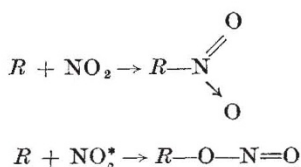


Radiation-induced Nitration of Aliphatic Hydrocarbons

THE behaviour of fission product iodine in a tributyl phosphate-kerosene system for reprocessing pile-irradiated uranium fuels has recently been studied in this laboratory. It was found that the principal mode of fixation of iodine in the hydrocarbon diluent was scavenging by hydrocarbon radicals produced by the action of the fission product radiation. However, it was observed that the *G*-value for fixation under process conditions was only about 0.1. This is very much lower than the values of about 7.0 reported for air-free *n*-heptane¹ and 5.6 for air-free cyclohexane², which are generally accepted as giving some indication of the total yield of radicals in irradiated aliphatic hydrocarbons.

It was considered that other radical scavengers must be present in the process solutions in addition to the iodine. Atmospheric oxygen will certainly be at least partly responsible for the low uptake of iodine; but it was surmised that the nitrogen oxides, always present in radioactive nitrate solutions, may be more important in some cases. The oxides NO and NO₂ both have an 'odd electron' structure and are paramagnetic; they would therefore be expected to combine with alkyl radicals rapidly and with little activation energy requirement. To test this idea, *n*-dodecane containing 10 gm. NO₂/litre was irradiated using a 7.2-c. strontium-90 β-source. The mean radiation dose-rate was 2 × 10¹⁸ eV./ml. hr. and the duration of the irradiation was 114 hr. No special precautions were taken to exclude air. Infra-red spectral examination of the irradiated dodecane showed strong *R*-NO₂ (1,555 cm.⁻¹, 1,350 cm.⁻¹) and *R*-COOH (1,720 cm.⁻¹) bands. Slight absorption peaks at 1,680 cm.⁻¹ and 1,645 cm.⁻¹ were attributed to alkyl nitrite and alkyl nitrate, respectively. Comparison with standard substances showed that the *G*-value for *R*-NO₂, assumed to be nitrododecane, was 5.0. The yield of carboxylic acid, taken as dodecanoic acid, was about 1.0. No change could be detected in a dodecane solution of NO₂ which had been allowed to stand in the absence of radiation for a similar length of time. Carboxylic acid formation is presumably the end result of radical scavenging by atmospheric oxygen: in an earlier experiment, in which the dissolved NO₂ became exhausted, the yield of carboxylic acid was more than doubled.

These results are in good agreement with previous work on iodine scavenging in oxygen-free hydrocarbons^{1,2} and suggest that one of the most important solvent degradation phenomena in highly active tributyl phosphate-hydrocarbon processes may be radiation-induced nitration. It is probable, in NO₂ solutions that are completely devoid of oxygen, that the only products arising from the alkyl radicals will be nitroalkanes together with small amounts of alkyl nitrites, the latter possibly arising from a reaction of alkyl radicals with excited NO₂ molecules:



The radiation chemistry of aliphatic hydrocarbon-nitrogen oxide systems seems to be worthy of further study since information thus obtained should be of considerable value in elucidating organic radiation chemical mechanisms in general, and would provide a unique opportunity of obtaining unequivocal evidence regarding some of the fundamental processes proposed in contemporary theories of aliphatic nitration such as, for example, those reviewed by A. V. Topchiev³.

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Role of Oxygen in the Cross-linking and Degradation of Deoxyribonucleic Acid by Ionizing Radiations

WHEN deoxyribonucleic acid in dilute aqueous solutions is irradiated with X-rays, the attack by the free radicals produced in water leads to main-chain scission, and this reaction is essentially the same in the presence as in the absence of oxygen¹. Irradiation of nucleic acid in the solid state and containing less than 25 per cent of water leads to a complex series of reactions which, judged by physico-chemical measurements, were largely unaffected by oxygen. With nucleic acid gels having a water content between these two extremes, oxygen was found to exert a pronounced influence on the changes produced by irradiation with 1-MeV. electrons. Since deoxyribonucleic acid is present in the cells in the form of a relatively concentrated gel, the response to radiation in this form is more likely to be of biological significance than the behaviour of dilute solutions or nearly dry solid.

The nucleic acid used in these gel experiments was obtained from salmon sperm, contained little salt (less than 3 per cent sodium acetate) and was free from protein (less than 0.02 per cent). Its molecular weight was 10⁷ and its physico-chemical properties have been described in detail (see ref. 2). The molecular weight (determined by light-scattering) of nucleic acid in the dry or nearly dry state initially falls on exposure to 1-MeV. electrons to about two-thirds of its starting value and then increases again, while the intrinsic viscosity falls continually with dose. From these and other data, Alexander, Lett, Moroson and Stacey³ concluded that irradiation produced