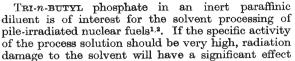
Radiolysis of Tri-n-butyl Phosphate



on plant efficiency, since it leads to the simultaneous production of di-n-butyl phosphate and mono-nbutyl phosphate. Under certain conditions, these acidic esters exhibit a high complexing power towards plutonium, uranium and some fission-products3. The consequences are poor decontamination of the fuel material and re-

duced efficiency in stages designed to wash back these materials into an aqueous phase.

Experiments carried out in recent years by us have given the following results. Irradiation of pure tri-n-butyl phosphate with 1 MeV. electrons from a Van de Graaff generator gave yields of acid phosphate and gas, the amounts of which were proportional to energy input (Williams, T. F., and Wilkinson, R. W., unpublished work). The acidic material was extracted from the solvent and was shown by infra-red analysis and paper-chromatography⁴ to consist of two acids identified as di- and mono-n-butyl phosphate. The ratio of the yields of the two acids was constant over a wide range of energy deposition. These yields, expressed as molecules per 100 eV. of energy absorbed, were,

G (di-n-butyl phosphate)	—	1.5
G (mono-n-butyl phosphate)	==	0.17
G (gas, volatile at - 196° C.)	8	1.1

This non-condensable gas consisted of 95 per cent hydrogen and 5 per cent methane. The C_2 hydro-carbons were separated at -120° C., and analysis using the Blacet-Leighton technique⁵ indicated a mixture of ethane and ethylene with a total G = 0.2. At higher temperatures (- 70° C.) a mixture of C₃ and C4 hydrocarbons was collected. The solubility of these gases in the solvent caused difficulty in their extraction and some variation in the measured yield, G = 0.4. Higher hydrocarbons may have been present, but could not be extracted by the technique employed. At the high rate of energy input used $(3.5 \times 10^{19} \text{ eV./ml./min.})$, no difference could be detected in the acid yield between irradiations carried out in air and in vacuo.

If, prior to irradiation, tri-n-butyl phosphate was saturated with water to give a solution containing 6.4 wt. per cent of water, a total yield G(di - monon-butyl phosphate) = 0.9 was obtained (Williams, T. F., and Wilkinson, R. W., unpublished work). This decrease in yield cannot be explained simply on the partition of energy absorption by the two components. A sample of water-saturated tri-n-butyl phosphate which had been irradiated to a total dose of 8 \times 10²¹ eV./ml. was also subjected to vapour-phase chromatographic analysis using a Griffin V.P.C. apparatus, type S 18-750. The chromatogram was compared with one obtained from a non-irradiated sample spiked with 5 per cent n-butanol and 5 per cent n-butyraldehyde. The non-irradiated sample gave very clear alcohol and aldehyde peaks. No trace of them could be found in the irradiated sample (Rigg, T., unpublished work). It was concluded that these substances were not major products of the radiolysis of tri-n-butyl phosphate.

The suggestion of Cathers⁶ that a radiation-induced hydrolysis is responsible for the breakdown of tri-nbutyl phosphate is not supported by these findings. The actual mechanism of radiolysis may involve both 'radical' and 'ultimate-molecule' processes, arising from a 'direct' effect caused by energy absorbed by the ester itself.

Tri-*n*-butyl phosphate

$$HO$$

 BuO
 $P \rightarrow O + 'C_4H_8'$ or degradation
products of C_4H_8
 HO
 HO
 BuO
 $P \rightarrow O + 2'C_4H_8'$ or equivalent
degradation
products

It is conceivable that some of the hydrocarbon residue products may contain more than four carbon atoms formed by radical recombination⁷. Our failure to detect these may account for the lack of a stoichiometric balance between the production of the acidic esters and total carbon measured in terms of gaseous products.

We wish to express our gratitude to Messrs. Marchon Products, Ltd., of Whitehaven, who kindly placed the vapour phase chromatography apparatus at our disposal, and to the United Kingdom Atomic Energy Authority for permission to publish this communication.

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Dispersion of the Photoelastic Constants of **Fused Silica**

Among amorphous substances, vitreous silica occupies a favoured place as it consists of a single chemical constituent. A systematic investigation of the dispersion of its photoelastic constants is therefore of great importance. Filon and Harris¹ measured the stress optical coefficient of fused silica over the range of wave-length 4600-6500 A. Although they reported the presence of dispersion of the stress optic coefficient, the results were not conclusive, for the range of wave-lengths studied by them was restricted. The piezo-optic constants q_{11} and q_{12} and the stress

optical coefficient $C \left[= \frac{n^3}{2} (q_{12} - q_{11}) \right]$ have been

measured by us for the range of wave-lengths 2250-5700 A. The specimen of fused silica used in the present experiments was obtained from the Thermal Syndicate, Ltd., England. The values of q_{11} and q_{12}