alkyl radicals[2,5], and not 13·3 gauss as found in this case. (A seven-line spectrum is observed at low temperature with a proton splitting constant of 23·5 gauss[6].) By analogy with the Pr_4NX salts the radical stable at room temperature in irradiated Bu_4NBr is probably a methyl allyl radical (1) $\dot{C}H_2$—(2) CH=(3) CH—(4) CH_3 in which the protons on carbons (1), (3) and (4) have similar splitting constants. The unpaired electron density on carbon (2) is opposite in sign to that on carbons (1) and (3) and will give rise to the observed slight doubling of some of the lines observed in the Bu_4NBr spectrum.

The mechanism of the production of these olefinic radicals on irradiation of tetra-alkyl ammonium halides is not known, but the elimination of olefines when the hydroxides of such tetra-alkyl ammonium compounds are heated is well known[10]. Work on these and similar compounds is being continued and further details will be published shortly.

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1 Fujimoto, M., and Ingram, D. J. E., *Trans. Farad. Soc.*, **54**, 1304 (1958).
2 Smaller, B., and Matheson, M. S., *J. Chem. Phys.*, **28**, 1169 (1958).
3 Cochran, E. L., Adrian, F. J., and Bowers, V. A., *J. Chem. Phys.*, **34**, 1161 (1961).
4 Tench, A. J., *J. Phys. Chem.* (to be published).
5 Ayscough, P. B., and Thomson, C., *Trans Farad. Soc.*, **58**, 1477 (1962).
6 Tench, A. J. (unpublished results).
7 Heller, C., and Cole, T., *J. Chem. Phys.*, **37**, 243 (1962).
8 Fessenden, R., and Schuler, R. H. (to be published).
9 Burrell, E. J., *J. Chem. Phys.*, **32**, 955 (1960).
10 Ingold, C. K., *Structure and Mechanism in Organic Chemistry*, 419 (Cornell, New York, 1953).

A Nitric Oxide Induced Electron Spin Resonance Signal in Polymethacrylates

During investigations into the effect of nitric oxide on various polymers it was discovered that a strong electron spin resonance signal could be induced in a number of them. This effect was initially mentioned earlier[1].

The signal (first differential) shown in Fig. 1 is that obtained when granules of the polymers polyethylmethacrylate, polymethlymethacrylate and poly (*n*-butyl) methacrylate are left in the presence of nitric oxide for a number of days; no change was observed in the signal when the nitric oxide was removed with a vacuum pump. Further electron spin resonance and ultra-violet observations suggest that this signal results from the nitric oxide reacting with the ester side-groups of the polymer. The reaction, which is influenced by the alkyl group, is considered to occur at the double bond of the ester (C=O).

Analysis of the electron spin resonance signal has indicated that it is a mixture of three separate signals, two of these being strong singlets with g values of 2·0047 and 2·0170, and the third being a weak triplet the centre peak of which has a g value close to 2·0047. Shown in Fig. 2 are the two molecular configurations considered responsible for the signal. The configuration of Fig. 2*a* would provide the strong singlet with $g = 2·0047$ whereas that of Fig. 2*b* would provide the other singlet and the weak triplet which are the result of the different orientations which the nitric oxide group can have about the C′O′ bond. Some of these orientations allow an interaction between nitrogen nucleus and the unpaired electron, which gives rise to the triplet, while others, which do not allow

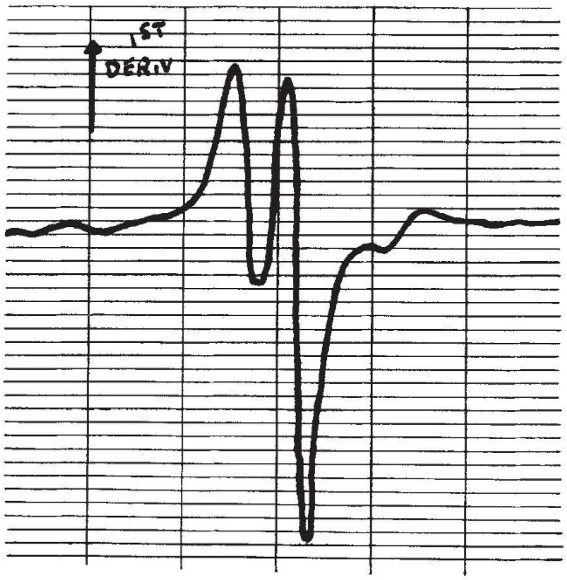

Fig. 1

the interaction, give rise to the singlet. The singlet would be larger than the triplet since the number of orientations which allow this interaction is small.

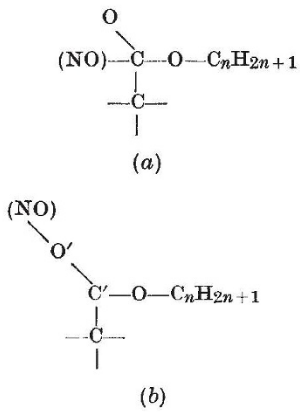

Fig. 2

Effects of Electron Irradiation. Irradiation of the nitric oxide treated polymethacrylates with electrons from an 8-MV linear accelerator has shown that the main chain degradation which normally occurs in these polymers is reduced. The amount of internal protection has been established by viscosity measurements to be 27 per cent for an electron dose of 10^7 rads with lower degrees of protection for higher doses.

A complete account of this work will be published later.

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1 Ebert, M., *Chemical Mechanisms of Some Agents which Modify Biological Radiation Responses: Radiation Effect Milieu*, edit. by Fritz-Niggli, H. (Urban and Schwarzenberg, Berlin, 1962).