol dm^{-3}	[aldehyde]	[ketone]	[BuNO$_2$]		[BuONO]		[BuNO$_3$]	
			1-	2-	1-	2-	1-	2-
0	0	0	0.075	0.52	0.065	0.32	0.003	0.029
0.638	[a]	0.031	0.037	0.13	0.024	0.087	0.042	0.57
1.10	[a]	0.043	0.027	0.089	0.017	0.057	0.079	0.70
4.29	0.004	0.051	0.012	0.032	0.006	0.020	0.11	0.90
6.40	0.012	0.072	0.007	0.016	[a]	0.011	0.095	0.87

[a] Too small for accurate measurement.

Table 4. Product yields (in μmol dm^{-3}) from $H_2O_2+NO_2+N_2+n\text{-}C_5H_{12}+O_2$ systems at 298 K and total pressure of 40 kPa with $[H_2O_2]_0 = 2.8\times10^{-6}$, $[NO_2] = 5.5\times10^{-5}$ and $[n\text{-}C_5H_{12}] = 1.7\times10^{-3}$ mol dm^{-3}

$[O_2]$ /10^{-3} mol dm^{-3}	[Ox]	[PeNO$_2$]			[PeONO]	[PeNO$_3$]	
		1-	2-	3-		1-	2- and 3-
0	0	0.057	0.35	0.20	0.34	[a]	0.023
0.982	0.043	0.023	0.064	0.037	0.074	0.036	0.92
2.60	0.056	0.011	0.035	0.020	0.035	0.027	1.00
3.73	0.062	0.009	0.024	0.014	0.021	0.030	1.06
5.67	0.074	0.004	0.015	0.008	0.012	0.029	0.95
7.17	0.11	0.004	0.012	0.007	[a]	0.031	1.01

[a] Too small for accurate measurement.

corresponding to 2-PeNO$_2$, and these could not be resolved. However, the yield of 3-PeNO$_2$ must preserve a constant ratio with that of 2-PeNO$_2$: accordingly the value of this ratio in the system not containing O_2 (when the PeNO$_3$ yield is negligible) was used to derive the yields of 2-PeNO$_2$ from those measured for 3-PeNO$_2$ in the systems with O_2 present. The yield of 1-PeNO$_3$ was then deduced from the residual area of the combined peak. The isomers of PeONO had short retention times and gave coincident peaks so that only the total yields of PeONO were derived. Another peak corresponding to n-valeraldehyde and/or pentanones was observed, these substances being indistinguishable with the present analytical system: the corresponding yield is denoted by [Ox] in table 4, which showing a representative selection of results. As very little PeNO$_3$ is produced in the absence of O_2 (see preceding paper) the total yields of PeNO$_3$ are ascribed to a mechanism commencing with the reaction of n-pentyl radicals with O_2, *i.e.* step (8). Further results for this system appear in fig. 1.

DISCUSSION

In the systems containing propane, n-butane and n-pentane, at the highest concentrations of O_2 used, > 90% of the product is in the form of the alkyl nitrate. Thus we have here a single-stage gas-phase process for introducing a functional group into the alkane *via* a thermal reaction operating at ambient temperature. This is unusual, perhaps unique, for an alkane and may be of industrial value.

The highest efficiencies with which H_2O_2 produced $RONO_2$ in the present work were 26% (C_2H_6), 35% (C_3H_8), 36% (C_4H_{10}) and 39% (C_5H_{12}). The upper limit to this efficiency is the efficiency with which the surface produces OH from H_2O_2 by the initiating reaction

$$H_2O_2+NO_2\xrightarrow{\text{wall}}OH(g)+HNO_3 \tag{1}$$

which in the present work was 43 ± 5%.[1] However, boric-acid-coated surfaces have been produced in our previous work[6] with approximately double this efficiency. Moreover, the efficiency of the surface for reaction (1) does not appear to be affected by the presence of O_2 since the total product yields remained effectively constant throughout the present work.

The general nature of the mechanism in the presence of O_2 seems clear. Under our conditions the OH radical from reaction (1) will react predominantly with RH to generate alkyl radicals, R. Thereafter there is competition between the NO_2 and O_2 for reaction with R, the former leading to nitroalkane, alkyl nitrite and some alkyl nitrate, the latter combining with R to form alkylperoxy radicals, RO_2. Abstraction from R by O_2 to yield the alkene and HO_2, which is important at higher temperatures (*e.g.* 773 K[7]), would not be expected to be important at ambient temperatures. In exemplification, the work of Plumb and Ryan[8] may be quoted: for C_2H_5 reaction with O_2 at ambient temperature, the rate constant for the reaction

$$C_2H_5+O_2\rightarrow C_2H_4+HO_2$$

was only *ca.* 5% of the limiting second-order value of k_8, which will, in all probability, apply under our conditions. It is clear from the data in tables 1–4 that the ultimate products resulting from the RO_2 radicals are the alkyl nitrates and carbonyl species (the latter collectively denoted as Ox). Thus as $[O_2]$ increases, the yields of alkyl nitrate and Ox increase at the expense of the nitroalkane, alkyl nitrite and the part of the alkyl nitrate yield associated (RNO_3'') as a result of the two general competitive routes represented as

$$R+NO_2\rightsquigarrow RONO,\ RNO_2,\ RNO_3'' \tag{A}$$

$$R+O_2\rightsquigarrow RNO_3',\ Ox. \tag{B}$$

The total yields of respective products from these two pathways are determined by the relative rates of the initiating elementary steps:

$$R+NO_2(+M)\rightarrow RONO^*,\ RNO_2(+M) \tag{3)+(4}$$

$$R+O_2(+M)\rightarrow RO_2(+M). \tag{8}$$

On this basis we obtain the equation

$$\frac{k_8[O_2]}{(k_3+k_4)[NO_2]}=\frac{[RNO_3']+[Ox]}{[RONO]+[RNO_2]+[RNO_3'']}=\frac{\Sigma P(A)}{\Sigma P(B)}$$

where $\Sigma P(A)$ and $\Sigma P(B)$ represent the total product yields arising *via* pathways (A) and (B), respectively. Plots of $\Sigma P(A)/\Sigma P(B)$ against $[O_2]$ at constant $[NO_2]$ for ethane,

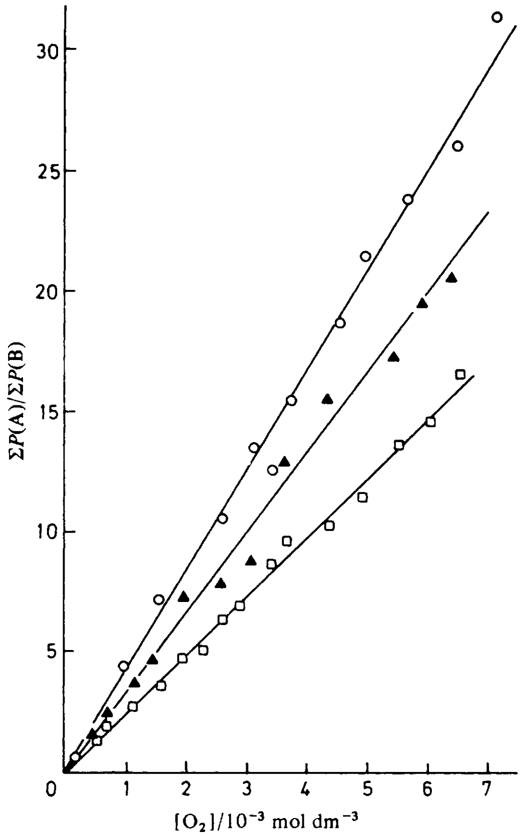


Fig. 1. Plots of $\Sigma P(\mathrm{A})/\Sigma P(\mathrm{B})$ (see text) against $[O_2]$ for $H_2O_2+NO_2+O_2+(N_2)+RH$ systems at 298 K and $[NO_2] = 5.5\times10^{-5}$ mol dm^{-3}, $[H_2O_2]_0 = 2.8\times10^{-6}$ mol dm^{-3}, a total pressure of 40 kPa and RH = ethane (□), propane (▲) and n-pentane (○).

Table 5. Parameters derived from linear plots of the type shown in fig. 1

alkane	gradient/10^3 dm^3 mol^{-1}	$k_8/(k_3+k_4)$
ethane	2.5 ± 0.1	0.14 ± 0.01
propane	3.1 ± 0.2	0.17 ± 0.01
n-butane	3.6 ± 0.2	0.20 ± 0.01
n-pentane	4.0 ± 0.2	0.22 ± 0.01

propane and n-pentane systems are shown in fig. 1. As expected these are linear and pass through the origin. A similar plot for the n-butane system was obtained but this is not shown in fig. 1 since these data crowd between the propane and pentane plots. Values of the rate-constant ratio $k_8/(k_3+k_4)$ derived from the gradients of the least-mean-squares lines fitted to these data are given in table 5. The error limits are one standard deviation. The data in table 5 show that as R increases in size, under our conditions its reaction with O_2 is favoured over its reaction with NO_2.

The results can also be used to derive values for the relative reactivities of O_2 and NO_2 at the primary and secondary radical centres of the R species. For reaction at the primary centres the equation is

$$\frac{k_8(1)[O_2]}{\{k_3(1)+k_4(1)\}[NO_2]} = \frac{[1\text{-}RNO_3'] + [\text{aldehyde}]}{[1\text{-}RNO_2]+[1\text{-}RONO]+[1\text{-}RNO_3'']}$$

where $k_8(1)$, $k_3(1)$ and $k_4(1)$ refer to the rate constants for reactions (8), (3) and (4), respectively, at a primary carbon atom. A similar equation may be written in terms of rate constants $k_8(2)$, $k_3(2)$ and $k_4(2)$ for the reactions at secondary carbon atoms, involving ketone rather than aldehyde concentrations. Plots of the right-hand side of this equation [denoted as $\Sigma P(A)/\Sigma P(B)$] against $[O_2]$ at constant $[NO_2]$ proved to be linear, as exemplified by the data for n-butane shown in figure 2. The rate constant ratios derived are shown in table 6. In the case of n-pentane where separate measurements of aldehyde and ketones were not made, it was assumed that the ratios [aldehyde]/[ketones] and $[1\text{-}RNO_3]/([2\text{-}RNO_3]+[3\text{-}RNO_3])$ would be equal: this is of small significance since the combined aldehyde and ketone were only 10% at most of the alkyl nitrates in relative yields.

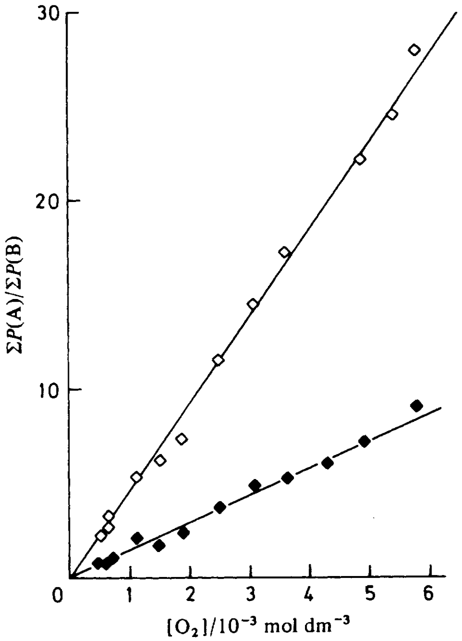


Fig. 2. Plots of $\Sigma P(A)/\Sigma P(B)$ (see text) against $[O_2]$ for $H_2O_2+NO_2+$n-butane$+O_2$ systems for 1-substituted (◆) and 2-substituted (◇) products and the same conditions as specified under fig. 1.

The data in fig. 2 and table 6 show that primary and secondary radical centres have distinctly different relative reactivities to O_2 and NO_2, O_2 being significantly favoured over NO_2 for reactions at a secondary carbon as compared to a primary carbon. Also, although separate data for the 2- and 3-positions in n-C_5H_{11} were not derived, the increased average value of $k_8(2)/[k_3(2)+k_4(2)]$ for n-pentane compared with those for propane and n-butane in table 6 may suggest that O_2 reaction at the 3-position is even more favoured over NO_2 reaction there than is the case for the 2-position. These trends might invite the simple interpretation that the larger NO_2 experiences a larger increase in steric hindrance than does the smaller O_2 when going from reaction at a primary to a secondary position. However, other factors may be involved.

Table 6. Ratios of rate constants $r(n) = k_8(n)/[k_3(n)+k_4(n)]$ for specific alkyl radicals (R) at 298 K

R	$10^2\,r(1)$	$10^2\,r(2)$
$1\text{-}C_3H_7$	7.6 ± 0.4	
$2\text{-}C_3H_7$		23 ± 1
$1\text{-n-}C_4H_9$	6.8 ± 0.3	
$2\text{-n-}C_4H_9$		22 ± 1
2- and $3\text{-n-}C_5H_{11}$		27 ± 1

There are no absolute values of k_3 and k_4 available and very few for k_8, so that comparison of our rate-constant ratios with literature values is not possible. Values of k_8 (second-order limiting) have been determined for $R = C_2H_5$ and values of $k_8(1)$ and $k_8(2)$ for $1\text{-}C_4H_9$ and $2\text{-}C_4H_9$, respectively. For C_2H_5 a measured mean value of 4.2×10^9 dm^3 mol^{-1} s^{-1} [9] and an extrapolated estimate of *ca.* 2.7×10^9 dm^3 mol^{-1} s^{-1} [8] come from the literature. The latter and more recent value, when combined with our rate-constant ratio, gives $(k_3+k_4) \approx 2.0 \times 10^{10}$ dm^3 for ethyl radicals. For $n\text{-}C_4H_9$ the literature values[10] are $k_8(1) = (4.5 \pm 0.8) \times 10^9$ dm^3 mol^{-1} s^{-1}, combining with our ratio to yield $k_3(1)+k_4(1) = (7.2 \pm 1.6) \times 10^{10}$ dm^3 mol^{-1} s^{-1}, and $k_8(2) = (1.0 \pm 0.1) \times 10^{10}$ dm^3 mol^{-1} s^{-1}, which yields $k_3(2)+k_4(2) = (4.9 \pm 0.7) \times 10^{10}$ dm^3 mol^{-1} s^{-1}. These absolute values show no obvious trends.

The mechanism by which the RO_2 radicals are converted to alkyl nitrates and carbonyl compounds in our systems is not clear. There are several possibilities but none is entirely consistent with all of the information available in the literature. We examine each in turn.

Under the conditions in our systems the RO_2 radicals will react overwhelmingly with NO_2 since any potential reaction channels with O_2 are strongly endothermic so that the corresponding rates at ambient temperature will be small. Three possible reaction channels with NO_2 are (using $R'CH_2O_2$ to denote the alkylperoxy radical):

$$R'CH_2O_2 + NO_2 \rightarrow R'CH_2OONO_2 \tag{9a}$$

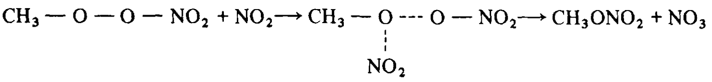
$$\rightarrow R'CHO + HONO_2 \tag{9b}$$

$$\rightarrow R'CH_2O + NO_3 \tag{9c}$$

where $R'CH_2O$ denotes an alkoxy radical. Previous studies of reaction (9) have concerned methylperoxy radicals only. Spicer *et al.*[3] have found that for CH_3O_2 channel (9*a*) accounted for 75 ± 5% of reaction (9) and channel (9*b*), leading to HCHO formation, accounted for 20 ± 10%. On this basis it would be surprising if channel (9*a*) did not play a major role in the case of higher alkylperoxy radicals while the occurrence of channel (9*b*) could account for the formation of the carbonyl compounds.

However, the evidence for the significant occurrence of channel (9*c*), generating alkoxy radicals which would be expected to combine with NO_2 to yield alkyl nitrates, is more controversial and is discussed later.

Despite the likely importance of channel (9*a*), alkyl peroxynitrates are not found as final products in our systems, just as was the case in the other studies[3,4] on CH_3O_2 radicals. In all cases alkyl nitrates are the major products. There is no doubt that some alkyl peroxynitrates are reasonably stable at ambient temperatures. Niki *et al.*[11] found that CH_3OONO_2 had a lifetime > 30 min, but, perhaps of significance for our work, this lifetime was more than halved if the reactor walls had not been conditioned. Spicer *et al.*[3] suggested that CH_3OONO_2 could react with NO_2 directly as follows:



$$CH_3-O-O-NO_2+NO_2\longrightarrow CH_3-\underset{\substack{\vdots\\ NO_2}}{O}\cdots O-NO_2\longrightarrow CH_3ONO_2+NO_3 \qquad (10)$$

However, in the system used by Niki *et al.*[11] NO_2 was present and this suggests that the above reaction cannot occur at a significant rate. Simonaitis and Heicklen[4] have also produced results which they interpreted as contrary to the occurrence of reaction (10) and of (9*c*), but the system which they used was complex and their interpretation is open to a number of criticisms[12] so that we consider that their work must be taken as being inconclusive in this respect. In particular the production of NO from NO_2 photodissociation and its effect on the reaction system were not accounted for fully in that work.

If $ROONO_2$ is transiently stable, the equilibrium

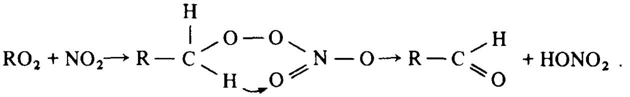
$$RO_2+NO_2 \rightleftharpoons ROONO_2$$

should be established in our system. For $C_3H_7OONO_2$ decomposition a rate constant of 1.9 s^{-1} at 300 K has been derived.[13] The activation energy was 83 kJ mol^{-1}, which is similar to the activation energy for $HOONO_2$ dissociation of 87 ± 2 kJ mol^{-1} measured by Graham *et al.*[14] These values will correspond roughly with the O—N bond strength and are likely to be applicable approximately to other alkyl peroxynitrate decompositions. Since the pre-exponential factors are not likely to vary greatly with R, we can therefore expect decomposition rate constants of the order of 2 s^{-1} for the other alkyl peroxynitrates. Adachi and Basco[15] have measured a rate constant of $(7.5 \pm 0.4) \times 10^8$ $dm^3\ mol^{-1}\ s^{-1}$ at ambient temperature for the reaction of $C_2H_5O_2$ with NO_2, which appears to be the only such data available. Again it would be surprising if this rate constant varied greatly with R in RO_2. At the concentration of NO_2 in our systems we therefore expect a pseudo-first-order rate constant for the reaction of RO_2 with NO_2 of the order of 4×10^4 s^{-1}. On the basis of the above rate constants we expect the above equilibrium to be established on a timescale of seconds with a concentration ratio of $[RO_2]/[ROONO_2]$ of the order of 5×10^{-5}.

The establishment of this small steady-state concentration of RO_2 provides the opportunity for reactions (9*b*) and (9*c*) to assume importance despite the much greater rate of (9*a*). As noted before, Spicer *et al.*[3] have shown that for CH_3O_2 channel (9*b*) is more important than channel (9*c*). In our work the yields of $RONO_2'$ are much greater than those of the carbonyl compounds, suggesting that the reverse is true for the higher RO_2 radicals. The feasibility of this suggestion depends on the rate parameters of channel (9*c*): Cox *et al.*[12] have considered this question for CH_3O_2. They concluded that the pre-exponential factor is likely to be *ca.* 2×10^9 $dm^3\ mol^{-1}\ s^{-1}$, but the endothermicity and hence the activation energy of channel (9*c*) is very uncertain, 28 ± 27 kJ mol^{-1} being quoted. If in fact the activation energy were as low as

10 kJ mol^{-1} then the rate constant k_{9c} is *ca.* 4×10^7 dm^3 mol^{-1} s^{-1} at ambient temperature, and under our conditions this leads to a pseudo-first-order rate constant for $ROONO_2$ removal through channel (9*c*) of *ca.* 0.1 s^{-1}. Upon integration of the relevant rate equation the time then required for 99% removal of the $ROONO_2$ *via* channel (9*c*) is *ca.* 50 s. The timescales in our flow system are *ca.* 70 s in the flowtube and some 500 s in the sampling system. On the basis of these times, the minimum value of k_{9c} compatible with channel (9*c*) being effective in removing $ROONO_2$ corresponds to an activation energy of *ca.* 17 kJ mol^{-1}. Channel (9*c*) could not be effective for the production of alkyl nitrates if its activation energy approached the mean value of the endothermicity deduced by Cox *et al.*[12] for CH_3O_2. However, it must be borne in mind that transformation of $ROONO_2$ on a timescale of the order of 10 min as required in our system does not seem compatible with the lifetime in excess of 30 min found for CH_3OONO_2 by Niki *et al.*[11] despite the different conditions of the experiments. Thus the evidence for the occurrence of channel (9*c*) is inconclusive.

Carbonyl compounds are found in our products, suggesting the occurrence of channel (9*b*). The yields of such products show a clear trend, decreasing in importance as the size of R increases. This could reflect the stabilizing effect of R on an energized intermediate in a process such as follows:



However, an alternative mechanism for the formation of carbonyl compounds needs to be considered if alkoxy radicals do in fact exist in the system [from channel (9*c*)]. An alkoxy radical (RCH_2O) can react with O_2

$$RCH_2O + O_2 \rightarrow RCHO + HO_2 \qquad (11)$$

and reaction (11) will be in competition with the step forming alkyl nitrate

$$RCH_2O + NO_2(+M) \rightarrow RCH_2ONO_2(+M) \qquad (12)$$

Cox *et al.*[12] studied the reactions of CH_3O corresponding to reactions (11) and (12), finding a rate-constant ratio of $k_{11}/k_{12} = 1.25 \times 10^{-4}$ at 298 K. In our systems the maximum $[O_2]$ is *ca.* 7×10^{-3} mol dm^{-3} and with $[NO_2] = 5.5 \times 10^{-5}$ mol dm^{-3}, reaction (12) would be *ca.* 60 times faster than reaction (11) if CH_3O were concerned. It therefore seems unlikely that for C_2H_5O under the same conditions, reactions (11) and (12) could have rates only differing by a factor of *ca.* 2, as required if reaction (11) is to be regarded as the sole source of the acetaldehyde yields shown in table 1. On the other hand, other values of k_{11}/k_{12} required to explain the yields of carbonyl compounds relative to alkyl nitrates on the basis that both originate solely from alkoxy (RO) are not unreasonable in comparison with that for CH_3O above: values of *ca.* 4×10^{-4} for $R = 2\text{-}C_3H_7$ and *ca.* 8×10^{-4} for $R = 2$- or $3\text{-}C_5H_{11}$ could be used to interpret data in tables 2 and 4. Moreover, it is of great significance that in tables 1–4 the yields of RNO_3' at the highest $[O_2]$ are always slightly lower than those at an intermediate $[O_2]$. This must indicate that the reaction of a precursor species to RNO_3' with O_2 is of significance. In the cases of R larger than C_2H_5 it must be likely that the species concerned is RO, which appears to be the only one with a known reactivity towards O_2. Nevertheless it seems unlikely that reaction (11) could be the only source of carbonyl compounds in our systems, particularly in the case of ethane.

One other possible route to the alkyl nitrate is through the mutual reaction of RO_2 radicals:

$$RO_2 + RO_2 \rightarrow 2RO + O_2. \qquad (13)$$

Reaction (13) was proposed to be significant in the decomposition of nitroperoxypropyl nitrate by Bandow *et al.*[16] If the RO_2 radicals (in equilibrium with $ROONO_2$) were distributed homogeneously in our bulk gas the value of $[RO_2]$ would not be sufficiently high for reaction (13) to compete with channel (9*b*) or (9*c*): however, as discussed in Part 1 of this series,[1] OH and hence R and possibly RO_2 are generated in a very thin layer of the gas phase close to the flowtube walls, so that local concentrations of RO_2 could be high in conjunction with depleted concentrations (compared with the bulk gas) of NO_2 in this boundary layer, both factors tending to promote reaction (13). However, there is sufficient information in the literature on the mutual reactions of alkylperoxy radicals to show that, in the cases concerned here, these would lead to quite different product distributions from those found in our work.

For $R = 2\text{-}C_3H_7$ it has been shown that the two main channels are as below:[17]

$$2(CH_3)_2CHO_2 \rightarrow (CH_3)_2CHOH + (CH_3)_2CO + O_2 \qquad (13a)$$

$$\rightarrow 2(CH_3)_2CHO + O_2 \qquad (13b)$$

with a rate-constant ratio $k_{13a}/k_{13b} = 0.72$ at 303 K. In our system the alcohol from channel (13*a*) would react rapidly with NO_2, as established for other alcohols,[18] leading to large yields of the nitrite *via* the equilibrium represented by

$$ROH + 2NO_2 \rightleftharpoons RONO + HNO_3.$$

In table 2 the acetone yield is small compared with the nitrate and there is little nitrite formed, both contradicting the significant occurrence of reaction (13).

The mutual reaction of $n\text{-}C_4H_9O_2$ radicals follows one main pathway:[19]

$$2n\text{-}C_4H_9O_2 \rightarrow n\text{-}C_3H_7CHO + n\text{-}C_4H_9OH + O_2.$$

The product yields in table 3 are totally incompatible with this as they show only small yields of carbonyl compounds. Thus we conclude that mutual reactions of RO_2 radicals are not significant under our conditions.

Finally, the conversion of the alkylperoxy nitrates to alkyl nitrates could be occurring by a heterogeneous process in our flow system. As mentioned before, Niki *et al.*[11] showed that the lifetime of the CH_3OONO_2 produced in their system depended upon the conditioning of the Pyrex walls of their reaction vessel. We have never observed any contribution of wall reactions, other than the initiating reaction (1), in this or previous work. Moreover, boric-acid-coated surfaces in higher-temperature systems are considered to have low activities for heterogeneous reaction of peroxy species. Nevertheless we have no positive evidence to preclude the possibility.

In summary then we find, in common with the other studies which have been mentioned, that the generation of RO_2 radicals in the presence of NO_2 leads predominantly to the formation of alkyl nitrates. It seems extremely probable that the reaction between RO_2 and NO_2 forms $ROONO_2$ in its initial stages. The most likely homogeneous process for the formation of the alkyl nitrates must be reaction between RO_2 and NO_2 *via* channel (9*c*) and hence through the alkoxy radicals as intermediates: in the case of $R = CH_3$ this was suggested by Cox *et al.*,[12] but there is little positive evidence for this. The only alternative seems to be the possibility of a heterogeneous process.

J. M. C. thanks the S.E.R.C. for the award of a CASE studentship, during the course of which this work was performed. We also thank Interox Chemicals Ltd for gifts of hydrogen peroxide solution and for their interest in the work.

[1] Part 1. G. J. Audley, D. L. Baulch and I. M. Campbell, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 599.

[2] Part 2. D. L. Baulch, I. M. Campbell and J. M. Chappel, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 609.

[3] C. W. Spicer, A. Villa, H. A. Wiebe and J. Heicklen, *J. Am. Chem. Soc.*, 1973, **95**, 13.

[4] R. Simonaitis and J. Heicklen, *J. Phys. Chem.*, 1974, **78**, 2417.

[5] G. J. Audley, D. L. Baulch and I. M. Campbell, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 2541.

[6] G. J. Audley, D. L. Baulch and I. M. Campbell, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 1237.

[7] R. R. Baldwin, I. A. Pickering and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 2374.

[8] I. C. Plumb and K. R. Ryan, *Int. J. Chem. Kinet.*, 1981, **13**, 1011.

[9] D. D. Dingledy and J. G. Calvert, *J. Am. Chem. Soc.*, 1963, **85**, 856.

[10] T. Lenhardt, C. E. McDade and K. D. Bayes, *J. Chem. Phys.*, 1980, **72**, 304.

[11] H. Niki, P. D. Maker, C. M. Savage and L. P. Breitenbach, *Chem. Phys. Lett.*, 1978, **55**, 289.

[12] R. A. Cox, R. G. Derwent, P. M. Holt and J. A. Kerr, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 2044.

[13] E. O. Edney, J. W. Spence and P. L. Hanst, *J. Air Pollut. Control Assoc.*, 1979, **29**, 741.

[14] R. A. Graham, A. M. Winer and J. N. Pitts, *Chem. Phys. Lett.*, 1977, **51**, 215.

[15] H. Adachi and N. Basco, *Chem. Phys. Lett.*, 1979, **67**, 215.

[16] H. Bandow, M. Okuda and H. Akimoto, *J. Phys. Chem.*, 1980, **84**, 3604.

[17] L. J. Kirsch, D. A. Parkes, D. J. Waddington and A. Woolley, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 2293.

[18] H. Niki, P. D. Maker, C. M. Savage and L. P. Breitenbach, *Int. J. Chem. Kinet.*, 1982, **14**, 1199.

[19] J. L. Currie, H. W. Sidebottom and J. M. Tedder, *Int. J. Chem. Kinet.*, 1975, symposium no. 1, 477.

(PAPER 3/1000)