to 7.5×10^6 rads M^{-1} (mean values) were obtained by means of a linear accelerator at the Atomic Energy Research Establishment, Wantage. Degassed samples were irradiated in break-seal tubes. Gaseous products were separated at -196° , -80° and in some cases also at -120° C and analysed by gas chromatography and mass spectrometry. Liquid products were analysed by gas chromatography, infra-red and ultra-violet spectroscopy, and chemical methods (Table 1). The solid residue left after low-temperature distillation was analysed chemically and by ultra-violet absorption spectroscopy in solution.

The production of water in the case of nitromethane was shown by the Carl Fischer reagent and the solid residue was found to contain the *cis* dimer of nitroso-methane. It is possible that the *trans* form could have been carried over with substrate during distillation, but this was not substantiated.

Some of the products quoted were a result of reactions occurring a considerable time after the initial irradiation. The yield of gaseous products from irradiated nitromethane was drastically reduced if after a short irradiation, such as that obtained by using a linear accelerator, the samples were immediately quenched in liquid nitrogen until analysis. Under these conditions $G(N_2)$, 0.19; $G(CO)$, 0.27; $G(NO)$, 0.38; $G(CH_4)$, 0.08; $G(H_2)$, 0.21; $G(CO_2)$, 0.31; $G(N_2O)$, 0.35; $G(CH_3ONO)$, 1.58; $G(C_2H_6)$, 0.09; $G(HCHO)$, 0.32; $G(cis-(CH_3NO)_2)$, 0.43. It was noted that the decrease in gaseous products was accompanied by an increase in the yield of *cis*-nitrosomethane dimer. Allowing the sample to stand at room temperature for varying lengths of time increased the yields of nitrogen, carbon monoxide, carbon dioxide and nitrous oxide up to the limiting values quoted in Table 1. The post-irradiation reaction effects were complete after 5 h at room temperature.

The addition of iodine as a radical scavenger had no detectable effect on the amount of gaseous products. Nitrous oxide, a potential electron scavenger, slightly increased the nitrogen and carbon monoxide yields.

Table 1. PRODUCTS FOUND (APPROXIMATE VALUES)

- (1) From nitromethane, $G(N_2)$, 0.86; $G(CO)$, 0.39; $G(NO)$, 0.34; $G(CH_4)$, 0.095; $G(H_2)$, 0.22; $G(CO_2)$, 0.68; $G(N_2O)$, 0.66; $G(CH_3ONO)$, 1.15; $G(HCHO)$, 0.26; $G(cis-(CH_3NO)_2)$, 0.22. Small amounts of dimethyl ether, methyl nitrite, formaldehyde, water and methanol were also detected.
- (2) From nitroethane, $G(N_2)$, 0.50; $G(CO)$, 0.094; $G(NO)$, 0.08; $G(CH_4)$, 0.02; $G(H_2)$, 0.08; $G(CO_2)$, 0.12; $G(N_2O)$, 0.73; $G(C_2H_6)$, 0.78; $G(C_2H_4)$, 0.18. Ethyl nitrite and acetaldehyde were also detected.
- (3) From 1-nitropropane, $G(N_2)$, 0.74; $G(CO)$, 0.08; $G(NO)$, 0.35; $G(CH_4)$, 0.02; $G(H_2)$, 0.02; $G(CO_2)$, 0.31; $G(N_2O)$, 0.71; $G(C_2H_6)$, 0.54; $G(C_2H_4)$, 0.08; $G(C_2H_2)$, 0.06. Propyl nitrite and propionaldehyde were also present.
- (4) From 2-nitropropane, $G(N_2)$, 1.48; $G(CO)$, 0.04; $G(NO)$, 0.21; $G(CH_4)$, 0.03; $G(H_2)$, 0.15; $G(CO_2)$, 0.13; $G(N_2O)$, 0.07; $G(C_2H_6)$, 1.31; $G(C_2H_4)$, 0.10. Isopropyl nitrite and acetone were also present.

An examination of the decomposition of pure nitromethane was made by the technique of pulse radiolysis using the apparatus developed by Dr. J. P. Keene of the Christie Hospital and Holt Radium Institute, Manchester³. Two absorbing species were found, the spectra of which showed an absorption which increased from 6000 Å as the absorbing wave-length decreased. One of the species decayed by a second-order process, the other seemed to be relatively stable and increased with increasing dose rate and repeated pulsing. The identity of these species has not been definitely established, but it is tentatively suggested that the long-lived material is monomeric nitrosomethane and the shorter lived species is CH_2NO_2 which is removed by a bimolecular acid-base reaction. Owing to the acidic nature of the solvent, the lifetime of the analogue of the hydrated electron in an aqueous medium would be very short-lived.

No simple scheme is capable of explaining the observations and it is not possible to discuss adequately the mechanism here. The nature of the products can be explained in terms of a free radical scheme involving initial production of an alkyl radical and nitrogen dioxide such as that advanced for the photolysis of nitromethane⁴. This is certainly an oversimplification and it is significant

that the proportions of products vary in the photochemical and radiation systems. For example, the low yields of paraffins suggest that primary processes other than homolytic fission are important. Ionic processes which occur in the mass spectrometer⁵ are feasible in the radiolysis of nitromethane; in particular:

Other reactions possible are:

Certainly all the products found can be explained in terms of reactions involving these intermediates.

We thank Dr. J. P. Keene and Mr. K. Melhuish for assistance, the Atomic Energy Research Establishment, Wantage, for use of facilities, and the U.K.A.E.A. for support.

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Improvements in Sensitivities with Flame Ionization Detectors

COMMUNICATIONS following our letter "Safety in Air Separation Plants—Determination of Atmospheric Pollutants by Gas Chromatography"¹ have indicated that some difficulty has been found in obtaining the quoted sensitivities. In order to obtain these detection levels, certain precautions are necessary which are not commonly adopted when using flame ionization detectors.

The use of oxygen in place of the more widely used air for combustion purposes provides about a five- to ten-fold increase in sensitivity, but of at least equal importance is the carrier and combustion gas purity. The carrier gas used throughout our experiments was helium, purified by the titanium-hopealite-molecular sieve train described by Berry², but it should be noted that less expensive argon may be similarly purified. The combustion gases were passed through 12 ft. ($\times 0.25$ in. o.d.) columns of Davison's silica gel, re-activated at regular intervals. The *in situ* generation of electrolytic hydrogen would be a preferred method³. Finally, the signal co-axial connecting cable between the detector and amplifier must be kept scrupulously clean, with all insulators having a resistance in excess of 100 M.ohm. In the present case it was found necessary to clean the signal cable thoroughly every 24 h.

We believe that a more rigorous purification of the combustion gases, in conjunction with improved precautions in order to maintain a high insulation, will improve sensitivity levels even further.

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