A New Method for the Synthesis of Nitroethane, Ethyl Nitrite, and Ethyl Nitrate

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When H_2O_2 vapour and NO_2 are mixed in an ethane carrier in a flow system in the presence of a boric acid-coated surface, ethyl nitrate, nitroethane, and some ethyl nitrite are synthesized; a mechanism is advanced in which OH· and C_2H_5· radicals are the intermediates.

A variety of methods exists for the synthesis of nitroalkanes, alkyl nitrites, and alkyl nitrates[1] but all require the use of a

compound which is a derivative of the parent alkane, such as the alcohol or the alkyl halide, for a one-stage process. Only

in photochemical systems has the direct synthesis of these compounds from the parent alkane been achieved,[2,3] but such systems are inefficient in energy terms. Industrially the production of alkyl nitrates involves conditions of relatively high temperature (370—730 K) and the use of highly corrosive reagents such as nitric and sulphuric acids,[4] so that the processes are expensive in terms of both energy and capital investment.

We report a single stage, gas phase process which operates at ambient temperature to convert ethane into a mixture of nitroethane and ethyl nitrate as the main products, together with a minor amount of ethyl nitrite. This operates with high conversion efficiency in terms of the prime reagent, hydrogen peroxide.

Previous reports from this laboratory[5-8] have described the reaction between H_2O_2 vapour and NO_2 gas, proceeding heterogeneously on the wall of the vessel to yield gas phase hydroxyl radicals in the initial step [equation (1)]. In the

$$H_2O_2 + NO_2 \rightarrow OH\cdot + HNO_3 \qquad (1)$$

earlier work the OH· radicals reacted predominantly with the carbon monoxide which was added to the system. In the present work, instead of CO, a large excess of ethane was added to convert the major part of the hydroxyl radical production into ethyl radicals according to equation (2). The

$$OH\cdot + C_2H_6 \rightarrow H_2O + C_2H_5\cdot \qquad (2)$$

$C_2H_5\cdot$ radicals then reacted overwhelmingly with NO_2 (present in a substantial excess over H_2O_2) to produce a mixture of ethyl nitrate ($C_2H_5ONO_2$), nitroethane ($C_2H_5NO_2$), and some ethyl nitrite (C_2H_5ONO).

The reaction was conducted in a flow system which has already been described in detail.[8] The main carrier gas was ethane, taken from a cylinder (B.O.C., CP grade 99%) without further purification. To this measured flow were added calibrated flows of nitrogen dioxide, taken from a Matheson Co. lecture bottle and purified by bulb to bulb distillation using liquid nitrogen as the refrigerant. The total pressure in the flowtube was ca. 40 kPa. Hydrogen peroxide vapour [carried in a small flow of nitrogen (B.O.C. White Spot)] was derived from the pure liquid.[5,8] The hydrogen peroxide vapour flow was added to the main flow through a jet inset into the flowtube. The tip of the jet, pointing downstream, was located within a lining tube of Pyrex glass (21 mm i.d.), inserted as a close fit into the flowtube and having an inner surface coated with boric acid which is known to promote reaction (1).[6,8]

The reacted gases were sampled by collection in bulbs (ca. 2 dm³ volume) downstream.[8] The contents of the isolated bulb were frozen down by slowly pumping them through a spiral trap maintained at 77 K. The unreacted ethane was removed by raising the temperature of the trap to 195 K using a cardice–acetone bath and pumping it off. The residual products were analysed by gas chromatography (Perkin Elmer, F-11) using a katharometer detector and a Chromosorb 102 column (Perkin Elmer, 6' × 1/8'') operated at 383 K. Peaks on the chromatograms were identified and calibrated

using pure samples of nitroethane (BDH Ltd.), ethyl nitrite (synthesised[9]), and ethyl nitrate (synthesised[10]).

In the experiments in which the carrier gas was ca. 30% CO in N_2, the procedure varied in that the CO_2 produced by the chain propagation cycle [equations (3) and (4)] was collected in the spiral trap maintained at 195 K and directly injected into the chromatograph operating with a column of activated charcoal (6' × $\frac{1}{8}$'').

$$CO + OH\cdot \rightarrow CO_2 + H\cdot \qquad (3)$$

$$H\cdot + NO_2 \rightarrow OH\cdot + NO \qquad (4)$$
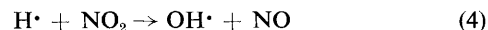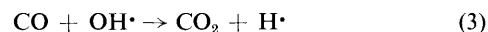
The total flowrate of the gases was of the order of 70 μmol s⁻¹ and the time for plug flow down the 1 m length of the lining tube some 80 s. This is quite adequate for essentially complete reaction since it is believed[6] that step (1) has a half-life of the order of 5 s under our conditions.

Table 1 shows some typical results obtained when the added concentration of hydrogen peroxide, $[H_2O_2]_0$, was maintained at 2.3×10^{-6} mol dm⁻³, $[C_2H_6]$ was 1.5×10^{-2} mol dm⁻³, and $[NO_2]$ was varied in the range (2.0—5.2) ×10⁻⁵ mol dm⁻³. Ethyl nitrite is a comparatively minor product, amounting to only ca. 10% of either ethyl nitrate or nitroethane, the two major products. A slight decrease in the total yield of these products with increasing $[NO_2]$: $[C_2H_6]$ ratio is expected since there is competition for OH· between step (2) and step (5). The sum of the yields in Table 1

$$OH\cdot + NO_2(+M) \rightarrow HNO_3(+M) \qquad (5)$$

is significantly less (43 ± 4%) than $[H_2O_2]_0$. Only ca. 10% of the total amount of OH· radicals produced is removed by reaction (5) under our conditions. However it is known that reaction (1) can proceed at less than 100% efficiency on boric acid surfaces,[6-8] so that the time-integrated yield of OH· radicals from this initial reaction, denoted as $[OH\cdot]_0$, is less than $[H_2O_2]_0$.

To test the efficiency of reaction (1) on the present boric acid surface, we performed a series of experiments with ca. 30% CO in N_2 as the main carrier gas. As described before,[8] when calibrated flowrates of an internal calibrant, S = diethyl ether, are added to the H_2O_2–NO_2–CO–N_2 system, the CO_2 yield from the propagation cycle [steps (3) and (4)] is depressed to an extent dependent upon [S], the rate constant (k_S) for reaction of OH· with S, and $[OH\cdot]_0$ when $[H_2O_2]_0$, $[NO_2]$, [CO], and the total pressure are kept constant. When S is a species like diethyl ether for which k_S is known (from our own work and other reports in the literature[8]), $[OH\cdot]_0$ can be deduced. At ambient temperature and a total pressure of ca. 40 kPa, this procedure yielded a value for the ratio $[OH\cdot]_0:[H_2O_2]_0$ corresponding to 0.45 ± 0.03:1, which is consistent with the total yields shown in Table 1, taking account of the relatively small effect of reaction (5). Such an efficiency of reaction (1) on a boric acid-coated surface lies within the range encountered before.[6,8] Since boric acid surfaces with efficiencies close to 100% have been obtained,[6] it is not unreasonable to expect that the yields shown in Table 1

Table 1. Yields of products in the $H_2O_2 + NO_2 +$ ethane system.

Added concentrations			Product concentrations		
$10^6[H_2O_2]_0$/mol dm⁻³	$10^3[NO_2]:[C_2H_6]$	$10^7[C_2H_5ONO]$/mol dm⁻³	$10^7[C_2H_5ONO_2]$/mol dm⁻³	$10^7[C_2H_5NO_2]$/mol dm⁻³
	1.36	0.35 ± 0.01	3.54 ± 0.18	4.16 ± 0.25
	1.52	0.42 ± 0.02	4.12 ± 0.22	5.42 ± 0.32
2.3	3.54	0.35 ± 0.01	4.09 ± 0.22	4.46 ± 0.27
	3.54	0.34 ± 0.01	4.47 ± 0.24	4.63 ± 0.33
	3.56	0.31 ± 0.01	3.88 ± 0.21	3.40 ± 0.21

could be doubled for the same $[H_2O_2]_0$ with other boric acid surfaces.

We interpret our results on the basis of the mechanism given by equations (6)—(10). The asterisk denotes a C_2H_5ONO species formed by combination and temporarily possessing sufficient internal energy to undergo step (8). We have incorporated step (8) on the basis that it seems unlikely that the combination rate constants for steps (6) and (7 + 7a) could differ by enough to explain the tenfold greater yield of $C_2H_5NO_2$ compared with C_2H_5ONO. Moreover according to Gray,[11] when NO_2 associates through an oxygen atom with an alkyl radical, the product is excited to the extent of some 230—250 kJ mol^{-1} of mainly vibrational energy. The dissociation energy of alkyl nitrites into alkoxy radicals and nitric oxide is 150—170 kJ mol^{-1}, so that a substantial amount of energy must be removed by collisional deactivation [as represented in step (7a)] to stabilise the nitrite species and to allow its appearance as a final product. Thus reaction (7), mainly followed by reaction (8) and thus (10), appears to be the likely explanation of the low yields of ethyl nitrite as compared with those of ethyl nitrate. However we cannot exclude reaction (9) since, by analogy with the corresponding reaction of methyl radicals,[12] this could be expected to have a
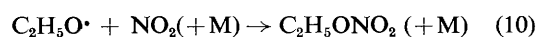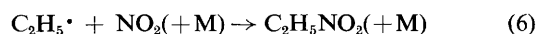
substantial rate constant value at ambient temperatures. Reaction (9) cannot, on the available evidence, be distinguished from the combined effect of reactions (7) and (8).

$$C_2H_5{}^{\bullet} + NO_2(+M) \rightarrow C_2H_5NO_2(+M) \tag{6}$$

$$C_2H_5{}^{\bullet} + NO_2(+M) \rightarrow C_2H_5ONO^*(+M) \tag{7}$$

$$C_2H_5ONO^* + M \rightarrow C_2H_5ONO + M \tag{7a}$$

$$C_2H_5ONO^* \rightarrow C_2H_5O^{\bullet} + NO \tag{8}$$

$$C_2H_5{}^{\bullet} + NO_2 \rightarrow C_2H_5O^{\bullet} + NO \tag{9}$$

$$C_2H_5O^{\bullet} + NO_2(+M) \rightarrow C_2H_5ONO_2 (+M) \tag{10}$$

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