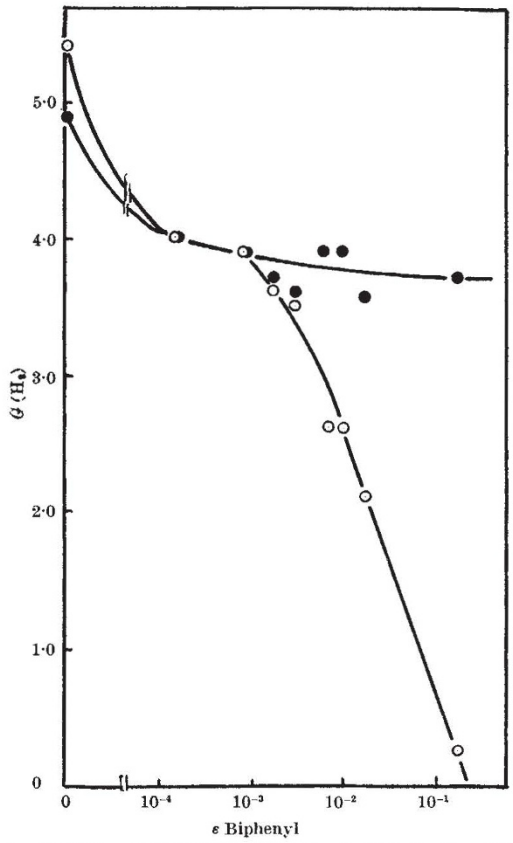

Fig. 1. Hydrogen yields in the radiolysis of mixtures of *cyclo*hexane and biphenyl at 20° C (○) and −196° C (●)

lysis of solid mixtures may provide interesting information as to the influence of structural factors on the energy transfer processes.

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CHEMISTRY

Pressure-programmed Gas-liquid Partition Chromatography

Normal chromatograms of wide-range samples obtained under constant column inlet and outlet pressures give high narrow peaks and low wide peaks at short and long retention times respectively for equal concentrations; this observation is the basis of the theoretical plate value calculation. At longer retention times there is a risk of compounds remaining undetected. Temperature programming has been used to minimize this risk and enables wider range samples to be analysed; this technique also tends to equalize peak widths.

Pressure programming is to increase progressively the inlet pressure of the column during the course of a chromatogram; normally the column exit pressure remains constant at that of the atmosphere. The method is most easily applied to capillary columns and it has the following advantages in addition to those noted above for temperature programming: (1) the column is immediately ready for use at the end of a chromatogram; there is no cooling-off period; (2) reproducible programming of pressure is easier to accomplish than that of temperature; (3) with suitable programming the chromatogram peaks of equal theoretical plate values should have equal widths; therefore the calculation using height times width at half height may be simplified to height measurement alone; (4) for homologous series, the peaks, notably those due to the higher members, become more nearly linearly spaced, thus aiding identification by extrapolation of data.

It is hoped to publish elsewhere the derivation that pressure programming, based on the following equation, leads to the advantages noted above.

$$\text{Log } P = kt + \log C$$

where $k = \dfrac{\log F - \log C}{T}$ and C, F, P are the inlet column pressures respectively at the start, finish and intermediate time, t, of a programme of duration, T.

Chromatograms, recorded under normal and logarithmic pressure programmed conditions, of a petroleum distillate are given in Fig. 1.

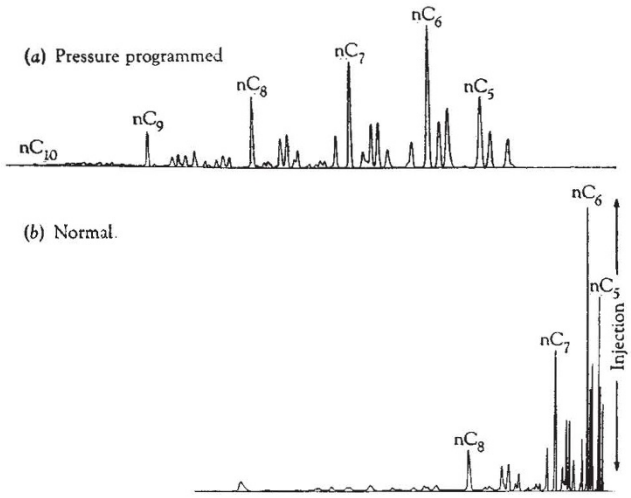

Fig. 1. Chromatograms of a petroleum distillate

I thank Dr. A. Newton for his advice, and Mr. A. L. Godier for constructing the chromatograph.

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Relation between Internal Rotational Barrier and Ionization Energy of Substituent Atoms in Ethyl Halides

A relationship can be found by plotting the potential barrier to internal rotation of ethyl halides against the ionization energy of the substituent halogen atom (Fig. 1). The results are given in Table 1.

The internal rotational barrier values shown in Fig. 1 and Table 1 represent a careful selection from the most recent and reliable microwave and infra-red spectroscopic measurements. The reliability of these chosen barrier values and hence the validity of the relation shown in Fig. 1 have been reaffirmed through our calculations of the

Table 1

Compound	Rotational barrier (cal/mole)	Ionization energy of substituent atom (ref. 6) (eV)
C_2H_5F	3,959 (ref. 1)	17·42
C_2H_5Cl	3,695 (ref. 2)	13·01
C_2H_5Br	3,567 (ref. 3), 3,684 (ref. 4)	11·84
C_2H_5I	3,220 (ref. 5)	10·44