

Formation of Organic Nitro-compounds in Flowing H₂O₂ + NO₂ + N₂ + Organic Vapour Systems

Part 2.—H₂O₂ + NO₂ + N₂ + Alkane System

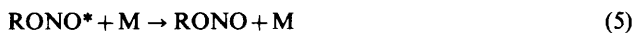
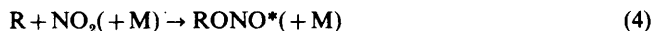
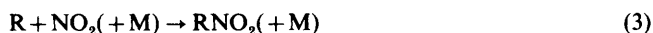
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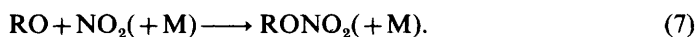
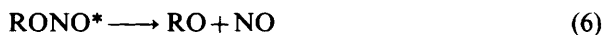
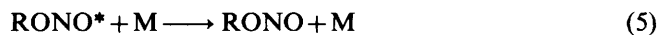
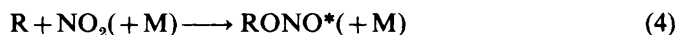
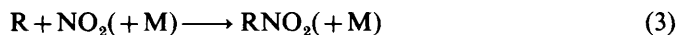
The principal products from the surface-initiated reactions in flowing mixtures of H₂O₂, NO₂, N₂ and RH, where RH = ethane, propane, n-butane and n-pentane, have been identified as the nitroalkane, alkyl nitrite and alkyl nitrate. The product yields have been measured; in the case of propane the variation of the yields with total gas pressure has also been studied.

Values have been obtained for the relative rates of primary and secondary H-atom abstraction from each alkane by OH and for the rate-constant ratios k_3/k_4 and k_5/k_6 at 298 K:



The trends in the product yields with variation of pressure and change of R indicate that RO radicals are produced *via* reactions (4)–(6) rather than by a direct single-step reaction of R with NO₂.

In Part 1 of this series,¹ it was reported that the organic products from the H₂O₂ + NO₂ + C₂H₆ gas-phase reaction system were ethyl nitrate and nitroethane in major yields and a considerably smaller yield of ethyl nitrite. Denoting the alkane as RH, the mechanisms for formation of these products were postulated to involve the following steps:



In the case of RH = C₂H₆, the species RONO* is an energised ethyl nitrite molecule possessing internal energy of ≥ 173 kJ mol⁻¹ and thus subject to dissociation to the ethoxy radical and nitric oxide in competition with collisional quenching. The observation that ethyl nitrate, resulting from combination of the ethoxy radical with

NO_2 , appeared with yields about an order of magnitude greater than those of ethyl nitrite was interpreted as indicating that only a minor fraction of $\text{C}_2\text{H}_5\text{ONO}^*$ species was eventually collisionally stabilised to $\text{C}_2\text{H}_5\text{ONO}$.

In this paper we report measurements of the yields of the organic products for $\text{H}_2\text{O}_2 + \text{NO}_2 + \text{RH}$ systems for $\text{RH} =$ propane, n-butane and n-pentane, incorporating the results for $\text{RH} =$ ethane from the preceding paper. The main interest is the change in the distribution of the products as R increases in size: on the basis of the mechanism postulated above, as the number of bonds in R increases, internal stabilisation of RONO^* might be expected to become more important so that alkyl nitrite yields should increase at the expense of alkyl nitrate yields. Furthermore, if collisional stabilisation of RONO^* is competitive with its dissociation to RO and NO, one would expect that yields of alkyl nitrite should decrease for a particular RH as the total pressure of the system is decreased, with a corresponding increase in the yield of alkyl nitrate.

Another significant aspect of $\text{H}_2\text{O}_2 + \text{NO}_2 + \text{RH}$ systems, which depend upon OH attack on RH, is that the subsequent reactions of NO_2 with R take place at the site at which the hydrogen atom was abstracted from RH. The alkanes used here contain varying relative numbers of primary and secondary hydrogen atoms: by analysis of the proportions of the isomeric products, nitro-substituted in different positions along the carbon chain, relative rate parameters for OH abstraction of primary and secondary hydrogen atoms of RH should be obtainable. This novel approach, based upon product analysis, is complementary to previous methods for obtaining such kinetic information, which have involved measurements of the total rate of disappearance of OH in the presence of an excess of a variety of alkanes.^{2,3} The total rate constants for each RH were expressed as the sum of rate constants for each hydrogen atom in RH, so that absolute rate constants for OH abstraction of a single primary and single secondary H atom in alkanes were derived by solving the set of simultaneous equations over the set of RH species.^{4,5} We compare our relative rate parameters with those predicted by combination of the available absolute values in the literature.

EXPERIMENTAL

The experimental and analytical systems were basically the same as those used for $\text{RH} =$ ethane and described in the preceding paper.¹ The flow system was operated with the series of carrier gases composed of ca. 10% propane, n-butane or n-pentane in N_2 , total flowrates being ca. $70 \mu\text{mol s}^{-1}$. Propane vapour was taken directly from a lecture bottle (B.D.H. Ltd, 99.5% stated purity) and its flowrate was measured on a calibrated capillary flowmeter: n-butane (B.D.H. Ltd, 99% stated purity) was handled similarly. For n-pentane, the liquid (Fisons Ltd, 99% purity) was distilled and the middle fraction was used in a bubbler system held at 273 K by means of an ice bath, with calibrated flows of N_2 used as the pick-up gas. The resultant flowrates of n-pentane were established by diversion of the flow of $\text{N}_2 + \text{C}_5\text{H}_{12}$ through a sampling bulb of known volume. When this bulb was considered to contain a sample of gas representative of the $\text{N}_2 + \text{C}_5\text{H}_{12}$ flow, it was isolated from the flow and the contents slowly pumped through a spiral packed with glass helices maintained at 77 K by liquid nitrogen: upon isolation of the trap, warming and connection to a bulb of known volume, the pressures measured could be used to calculate the n-pentane flowrates.

The yields of the nitro-products were measured by gas chromatography using the procedure as before,¹ modified as follows. The products from all of the systems in turn were frozen down by passage through a trap cooled with liquid nitrogen to 77 K. For propane, most of the alkane was pumped off with the trap maintained at 157 K using a diethylether slush bath. In the cases of n-butane and n-pentane, this procedure was performed with acetone baths of slush at 178 K and cooled liquid at 213 K, respectively. Thereafter the residue was warmed and injected into

the gas-chromatography system as before.¹ In some of the analyses, a column consisting of a 10 m length of fused-silica capillary (0.2 mm i.d.) coated internally with Reoplex 400 was used. This proved satisfactory for alkyl nitrates and nitroalkanes, but the peaks of the alkyl nitrites, which had relatively short retention times, could not be resolved from the tail of the large peak corresponding to residual alkane. A column consisting of a 2 m length of stainless-steel tube ($\frac{1}{4}$ in o.d.) packed with a 20% loading by weight of β , β' -oxydipropionitrile on 60–80 mesh Chromosorb W proved to give satisfactory resolution of all the product peaks, the column being temperature programmed between 20 and 60 °C. The identification and calibration of the product peaks on the chromatograms were performed using injections of known amounts of pure compounds. Standard synthetic methods were used to prepare samples of all of the alkyl nitrite isomers (using the corresponding alcohol and nitrous acid)⁶ and alkyl nitrate isomers (using the corresponding alkyl bromide and silver nitrate in acetonitrile)⁷ with the exception of 1-butyl nitrate for which a commercial sample was used (Pflatz and Bauer). Commercial samples of nitroethane (B.D.H. Ltd), 1-nitrobutane (Fluka) and 1-nitropentane (Fluka) were used. The remaining nitroalkane isomers were prepared from the corresponding alkyl bromide and sodium nitrite in dimethyl sulphoxide.⁸

Hydrogen peroxide vapour was added using N₂ bubbling through the pure liquid maintained at 293 ± 1 K as before.^{1,9} All experiments were performed with a hydrogen peroxide concentration added to the flowtube, $[\text{H}_2\text{O}_2]_0$, of 2.8×10^{-6} mol dm⁻³, with the exception of the experiments with ethane where the concentration was 2.3×10^{-6} mol dm⁻³. Nitrogen dioxide was added using a bubbler system as before,^{1,9} the concentration being maintained at 5.5×10^{-5} mol dm⁻³ throughout. The alkane concentration was 1.6×10^{-3} mol dm⁻³ in all experiments other than those with ethane, where it was 1.5×10^{-2} mol dm⁻³. Most of the experiments were conducted with a total pressure in the flowtube of 40.0 kPa but with propane some experiments were performed at total pressures of 13.3 and 93.3 kPa. The flowtube temperature was maintained at 298 K by means of thermostatted water circulating in an external jacket. The boric acid coating on the internal surface of the tube lining the flow system was the same one used in the preceding experiments with ethane.¹

RESULTS

The products identified, and their yields, for each of the alkanes are given in table 1. In the ethane system the carrier gas was essentially all C₂H₆, whereas in all the other systems the carrier gas, at a pressure of 40 kPa, was N₂ containing 10% of the alkane.

The nitrate yields from pentane and butane are small and may be subject to a systematic error arising from the possible presence of traces of O₂ in the system. In the following paper in this series it is shown that small amounts of O₂ can enhance the nitrate yield at the expense of nitrite. The total product yields indicate that *ca.* 40% of the H₂O₂ produces OH radicals *via* reaction (1). If all of the remaining H₂O₂ were to yield O₂ as a product it would be sufficient to enhance the nitrate yields from the pentane and butane by up to 25 and 30%, respectively. Because the nitrate yields for propane and ethane are so much larger, in these cases any error arising from O₂ at this level is relatively small (< 3 and < 1%, respectively).

The effect of pressure on product yields was studied at three different total pressures for the propane system. The results are given in table 2.

DISCUSSION

For each alkane the total yield of products is in the range 35–39% of the initial H₂O₂ concentration, demonstrating the constancy of the efficiency of the surface in producing OH radicals *via* reaction (1). This step is well established from previous studies.^{9, 10}

The relative amounts of the 1-, 2- and 3-isomers in the products reflect the

Table 1. Major product^a yields from the H₂O₂ + NO₂ + RH + (N₂) system at 298 K

RH	isomer	[RONO] /10 ⁻⁷ mol dm ⁻³	[RONO ₂] /10 ⁻⁷ mol dm ⁻³	[RNO ₂] /10 ⁻⁷ mol dm ⁻³
C ₂ H ₆ ^b	—	0.21 ± 0.06(3) ^c	3.63 ± 0.17(45)	4.06 ± 0.13(50)
C ₃ H ₈	1-	0.76 ± 0.17(7)	0.51 ± 0.05(5)	1.5 ± 0.1(14)
	2-	1.3 ± 0.3(12)	1.7 ± 0.2(16)	5.0 ± 0.5(46)
C ₄ H ₁₀	1-	0.65 ± 0.15(6)	0.03 ± 0.01(0.3)	0.75 ± 0.07(7)
	2-	3.2 ± 0.7(31)	0.29 ± 0.06(3)	5.2 ± 0.5(51)
C ₅ H ₁₂	1-	0.28 ± 0.03(3)	< 0.03	0.57 ± 0.06(6)
	2-		0.14 ± 0.05(1)	3.5 ± 0.4(36)
	3-	3.1 ± 0.3(32)	0.09 ± 0.03(1)	2.0 ± 0.2(20)

^a For each alkane the products also contained traces of the corresponding carbonyl compounds. ^b In the case of C₂H₆, [H₂O₂]₀ = 2.3 × 10⁻⁶ mol dm⁻³, [C₂H₆] = 1.5 × 10⁻² mol dm⁻³ and [N₂] = 8.3 × 10⁻⁴ mol dm⁻³. For all other alkanes [H₂O₂]₀ = 2.8 × 10⁻⁶ mol dm⁻³, [RH] = 1.6 × 10⁻³ mol dm⁻³ and [N₂] = 1.45 × 10⁻² mol dm⁻³. ^c Figures in parentheses are percentages of the total product yields.

Table 2. Effects of pressure and carrier-gas composition on product yields and the rate-constant ratio k_8/k_5 for the H₂O₂ + NO₂ + C₃H₈ + (N₂) system at 298 K

Pressure /kPa	gas composition,		[RONO] /10 ⁻⁷ mol dm ⁻³	[RONO ₂] /10 ⁻⁷ mol dm ⁻³	[RNO ₂] /10 ⁻⁷ mol dm ⁻³	(k_8/k_5) /10 ⁻³ mol dm ⁻³
	[N ₂]/[RH]	isomer				
13.3	2.35	1-	0.44 ± 0.09	0.50 ± 0.02	1.4 ± 0.2	13.9 ± 2.9
		2-	0.73 ± 0.15	1.6 ± 0.2	5.1 ± 0.8	26.4 ± 6.3
40.0	9.0	1-	0.76 ± 0.17	0.51 ± 0.05	1.5 ± 0.1	15.1 ± 3.7
		2-	1.3 ± 0.3	1.7 ± 0.2	5.0 ± 0.5	29.3 ± 7.6
93.3	22.5	1-	0.79 ± 0.16	0.25 ± 0.04	1.4 ± 0.2	13.4 ± 3.5
		2-	1.4 ± 0.4	0.84 ± 0.13	4.9 ± 0.7	25.8 ± 8.4

relative ease of abstraction by OH of the corresponding H atoms in the parent alkane. General formulae for the rate constants of such reactions have been derived in which the overall rate constant for abstraction of H atoms is expressed as the sum of the rate constants for abstraction of the primary, secondary and tertiary H atoms, each term being weighted according to the number of H atoms of a particular type present. Darnall *et al.*⁴ have derived the expression.

$$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 6.08 \times 10^8 n_p \exp(-822 \text{ K}/T) \\ + 1.45 \times 10^9 n_s \exp(-428 \text{ K}/T) + 1.26 \times 10^9 n_t \exp(0 \text{ K}/T)$$

where n_p , n_s and n_t are the number of primary, secondary and tertiary H atoms in the alkane. At 298 K this gives

$$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 3.85 \times 10^7 n_p + 3.45 \times 10^8 n_s + 1.26 \times 10^9 n_t.$$

Table 3. Measured and predicted isomer ratios for OH abstraction from propane, butane and pentane at 298 K

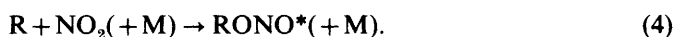
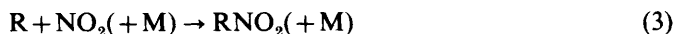
	[1-isomer]/[2-isomer]		[1-isomer]/[2-isomer + 3-isomer] pentane
	propane	butane	
experiment	0.35 ± 0.04	0.16 ± 0.03	0.096 ± 0.010
calculated	0.34	0.17	0.11

Table 4. Values of k_3/k_4 derived from isomer yields at 298 K

RH	isomer		
	1-	2-	3-
C ₂ H ₆	1.06 ± 0.06	—	—
C ₃ H ₈	1.18 ± 0.18	1.59 ± 0.25	—
C ₄ H ₁₀	1.10 ± 0.27	1.45 ± 0.35	—
C ₅ H ₁₂	2.04 ± 0.30	1.67 ± 0.21	

The analogous formulae due to Baldwin and Walker⁵ are almost identical. In table 3 values for the ratios of isomer yields calculated from the above expression are given together with the experimental values. The agreement between the two is excellent.

The yield of nitroalkane is fairly constant (50–62%) over all the alkanes, but closer inspection reveals some differences among the various isomers. The ratio of nitroalkane yield to that of other products reflects the ratio k_3/k_4 for the reactions

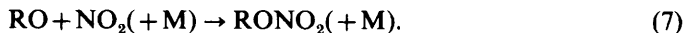


Values of k_3/k_4 derived from the yields are given in table 4. Separate values for the 2- and 3-isomers of pentane could not be obtained because of the difficulty of separately analysing for the 2- and 3-pentyl nitrates. The value of k_3/k_4 quoted in those cases is for the sum of the yields of the 2- and 3-isomers.

With the exception of the 1-isomer of pentane the figures yield a consistent picture with formation of nitroalkane relative to other products being slightly more favoured for the 2- and 3-isomers than for the 1-isomer. On purely statistical grounds (2 atoms of O to 1 of N in NO₂) k_4 might have been expected to be greater than k_3 . That this is not so may reflect small energy barriers in one or both of the reactions. There is no obvious explanation for the apparently high value of the ratio for the 1-isomers of pentane.

At the same total pressure, as the size of R increases, the yields of alkyl nitrites increase at the expense of the alkyl nitrates, the yields of the nitroalkanes being virtually independent of RH (table 1). In the propane system the ratio of nitrate to nitrite decreases with increasing total pressure, while both the nitropropane yield and the relative total yields of the 1- and 2-isomers do not vary significantly with pressure

(table 2). These findings are as expected on the basis of the proposed mechanism. If reaction (7) is the sole fate of the RO radical then the ratio [nitrate]/[nitrite] is given by $k_6/k_5[M]$



At the three pressures used in studying the propane system the composition of [M] varied as shown in table 2. If it is assumed that in reaction (5) the collisional-quenching efficiency of propane is a factor of five greater than that of N_2 , then self-consistent values of k_6/k_5 are obtained as shown in table 2, where k_5 is the rate constant for collisional deactivation by N_2 . The ratio of collisional efficiencies which must be assumed here is slightly larger than the value found experimentally (3.5) in thermal unimolecular reactions¹¹ but not unreasonably so in view of the different nature of the systems.

For collisions between N_2 and $\text{C}_3\text{H}_7\text{ONO}^*$ the collision number may be estimated to be $3 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. N_2 has typically a collision efficiency of 0.1–0.2,^{11,12} suggesting an approximate value of k_5 of $5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and hence, taking k_6/k_5 from table 2, $k_6 \approx 7 \times 10^8 \text{ s}^{-1}$. That such a value of k_6 is reasonable can be demonstrated using R.R.K. unimolecular rate theory. According to R.R.K. theory¹¹ the rate constant for dissociation of the internally excited RONO^* will be given by $k_6 = A[(E - E_0)/E]^S$, where A is the frequency factor for the process, E is the total internal energy contributing to the dissociation, E_0 is the critical energy for dissociation and S is the effective number of oscillators contributing to the reaction. Batt *et al.*¹³ have determined the dissociation energies, $D(\text{RO}-\text{NO})$ for $\text{R} = \text{C}_2\text{H}_5$, $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$ and $s\text{-C}_4\text{H}_9$; they are all very similar ($173 \pm 4 \text{ kJ mol}^{-1}$). For $n\text{-C}_3\text{H}_7$, $D(\text{RO}-\text{NO}) = 167 \text{ kJ mol}^{-1}$. Heats of formation of $n\text{-C}_3\text{H}_7$,¹⁴ $n\text{-C}_3\text{H}_7\text{ONO}^{13}$ and NO_2 give $D(n\text{-C}_3\text{H}_7-\text{ONO}) = 246 \text{ kJ mol}^{-1}$. Thus for $\text{R} = n\text{-C}_3\text{H}_7$, approximate values for E_0 and E are 173 and $246 + 15 \text{ kJ mol}^{-1}$, respectively, the extra 15 kJ mol^{-1} being a contribution to E from the internal modes of RONO , the magnitude of which was estimated from C_v . Values of A for bond-fission reactions lie typically in the range $10^{13}\text{--}10^{17} \text{ s}^{-1}$,¹² we use a value of 10^{15} s^{-1} . In R.R.K. calculations of this kind S usually turns out to be approximately half the number of vibrational modes in the molecule. Taking $S = 16.5$ together with the above values for A , E and E_0 gives $k_6 = 1.3 \times 10^8 \text{ s}^{-1}$. In view of the uncertainties in all of the quantities used at best only an order-of-magnitude agreement could be expected and in that respect the outcome is satisfactory.

The experimental results for $\text{R} = i\text{-C}_3\text{H}_7$ (table 2) give a value of k_6/k_5 a factor of 2 greater than for the $n\text{-C}_3\text{H}_7$. The uncertainties in the thermodynamic data for the species involved, and hence the uncertainties in E and E_0 , are sufficiently large to produce differences of at least a factor of two in the R.R.K. calculation of k_6 .

The ratio [nitrate]/[nitrite] decreases as the size of R increases, reflecting mainly the decrease in k_6 with increase in the size of R. Successive members of the homologous series of alkanes used here differ by a CH_2 group and, in principle, we might expect to be able to analyse the change in terms of the R.R.K. relationship used previously. However, a quantitative comparison is difficult because of (1) the large uncertainties in the small nitrite yields for $\text{R} = \text{C}_2\text{H}_5$ and the small nitrate yields for $\text{R} = \text{C}_4\text{H}_9$ and C_5H_{11} , (2) the possibility of a systematic error in the nitrate yields from butane and pentane and (3) differences in composition of the carrier gas in the ethane case as compared with the other experiments. However, the qualitative picture is quite clear

and in accord with proposed mechanism. As R increases in size the corresponding increase in the number of internal degrees of freedom in RONO*, at a given energy, will increase its lifetime, *i.e.* decrease k_6 . Since k_5 is not greatly changed by the size of R the ratio k_6/k_5 is expected to decrease rapidly as the homologous series is ascended leading to a corresponding increase in the nitrite yield [reaction (5)] at the expense of the nitrate [reaction (6)]. These are the trends found and this, together with the variation of nitrate and nitrite yields with pressure, could not easily be explained if RO formation were by a single-step bimolecular reaction between R and NO₂. A minor contribution from such a pathway cannot be ruled out in every case, but there seems little doubt that the main route to alkyl nitrate production is through formation and redissociation of the excited alkyl nitrite intermediate.

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