

however, there is a marked change, and the current increases with increasing field (curve *b*, Fig. 1). Above 10 kV./cm. the current varies with field as $E^{1.21}$.

Although the equipment used was not designed for mobility measurements, an estimate of the mobility of the negative ion in *n*-hexane can be made from the transient growth of current immediately after switching on the ultra-violet light, and the value so obtained (about 8×10^{-4} cm.²/V. sec.) is in rough agreement with other published data^{2,3}.

The experiments described here show that it is possible to inject an appreciable current into a dielectric liquid without having to subject the liquid to intense radiation. The fact that the current can be confined to the centre of the uniform field region is of great importance in the study of transient phenomena in which electrode edge effects can give rise to appreciable error. Also, the long time decay of current which is observed after the ultra-violet light is switched on would not be important if pulsed illumination were used, and the amount of charge injected into the liquid during the pulse would be considerably greater than that calculated from the magnitude of the steady current.

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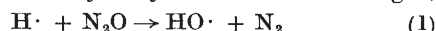
The Importance of Hydroxyl Radicals as Intermediates in the Cross-linking of High Polymers by γ -Irradiation

We have irradiated thin gelatin films (thickness 0.5–1.0 mm.) with cobalt-60 γ -rays at a dose-rate of 4.2×10^4 r. hr.⁻¹ at 10° C. The film was either suspended in a stoppered bottle containing oxygen or nitrogen or immersed in a liquid which filled the bottle. After irradiation of the film, attempts were made to dissolve it in 19 times its own weight of water at 40° C., and the viscosity of any resultant solution was measured. No increase in relative viscosity was observed when the irradiation was carried out in an atmosphere of oxygen or nitrogen, or when the film was suspended in liquid paraffin, benzene, ether, cyclohexanone, pyridine, acetone or an alcohol, even when the dose exceeded 1 mega-roentgen. In the presence of water, however, the gelatin became cross-linked, as was shown by the fact that it was merely swollen by treatment with boiling water.

In a second series of experiments, gels prepared by dissolving 50 gm. of gelatin in 1 litre of water at 40° C. followed by 1 hr. in an ice-bath were irradiated at 10° C. immediately after covering with a layer of an organic liquid. Liquids such as methanol, glycerol and ether markedly reduced the cross-linking in that part of the gel which they had penetrated. These experiments indicate that cross-linking of gelatin induced by radiation is dependent on generation of free radicals by the action of the γ -rays on water, and that these radicals attack gelatine in reactions which probably involve abstrac-

tion of hydrogen atoms, thereby forming free radicals on the gelatin chains which become the cross-linking sites. Any organic liquid present diminishes the cross-linking either by competing with the gelatin for radicals from the water or by interfering with the cross-linking process.

If, as our results suggest, radicals play an important part in radiation-induced cross-linking of polymers, the otherwise anomalous results of Okada, Ito and Amemiya¹ may readily be explained. These authors observed that an atmosphere of nitrous oxide promotes the cross-linking of polyethylene induced by γ -irradiation, whereas an atmosphere of oxygen retards it. Dainton *et al.*² have shown that nitrous oxide reacts rapidly with hydrogen atoms (reaction 1) with formation of hydroxyl radicals and nitrogen,



and it is known that oxygen 'scavenges' hydrogen atoms to form $\text{HO}_2\cdot$ radicals which are likely to be less effective than $\text{HO}\cdot$ radicals in causing cross-linking.

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CHEMISTRY

Prediction of Retention Data in Gas-Liquid Chromatography from Molecular Formulæ

As a result of the introduction of the R_{x_0} method¹⁻³ of presenting gas-liquid chromatographic retention ratios, it has been possible to derive a simple method of predicting retention data from a knowledge of molecular weight and structure. Preliminary investigations have indicated its value in the structural analysis of organic compounds.

The retention index (*I*) of Kovats⁴ is closely related to R_{x_0} by the following expression (ref. 2):

$$I' = \frac{\log R_{x_0}}{b} + 9$$

where I' is $I/100$ and b the slope of the log plot for *n*-paraffins. I' can be interpreted as the carbon number of a hypothetical *n*-paraffin having the same retention as the solute to which I' refers. The formula of the hypothetical *n*-paraffin equivalent to the solute is $\text{C}_{I'}\text{H}_{2I'+2}$ and will have a molecular weight given by $M_e = 14.026 I' + 2.016 = 14.026 \frac{\log R_{x_0}}{b} + 128.25$.

This can be regarded as the 'effective' molecular weight of the solute. We have found the difference between the effective and true molecular weights of the solute (ΔM_e) to be a useful parameter for correlating retention data with chemical structure for the following reasons:

(1) ΔM_e is a conceptually simple parameter having the familiar dimensions of molecular weight.

(2) It is virtually constant throughout a homologous series (Table 1).

(3) It has no, or only a slight linear, variation with temperature (Table 2).

(4) ΔM_e is an additive function of the structural features of a molecule (Table 3) (except when specific group-group interactions occur).