Notes

Structural effects on quantitative gas-chromatographic detector response

Methyl esters of dicarboxylic acids

The use of gas–liquid chromatographic techniques for quantitative analysis implies that the detector responds uniformly to the various compounds to be assayed. Previous work relevant to this assumption has involved the response of thermal detectors[1–4]. The response of the β-ray argon detector has not been studied extensively, although Lovelock[5–7] indicates a trend towards constant sensitivity with increasing molecular weight for several types of organic compounds. It has been predicted that schemes similar to those found for thermal conductivity cells will be necessary if β-ray detectors are to be used for compounds of low molecular weight, with the response leveling off at a constant value on a weight basis at increasing molecular weights[8].

The present study is an investigation of the molar responses of a β-ray argon detector towards the dimethyl esters of the straight chain α,ω-dicarboxylic fatty acids.

Experimental

The gas chromatograph was a Barber-Colman Model 15 with radium ionization detector. The column was 7.5% diethylene glycol adipate on Gas-chrom P, 100–140 mesh. The column temperature was 130°, that of the flash heater 170–220°, and the temperature of the detector 267°. The detector was operated at 750 V, scale 3. The argon flow rate was 24, or 6.7 ml/min. The areas under the peaks were independent of flow rate.

The compounds under investigation were introduced into the column in diethyl ether solution, using Hamilton syringes. Dimethyl malate was used in most of the determinations as an internal standard.

Results and discussion

The molar responses, both absolute and relative (dimethyl malate = 1), show an alternation of peak areas with the number of carbon atoms per molecule; this alternation, however, tends to level off at seven carbon atoms (Fig. 1, A to F). Such alternation of properties with the number of carbon atoms has often been observed in the aliphatic straight chain acids; it has been found for melting points, crystal spacings and solubilities[9]. The dicarboxylic acids also show alternations in the antisymmetric COO^- stretchings of the sodium and copper salts as well as the magnetic moments of the copper salts[10].

The influence of one carboxyl group upon the other for these properties, among the aliphatic acids and their derivatives, is of course most marked in oxalic acid. It drops off with insertion of methylene groups, being fairly strong in malonic acid

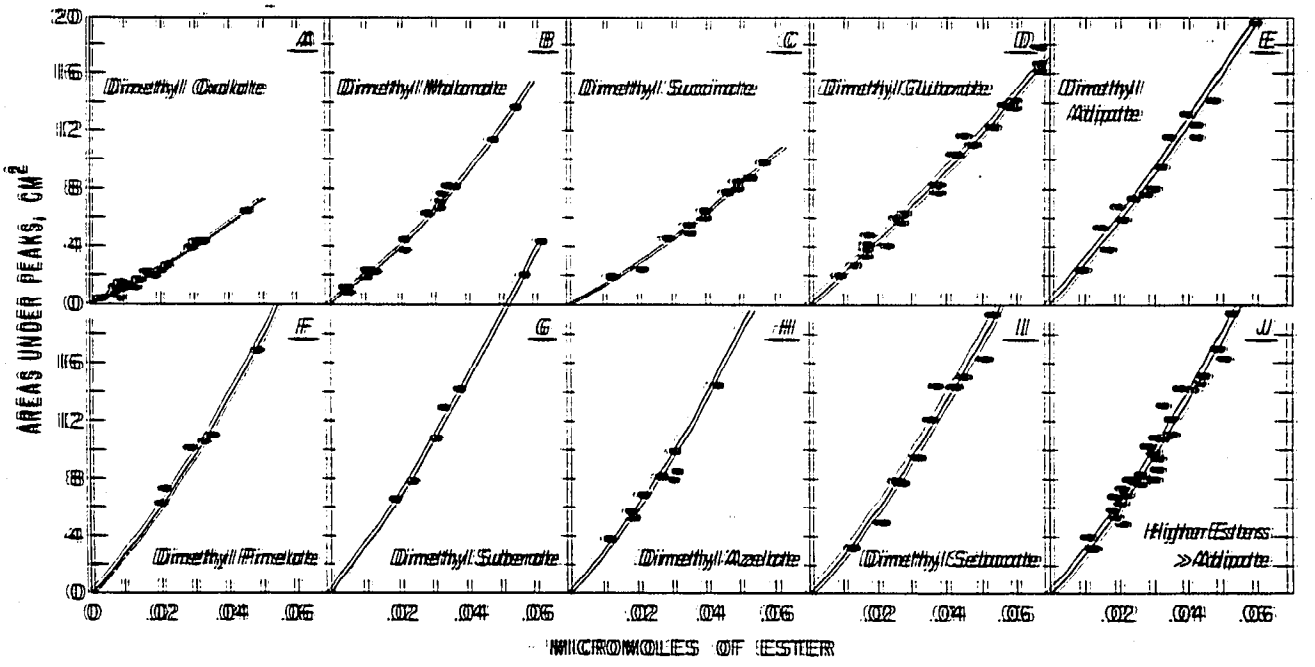

Fig. 1. Detector responses for dimethyl dicarboxylates. Areas under peaks ((cm^2)) as function of μmoles of ester.

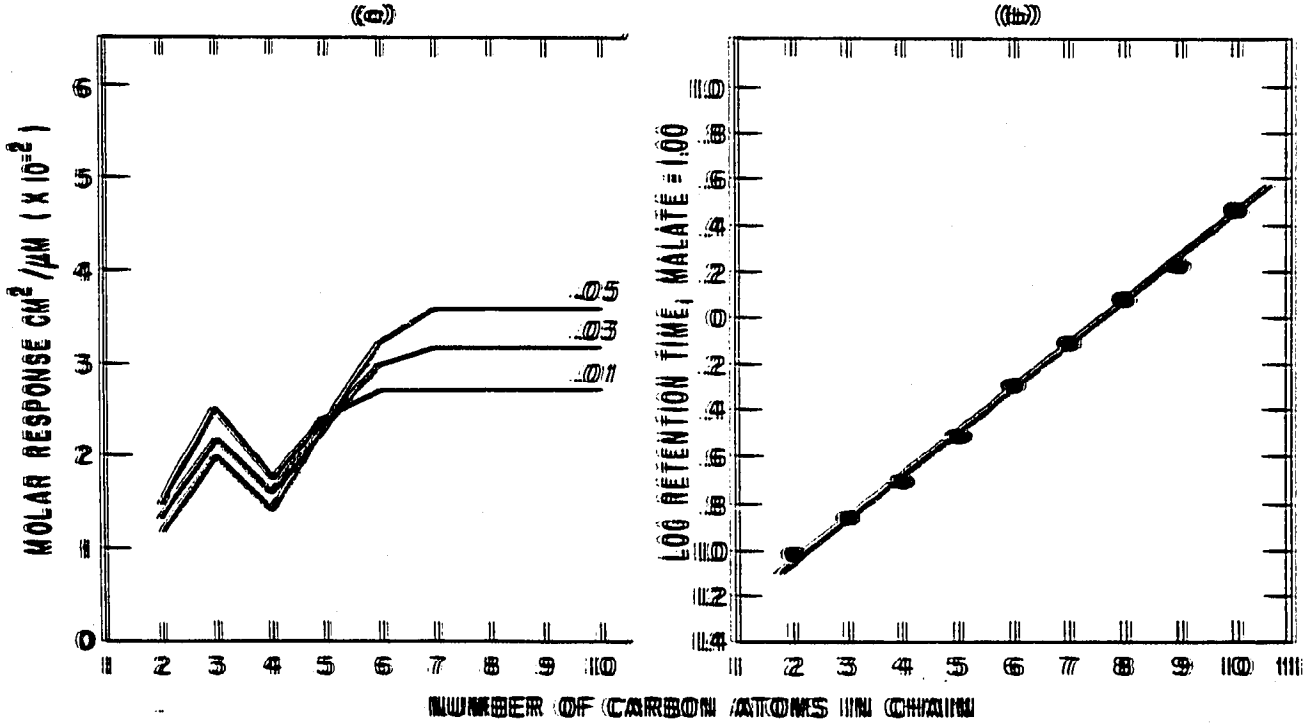

Fig. 2. (a) Alternation of molar responses (cm^2/μmole) with number of carbon atoms in chain, at varying amounts of ester, μmoles. (b) Retention times as function of number of carbon atoms in chain; dimethyl malonate = 1.00.

(one —CH_2—) and still apparent in succinic acid (two —CH_2—); when the functional groups are separated by three or more methylene groups the interaction disappears, probably owing to mutual repulsion of the two groups, which causes the chain to swing into a position allowing maximum distance between the groups. The succeeding members of the series follow a more smoothly changing course.

These effects are borne out in Figs. 1 and 2a. The difference in slopes in the first four esters (oxalate–glutarate) is readily apparent. For esters higher in the series than dimethyl adipate a common curve fits all within experimental error (Fig. 1J). Due to the curvature of the plots, molar responses increase with increasing amounts of ester, but the alternation in response persists up to the highest levels investigated (Fig. 2a).

As might have been expected, the retention times of this series follows the usual semi-logarithmic curve when plotted as a function of number of carbon atoms (Fig. 2b).

The basic cause of these alternations is probably the ionization potential of the molecule, although data to support such an hypothesis are scanty. FIELD AND FRANKLIN[10] list many ionization potentials of organic compounds, but none of the present series. In general, ionization potentials as function of the number of carbon atoms follow a smooth curve without alternations. In the series of the *n*-alkyl benzenes, the ionization potential is slightly lower for toluene than it is for either benzene or ethylbenzene[11], but this may be due to the direct influence of the benzene ring. Mass spectrometric data are available for a limited number of these methyl esters[12]. If the *m/e* value of the most intense peak of the pattern is used as criterion, some indications of similar effects are found. For even values of n ($n = 6, 8, 10, 20$ and 24) *m/e* is relatively low (< 100), while for the single compound listed for which n is odd ($n = 11$), *m/e* equals 152. Thus it is possible, although by no means really proven, that a relationship exists between responses and ionization potential.

Clearly, this possibility of alternations of response should be kept in mind when quantitation of mixtures by gas–liquid chromatography is attempted.

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