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Thermochemical study of the liquid phase equilibrium reaction of dihalomethanes by NMR spectroscopy

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Abstract

The liquid phase equilibrium reaction of dihalomethanes ($2CH_2BrI \rightleftarrows CH_2Br_2 + CH_2I_2$) has been investigated by NMR spectroscopy, as a function of the temperature and initial concentration of the reactants. The equilibrium constants have been experimentally determined for this reaction from the profile of the NMR spectra. Heat capacity measurements were carried out in the temperature range from 293.15 to 353.15 K by differential scanning calorimetry. The results relate the heats of formation of the three compounds and confirm the recently determined heat of formation of CH_2I_2 of 107.5 kJ mol^{-1}.

1. Introduction

The investigation of the thermochemistry of halogenated compounds have recently attracted increasing interest. Halomethane compounds have been found in different environmental media, and are now known to represent an important source of reactive halogens in the oceans as well as in the atmosphere [1–3].

Very limited experimental results on the thermochemistry of halomethanes in solution are available in the literature, due in part to the difficulty in obtaining accurate heats of formation for these compounds via standard calorimetric techniques. The gas phase thermochemistry of halomethanes, on the other hand, has been the object of recent experimental [4] and theoretical [5] investigations. The experimental study by threshold photoelectron photoion coincidence (TPEPICO) spectroscopy [4] suggested that the heat of formation of CH_2I_2 should be reduced to 107.5 ± 2.9 kJ mol^{-1}. Previous literature values were 117.6 ± 8.3 [6] and 119.5 ± 2.2 kJ mol^{-1} [7].

The present work was undertaking to check the self consistency of the TPEPICO study by investigating the equilibrium of the disproportionation reaction ($2CH_2BrI \rightleftarrows CH_2Br_2 + CH_2I_2$). This was carried out by equilibrating initial concentration mixtures in solution at various temperatures and analyzing the concentrations by NMR spectroscopy as a function of the reaction time. In order to determine the standard enthalpy of reaction ($T^0 = 298.15$ K) we have also employed differential scanning calorimetry (d.s.c) experiments to measure reliable solution phase heat capacities for each species in a range of temperatures.

2. Experimental

2.1. Materials

The high purity (>98%) dihalomethane reactants (CH_2Br_2, CH_2I_2, CH_2BrI), $(CH_3)_4NI$ as catalyst, and NMR-grade solvent, acetonitrile-d_3 (CD_3CN), were

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purchased from Sigma–Aldrich and used without further purification.

2.2. Reaction of equilibrium monitoring by NMR

The ^{1}H NMR spectroscopy was employed in the investigation of the liquid phase equilibrium reaction of diluted (~5%) dihalomethanes in CD_3CN solvent, and $(CH_3)_4NI$ as catalyst, over the temperature range from 338 to 353 K. A Bruker Avance 400 MHz wide bore magnet QNP instrument was used for obtaining ^{1}H NMR spectra. The error affecting the areas of the NMR peaks is estimated to be less than 1% [8].

Two mixtures of liquid solutions were prepared and placed into sealed NMR Pyrex cells in approximately 1:3:1 and 2:3:3 (CH_2Br_2, CH_2BrI, and CH2I2, respectively) concentration ratios. The cells were placed in a glycerin bath and maintained at temperatures constant to within ±0.2 K. The cells were removed from bath and quenched in cooled water for several minutes before each NMR measurement. Measurements were performed at different temperatures, $T = 338.15$, 343.15, 348.15 and 353.15 K. This temperature range was dictated by the very slow rate of halogen atom exchange at low temperatures, and the boiling point of the solution at high temperatures.

A differential scanning calorimeter (d.s.c.), Perkin–Elmer DSC-2C, was used to determine the heat capacity values in the range from 293.15 to 353.15 K, using a heating rate of $0.17\ \mathrm{K\,s^{-1}}$, and with a sensitivity of 0.008 W at full scale. The accuracy of the molar heat capacities was estimated between 1% and 2% [9].

3. Results and discussion

The equilibrium reaction for these dihalomethanes in solution is described in Eq. (1). The corresponding equilibrium constant (K_{eq}) have been determined in the usual way (Eq. (2)). This reaction takes place in a dilute and homogeneous liquid medium, so that the solution has properties that resemble those obtained for infinitely dilute solutions.

$$2CH_2BrI \rightleftarrows CH_2Br_2 + CH_2I_2 \quad K_{\mathrm{eq}},\ \Delta_r H_m(\mathrm{l}) \tag{1}$$

$$K_{\mathrm{eq}} = \frac{[CH_2Br_2]\cdot[CH_2I_2]}{[CH_2BrI]^2} = \frac{I_1 \cdot I_2}{I_3^2}. \tag{2}$$

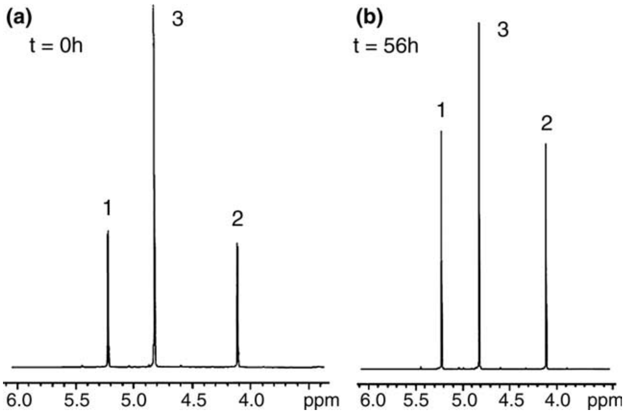

Fig. 1. ^{1}H NMR spectra for CH_2Br_2 (**1**), CH_2I_2 (**2**), CH_2BrI (**3**) in CD_3CN solution at $t = 0$ h (a) at non-equilibrium condition, and at $t = 56$ h (b) after reaching equilibrium at $T = 338.15$ K.

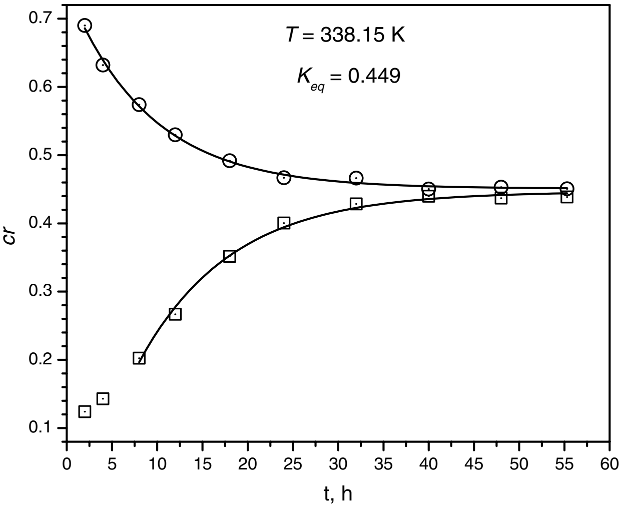

Fig. 2. Evolution of concentration ratio (*cr*) of reaction (1) at $T = 338.15$ K.

The concentration of each species was taken as proportional to the intensity of its corresponding NMR peak area (I_x, $x =$ **1**[CH_2Br_2], **2**[CH_2I_2], **3**[CH_2BrI]), which in turn is proportional to the number of the corresponding protons (i.e., protons with same NMR chemical environments) in the solution [10]. Fig. 1 shows typical ^{1}H NMR spectra for the dihalomethanes studied in CD_3CN solution.

The evolution of the concentration ratio (*cr*) of reaction (1), given by: $cr = \frac{I_1 \cdot I_2}{I_3^2}$, was examined for two

Table 1
Average value of K_{eq} obtained from the *cr* curves for each temperature studied

T (K)	338.15	343.15	348.15	353.15
K_{eq}	0.449 (0.006)	0.444 (0.005)	0.441 (0.006)	0.438 (0.005)

Values between parentheses correspond to the uncertainties obtained from fit *cr*-curves.

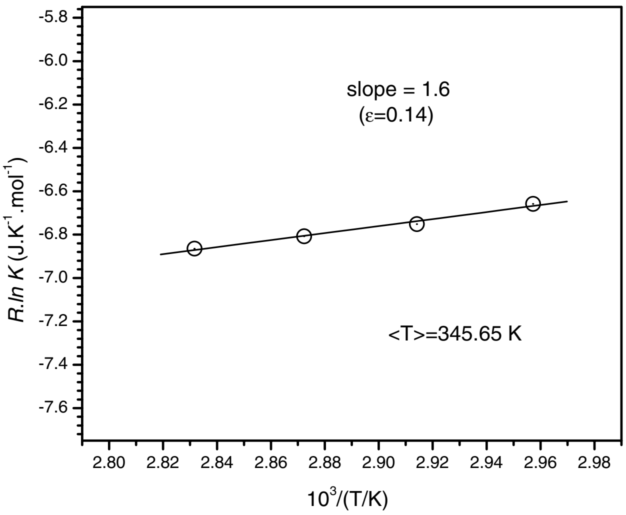

Fig. 3. Plot of $R \cdot \ln K_{eq}$ versus $10^3/T$.

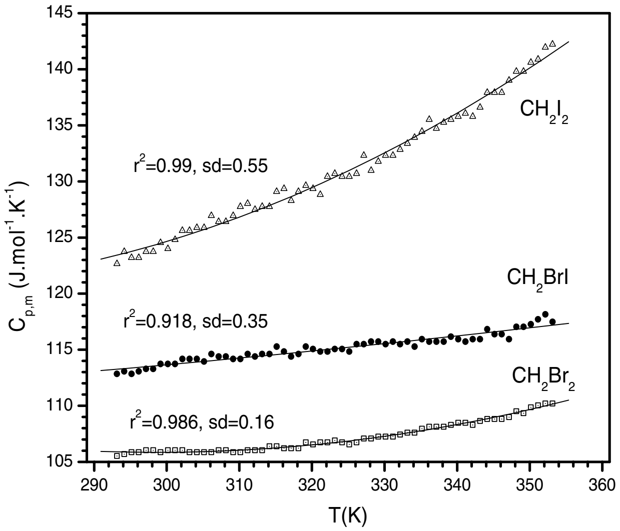

Fig. 4. Experimental heat capacities for each dihalomethane in liquid phase, $C_{p,m}(\mathrm{l}, T)$ fitted to polynomial functions.

different mixtures of halomethanes, starting with ratios of approximately $cr = 0.1$ and 0.7. A typical example of such study is presented in Fig. 2. It is clear from Fig. 2 that the same equilibrium concentration is reached in both cases after about 60 h of reaction. Furthermore, these experiments provide K_{eq} as the limiting value for the fitting of the cr curves (fitted with $r^2 > 0.98$). The experimental data are presented in Table 1, where the average values of K_{eq} have been obtained at different temperatures.

The molar Gibbs energy ($\Delta_r G_m$) and molar enthalpy ($\Delta_r H_m$), for reaction (1), can be calculated by using the well-known thermodynamic relations

$$\Delta_r G_{m,T} = -R \cdot T \cdot \ln K_{eq}, \tag{3}$$

and

$$\Delta_r H_{m,T} = -R \cdot \frac{\mathrm{d} \ln K_{eq}}{\mathrm{d}(1/T)}. \tag{4}$$

The plot of $R \cdot \ln K_{eq}$ versus $10^3/T$ values is represented in Fig. 3. The linear fitting is represented by equation: $R \cdot \ln K_{eq} = 1.6 \cdot (10^3/T) - 11.4$ (J K^{-1} mol^{-1}) ($r^2 = 0.986$, s.d. = 0.013). The molar enthalpy for reaction (1) obtained at the mean temperature ($\langle T \rangle = 345.65$ K) of the experimental range of temperatures is $\Delta_r H_{m,345.65} = (-1.6 \pm 0.3)$ kJ mol^{-1}. It has been calculated from the corresponding slope taken from the linear fitting of the data. The uncertainty assigned to the $\Delta_r H_{m,345.65\ K}$ value was calculated from the error ε of the corresponding slope. The constant term in the linear fit equation can be considered as the entropy at the mean temperature $\Delta S_{r,345.65\ K} = -11.4$ J K^{-1} mol^{-1}, which matches with the expected statistical entropy term, $R \cdot \ln(0.25) = -11.53$ kJ mol^{-1}, for this exchange reaction. The origin of this term lies in the rotational symmetry numbers of reactants and products, which are 2 for the di-bromo and di-iodo methanes, but only 1 for the mixed compound.

The value for the enthalpy of reaction (1) at the standard temperature ($T^0 = 298.15$ K) was computed from Kirchoff's Eq. (5) [11]

$$\Delta_r H^0_m(\mathrm{l}) = \Delta_r H_{m,345.65\ K} + \int_{345.65\ K}^{298.15\ K} \Delta C_{p,m}(\mathrm{l}, T)\,\mathrm{d}T, \tag{5}$$

where $C_{p,m}(\mathrm{l}, T)$ corresponds to the experimental heat capacity curves obtained from the d.s.c. measurements (Fig. 4).

Table 2
Parameters of polynomial-fit functions for the heat capacities

Dihalomethane	$C_{p,m}(\mathrm{l}, T) = a + b \cdot T + c \cdot T^2$ (J mol^{-1} K^{-1}) ($293.15 \leqslant T \leqslant 353.15$) K			$C^0_{p,m}(\mathrm{l})$[a] (J mol^{-1} K^{-1})	
	a	b	c	This work	From NIST Database [12]
CH_2Br_2	235.04	−0.865	1.45×10^{-3}	106.0 ± 2.1	104.1 ± 0.2[b] 105.3[c]
CH_2I_2	273.77	−1.188	2.3×10^{-3}	123.7 ± 2.5	112.8 ± 0.2[b] 133.8[d]
CH_2BrI	109.23	−0.029	1.46×10^{-4}	113.3 ± 2.3	–

[a] Experimental value at $T = 298.15$ K.

[b] Shehatta [13] determined these values using a micro drop heat-capacity calorimeter.

[c] Harrison and Moelwyn-Hughes [14].

[d] Carson et al. [15] reported this value as specific heat capacity.

The experimental values of $C_{p,m}(l, T)$ were fitted by quadratic polynomial functions using the least-squares method. Table 2 shows the parameters from those fittings and also the available experimental standard $C^0_{p,m}(l)$ values. It is noteworthy to mention that the $C_{p,m}(l, T)$ values for CH_2BrI were not available in the literature, and were determined for the first time in the present work. In addition, we also should point out that the measured heat capacities for CH_2I_2 at $T = 298.15$ K is significantly different from those found in the literature (see Table 2). On the other hand, the literature value of $C_{p,m}(l, T)$ for the CH_2Br_2 is in agreement with our measured value. The contribution of the last term in Eq. (5) was evaluated, and found to be -0.34 kJ mol^{-1}. Thus, the value of enthalpy of reaction (1) in solution, determined using this procedure is, $\Delta_r H^0_m(l) = -1.9 \pm 0.3$ kJ mol^{-1}.

By taking into account the equilibrium constant K_{eq} or the molar Gibbs energy and enthalpy values for reaction (1), we conclude that in this reaction the negative entropy terms dominates over the negative enthalpy term.

The calculation of the reaction enthalpy in the gas phase, $\Delta_r H^0_m(g)$ from $\Delta_r H^0_m(l)$ requires a knowledge of the enthalpy of vaporization ($\Delta_v H^0_m$) for each species. We list both experimental and estimated values in Table 3. In order to estimate $\Delta_v H^0_m$ we have used the Wadsö equation [16]: $\Delta_v H^0_m = 20.92 + 0.172 \cdot (T_{bp} - 273)$ (in kJ mol^{-1}), where T_{bp} is the normal boiling point. We also used the following literature values for $T_{bp} = 370.15$, 412.15 and 455.15 K for CH_2Br_2, CH_2BrI and CH_2I_2, respectively. It is found that the total contribution of $\Delta_v H^0_m$ to the change in the enthalpy of the reaction studied is $\Delta(\Delta_v H^0_m) = 0 \pm 0.8$ kJ mol^{-1}. Thus, the value of $\Delta_r H^0_m(g)$ is -1.9 ± 0.9 kJ mol^{-1}. The derived $\Delta_r H^0_m(g)$ can be compared to the value obtained from the standard enthalpy of formation $\Delta_f H^0_m(g)$ for each species (shown in Table 3), recently obtained by Lago et al. [4] from gas phase dissociative photoionization experiments. The value obtained by this way is $\Delta_r H^0_m(g) = 0.7 \pm 3.7$ kJ mol^{-1}. These results show that the values of $\Delta_r H^0_m$ determined by the two methods are in agreement within the uncertainty limits. In addition, the results obtained in this work also confirm the consistency of the gas phase $\Delta_f H^0_m(g)$ values reported by Lago et al. [4]. The only condensed phase heat of formation value found in the thermochemical tables from the literature is the one for CH_2I_2, $\Delta_f H^0_m(l) = 68.5 \pm 0.8$ [7]. This can be compared to a value obtained by subtracting the heat of vaporization from Lago's. [4] gas phase value of 107.5 kJ/mol. Depending on the value of the vaporization energy used (see Table 3), we obtain 55.3 and 61.9 kJ/mol. Both of these values are lower than the 68.5 kJ/mol, but the experimental heat of vaporization gives a better agreement.

Table 3
Standard molar enthalpies of formation $\Delta_f H^0_m(g)$ and vaporization $\Delta_v H^0_m$ for dihalomethanes

	CH_2Br_2	CH_2BrI	CH_2I_2
$\Delta_f H^0_m(g)$[a]	3.2 ± 3.4[b]	55.0 ± 3.4[b]	107.5 ± 4.5[b]
$\Delta_v H^0_m$[a]	37.6[c]	44.9[c]	52.2[c]
	36.97 ± 0.10[d]	41.2[e]	45.6 ± 0.6[d]

[a] In kJ mol^{-1}.

[b] Values taken from [4].

[c] Value estimated from Wadsö's equation [16].

[d] Experimental values taken from NIST Standard Reference Database [12].

[e] Value estimated by simple interpolation among experimental data of CH_2Br_2, CH_2I_2 and the corresponding boiling points.

4. Conclusions

The equilibrium reaction ($2CH_2BrI \rightleftarrows CH_2Br_2 + CH_2I_2$) has been studied by using NMR spectroscopy to determine the equilibrium concentrations. Equilibrium constants have been obtained from the profile of the NMR spectra and the heat capacities were determined for each dihalomethanes from d.s.c. experiments. The heat capacity of CH_2BrI has been experimentally measured for the first time in this work. The results for the equilibrium constant K_{eq} (~0.44) and the molar Gibbs energy suggest that the reaction among dihalomethanes ($2CH_2BrI \rightleftarrows CH_2Br_2 + CH_2I_2$) is dominated by entropy effects. The heats of vaporization of the three compounds are such that the solution phase heat of reaction should be equal to the gas phase heat of reaction. The heat of reaction derived in the present work, $\Delta_r H^0_m = -1.9 \pm 0.9$ kJ mol^{-1}, agrees within experimental error to the value derived from the measured gas phase heats of formation in a recent PEPICO experiment, $\Delta_r H^0_m = 0.7 \pm 3.7$ kJ mol^{-1} [4].

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