Determination of Conformational Volume Changes in Liquid 1-Bromoalkanes at High Pressure by Raman Spectroscopy

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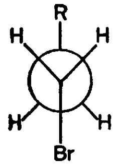
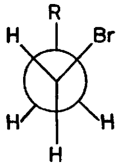
Summary An increase of pressure induces a shift of conformational equilibrium from P_C to P_H conformers in liquid 1-bromoalkanes, and is accompanied by a measurable change in molar volume.

DETERMINATIONS of pressure-induced conformational changes in liquids are few,[1–3] particularly using Raman spectroscopy. In this study we have not only detected a conformational change, but have also measured the associated conformational volume change. The liquids 1-bromobutane, 1-bromopentane, and 1-bromohexane were pressurised in a stainless steel cell having three sapphire windows allowing the collection of 90° Raman scattered light. This equilibrium cell avoids the possible problems of pressure gradient encountered with diamond anvil cells.



P_C



P_H

The two rotational isomers of interest here are designated as P_C and P_H. The ν(C-Br) modes differ significantly for each conformer, occurring in the range 642—645 cm^{-1} for P_C and 564 cm^{-1} for P_H. The integrated intensity under each of these bands, obtained by weighing, was determined over a range of pressures. At each pressure up to ten repeat scans were recorded in order to reduce error. For each liquid the ratio $\log (P_H/P_C)$ was plotted as a function of pressure. The least-squares straight line fits to these data are shown in the Figure. It can be seen that for all three liquids an increase in pressure increases the P_H conformer population. This is consistent with the behaviour of long-chain hydrocarbons,[3] where an increase in the number of *gauche* over *trans* bonds has been observed at higher pressures.

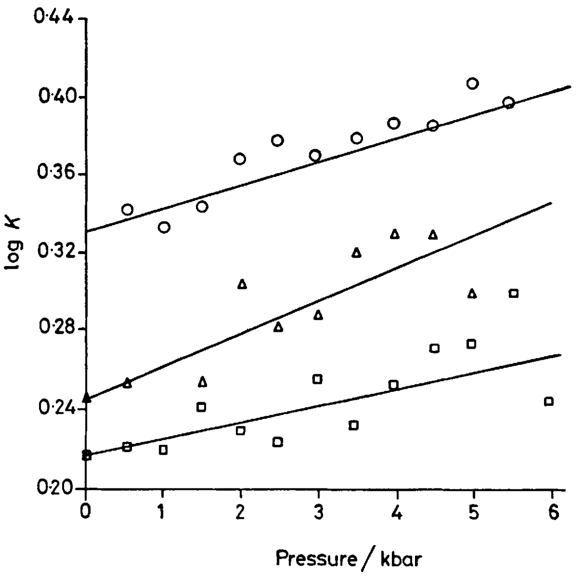


FIGURE. Plots of $\log K$ [$= \log (P_C/P_H)$] *vs.* pressure for (○) 1-bromobutane, (△) 1-bromopentane, and (□) 1-bromohexane.

From the relationship $\Delta V = -RT\,\delta \ln K/\delta P$ the change in molar volume in going from P_C to P_H, *i.e.* the conformational volume change, can be calculated. This assumes that the principal effect of pressure is to induce a conformational change as a result of a difference in molecular volume between the P_C and P_H conformers and that other pressure effects are negligible. The Table presents our results and includes the percentage volume change based upon two methods of calculating the molar volume (i) from the sum of the van der Waals volumes[4] and (ii) from the density.

TABLE

Liquid	ΔV/m^3 mol^{-1} × 10^6	Percentage volume change (i)[a]	(ii)[a]
1-Bromobutane	−7·9 ± 2	1·3 ± 0·3	0·7 ± 0·2
1-Bromopentane	−9·7 ± 3	1·4 ± 0·5	0·8 ± 0·3
1-Bromohexane	−4·6 ± 3	0·6 ± 0·3	0·3 ± 0·2

[a] See the text.

Our results indicate a smaller, yet same order of magnitude change, than that deduced from i.r. measurements on the axial–equatorial *trans*-1,4-dibromocyclohexane system[2] and are also comparable with the −6% molar volume change reported for liquid 1,1,2-trichloroethane *trans* to *gauche* rotation from ultrasonic relaxation measurements.[5] It further appears that the percentage volume changes for 1-bromobutane and 1-bromopentane are similar but that the percentage volume change for 1-bromohexane is smaller. This interpretation assumes however that the principal effect of pressure is to rotate the C(1)–C(2) bond and that the rest of the alkyl chain, being reasonably short, acts as a single unit of constant volume.

Preliminary studies of 1-iodopentane show similar behaviour though in this case the effect of pressure is more marked.

(*Received*, 20*th November* 1980; *Com.* 1242.)

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