

SHORT COMMUNICATIONS

DIELECTRIC ABSORPTION IN METHYL AND ETHYL ESTERS OF LONG-CHAIN ACIDS

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Methyl esters of aliphatic acids have occupied an important position in the study of dielectric absorption in long-chain molecular crystals. They were the first to be studied over a wide frequency range^{1,2} over a range of temperatures.³ These studies showed that methyl esters have two absorptions, one at microwave frequencies, the other in the radio frequency range. The former, which does not depend on the chain-length of the molecule and which is absent⁴ in compounds having the dipole close to the middle of the chain, appears to be due to motion of the end dipole of the molecule. It will not be considered further in the present communication.

The lower frequency absorption is strongly dependent on the chain-length of the molecule. Similar dependence on chain-length is found for the corresponding absorption in ethyl esters.⁴ It is believed that the absorption is due to rotation of the whole molecule, occurring near an imperfection of the crystal lattice.^{5,6}

At present the crystal structures of only these two series of aliphatic esters (methyl esters⁷ and ethyl esters⁸) are known in any detail, so that the two series are critical to discussion of mechanism. They have essentially the same side-by-side packing of chains, but differ in end packing.

Unfortunately the activation energies for these series reported from this Laboratory are of low accuracy, illustrated by the discrepancy between our value for methyl stearate (11 kcal/mole) and a value (12.7 kcal/mole) determined recently by Broadhurst.⁹ The inaccuracy is due mainly to the use of a limited temperature range for the measurements.

It appeared desirable to remeasure these activation energies before attempting deductions from the way in which they vary with chain-length. We have therefore

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¹ Dryden, J. S., and Jackson, W., *Nature*, 1948, **162**, 656.

² Jackson, W., *Nature*, 1949, **164**, 486.

³ Dryden, J. S., and Welsh, H. K., *Aust. J. scient. Res. A*, 1951, **4**, 616.

⁴ Dryden, J. S., and Dasgupta, S., *Trans. Faraday Soc.*, 1955, **51**, 1661.

⁵ Welsh, H. K., *Trans. Faraday Soc.*, 1959, **55**, 52.

⁶ Dryden, J. S., and Welsh, H. K., *Trans. Faraday Soc.*, 1964, **60**, 2135.

⁷ Aleby, S., and Sydow, E. von, *Acta crystallogr.*, 1960, **13**, 487.

⁸ Aleby, S., *Acta crystallogr.*, 1962, **15**, 1248, but see Mathieson, A. McL., and Welsh, H. K., *Acta crystallogr.*, 1965, **18**, 953.

⁹ Broadhurst, M. G., private communication.

remeasured the esters previously reported from room temperatures down to -70°C and have taken the opportunity to extend the range of chain-lengths. Good linear Arrhenius plots were obtained from which the activation energy, ΔE , and logarithm

TABLE I
ACTIVATION ENERGIES OF METHYL AND ETHYL ESTERS
OF LONG-CHAIN ACIDS
 ΔE and ΔE_0 in kcal/mole

Compound	n	ΔE	$\log A$	ΔE_0
Methyl tetracosanoate	26	15.9	17.7	1.7
Methyl docosanoate	24	15.2	17.6	0.8
Methyl octadecanoate	20	12.9	16.5	1.3
Methyl octadecanoate ^a	20	12.7	16.5	1.1
Methyl hexadecanoate	18	11.7	16.3	1.1
Ethyl tetracosanoate	27	17.2	18.6	1.2
Ethyl docosanoate	25	14.8	16.7	1.2
Ethyl octadecanoate	21	12.9	16.6	1.3
Ethyl hexadecanoate	19	11.8	16.2	1.2

^a Broadhurst, M. G., private communication.

of the frequency factor, $\log A$, were determined. These are listed in Table 1, together with the chain-length, n , and the energy gap, ΔE_0 , which was determined from the temperature variation of the intensity.

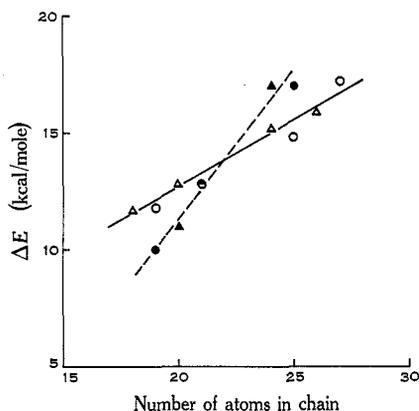


Fig. 1.—Variation of activation energy as a function of chain-length.

Previous work:

▲ methyl esters;³

● ethyl esters;⁴

--- chain-length dependence.

Present work:

△ methyl esters;

○ ethyl esters;

— chain-length dependence.

When plotted as a function of chain-length (Fig. 1) both series lie on the same line, with slope 0.5 kcal/mole/chain atom. Such a relationship had also been suggested by the earlier results¹⁰ but with a distinctly different slope (1.3). The identity of slope for the two series is compatible with the general similarity of chain packing. The fact that both series lie on the same line suggests that end packing has little effect on barrier height.

¹⁰ Dryden, J. S., and Meakins, R. J., *Rev. pure appl. Chem.*, 1957, **1**, 15.

An attempt¹¹ has been made to identify the temperature for maximum mechanical absorption at 1 Hz in a number of normal paraffins with that for dielectric absorption at the same frequency, calculated from the data which have now been corrected. It is remarkable that the revision of the dielectric parameters has little effect on the trend of the calculated temperatures. This insensitivity to major changes in parameters tends to confirm the suggestion¹² that the difference between chain-length dependence of the two sets of temperatures is significant, indicating that different processes are involved.

¹¹ Hoffman, J. D., Williams, G., and Passaglia, E., *J. Polym. Sci. C*, 1966, **14**, 173.

¹² Welsh, H. K., *J. Polym. Sci.*, in press.