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Pressure Effect on Conformational Equilibria of 1,2-Dichloroethane and 1,2-Dibromoethane by Means of Raman Spectroscopy

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Synopsis. The conformational equilibria of 1,2-dichloroethane and 1,2-dibromoethane have been investigated through a study of the pressure and temperature dependences of these materials in pure liquid states. The volume changes estimated here under a trans-gauche transformation of 1,2-dichloroethane and 1,2-dibromoethane are −2.7±0.4 and −5.2±0.5 cm^3/mol, respectively.

Many compounds, as mixtures of conformers, have vibrational modes characteristic to each conformer. Measurements of the quantitative intensity of certain vibrations as a function of the variation in pressure and temperature provided volume and enthalpy differences between the conformers.

In the present work, the enthalpy and volume differences between the trans and gauche conformers of 1,2-dichloroethane and 1,2-dibromoethane in a neat liquid state were determined by means of Raman spectroscopy. The trans conformer of 1,2-dichloroethane and 1,2-dibromoethane has one Raman-active C–X (X= halogene) stretching vibration (A_g species) at 754 cm^{-1} and 658 cm^{-1}, respectively. The gauche form exhibited two bands which were assigned to the symmetric and antisymmetric stretching vibrations, respectively (655 cm^{-1} and 678 cm^{-1} for 1,2-dichloroethane and 522 cm^{-1} and 588 cm^{-1} for 1,2-dibromoethane).[1,2]

The Raman spectra under high pressure were recorded using a Laser Raman Spectrometer consisting of an argon-ion laser (NEC, GLG 3200, 2W) and a Spec 1403 double monochromater. The high-pressure Raman cell used is shown in Fig. 1. This high-pressure optical cell with three quartz glass windows (10×10 mmϕ) is made of stainless steel, SUS 630 (Hitachi PSL stainless steel). The cell is similar to that used by Taniguchi *et al.*[3] Sample liquids were inserted directly into the cell and compressed hydrostatically by a piston (Hand pump. UP-21, Rikenkiki Co., Ltd.) connected to a intensifier (Model 15770-1, manufactured by Haskel Co., Ltd.). The pressure was measured using a Heise precision Bourdon-type guage (Heise Guage, Model CM, manufactured by Dresser Co., Ltd.). This guage works well up to 7.0×10^8 Pa, with a scale graduated to 5×10^5 Pa. The measurements involving pressure effects were carried out at room temperature (about 298 K) for 1,2-dichloroethane, but at 323 K for 1,2-dibromoethane since 1,2-dibromoethane solidifies at about 7×10^7 Pa at room temperature. The spectra were recorded at intervals of about 2.5×10^7 Pa. The temperature dependence of the Raman spectra was also measured at atmospheric pressure. Temperatures ranged from 292 to 363 K. A variable-temperature cell of the Harney-Miller type was used. The spectra were recorded three to five times at each temperature and pressure. The integrated intensities of each band were determined by weighting five Xerox copies of the spectral charts.

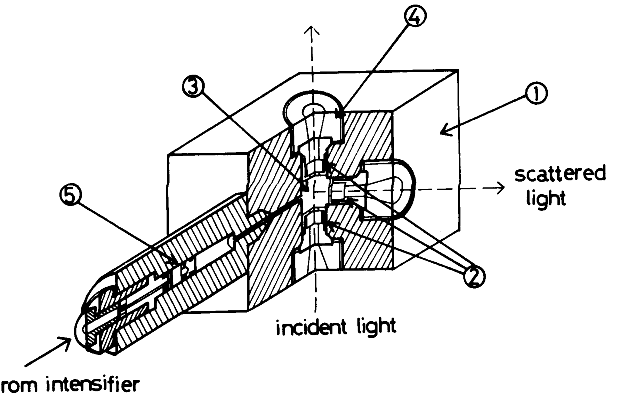

Fig. 1. High pressure optical cell.
1: Pressure bomb, 2: Quartz glass winodw, 3: Sample room, 4: Plug, 5: Piston.

The ratios of the sum of the integrated intensities of the two C–X stretching bands of the gauche form (I_g) to the intensity of the C–X stretching band of the trans form (I_t) were obtained as a function of temperature and pressure.

The enthalpy and volume differences between the two conformers can be estimated by the following equations.

$$\Delta H = -8.31 \times \left(\frac{\partial \ln [I_g/I_t]}{\partial \ln [1/T]}\right)_P \quad [\text{J/mol}] \qquad (1)$$

$$\Delta V = -8.21 \times 10^6\, T\left(\frac{\partial \ln [I_g/I_t]}{\partial P}\right)_T \quad [\text{cm}^3/\text{mol}]. \qquad (2)$$

Figure 2 shows $\ln[I_g/I_t]$ *vs.* P plot for 1,2-dichloroethane. The open circles indicate the paralell components and the solid ones are those for the perpendicular components, using 90° scattering and linearly polarized light. As is seen in Fig. 2, a linear relationship was obtained within the experimental error and the slopes for different polarization components coincide with each other. The volume changes obtained here for the trans-gauche transformation of 1,2-dichloroethane and 1,2-dibromoethane are −2.7±0.4 and −5.2±0.5 cm^3/mol, respectively. The enthalpy differences of 1,2-dichloroethane and 1,2-dibromoethane are 0.0 and 3.6±0.6 kJ/mol, respectively and are in good agreement with those reported previously.[4–6]

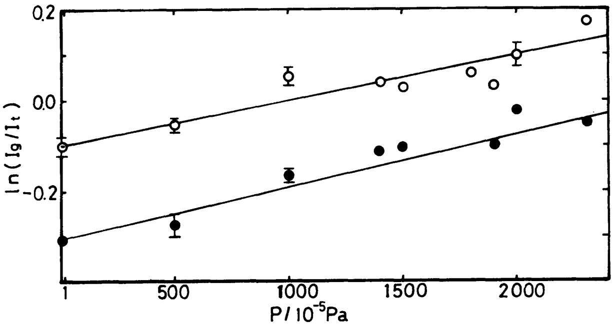

Fig. 2. Relationship between the logarithmic ratio of the integrated intensities of C–Cl stretching bands of *gauche*- and *trans*- 1,2-dichloroethane against the pressure at room temperature.
○: Parallel scattered light, ●: polarized scattered light.

If we assume that $V=M/d$, where d is the bulk density of liquid, the volume change ratios, $\Delta V/V$'s are $-3.4\pm0.5\%$ for 1,2-dichloroethane and $-6.0\pm0.6\%$ for 1,2-dibromoethane. The value of 1,2-dibromoethane is in good agreement with that obtained by ultrasonic work,[7] but that of 1,2-dichloroethane is about a half of the one obtained by their method.[8] At this stage, the discrepancy can not be interpreted.

Devaure and Lascombe,[9] starting from a thermodynamical consideration, derived the following equation for the relation between the enthalpy and volume differences of the conformational equilibria in liquids.

$$\Delta H_{\rm liq} - \Delta H_{\rm gas} = RT^2\left(\frac{\partial f}{\partial T}\right)_p + \Delta V_{\rm liq}\frac{\alpha}{\beta}T \qquad (3)$$

where α and β are the expansion coefficient and isothermal compressibility, respectively and f is $\ln[K/K_0]$, in which K is the equilibrium constant in liquid state and K_0 in gaseous state. They claimed that the first term in Eq. 3 is negligible, as predicted by Pratt-Chandler's theory.[10]

The enthalpy differences of the trans-gauche transformation of 1,2-dichloroethane and 1,2-dibromoethane in a gaseous state, $\Delta H_{\rm gas}$, have been found to be 5.10 and 6.94 kJ/mol (on the average),[4–6] respectively. We can estimate the left hand side of Eq. 3, $\Delta=\Delta H_{\rm liq}-\Delta H_{\rm gas}$, to be -5.10 and -3.34 kJ/mol for 1,2-dichloroethane and 1,2-dibromoethane, respectively. The second term of the right hand side of Eq. 3 can also be calculated, from data on thermal-expansion coefficients[11] and isothermal compressibilities (where isothermal compressibility was calculated from the data of adiabatic compressibility,[12] β_s, heat capacity,[13] C_p, and molar volume, V using the equation of $\beta=\beta_s+\frac{TV\alpha^2}{C_p}$). The values of $\Delta V_{\rm liq}\frac{\alpha}{\beta}T$ were -1.15 and -2.12 kJ/mol for 1,2-dichloroethane and 1,2-dibromoethane, respectively. Comparing the values of Δ with $\Delta V_{\rm liq}\frac{\alpha}{\beta}T$, the first term in the right hand side of Eq. 3 can not be neglected in comparison with the second term, at least in this case, even if taking into account of the experimental errors.

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