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Raman Study of Hydration Effect on Conformational Equilibria of Haloacetones

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The conformational equilibria of chloroacetone and bromoacetone in various solvents were investigated using temperature and pressure-tuning Raman spectroscopy. Three conformational equilibria of *gauche* ⇆ *trans*, *gauche* ⇆ *trans′* (*trans* conformer whose halogen atom forms hydrogen bonds with water), and *trans* ⇆ *trans′* were observed in water. Thermodynamic quantities between the conformers of both haloacetones in various solvents were evaluated from the temperature and pressure dependence of the Raman intensities of the C–X (X: Cl and Br) stretching modes. The effects of the substitution of halogen atoms were observed in the enthalpy and volume differences between the conformers in water. From the present results together with the previous results for fluoroacetone, a good correlation between the conformational thermodynamics for haloacetones in water and the polarizabilities of the halogen atoms was shown.

The conformational equilibrium of a chain molecule in aqueous systems is directly related to the hydration structure of the molecule. The hydration effect on the molecular conformation is of importance for understanding the structural stability of biopolymers. As a model study, we investigated the conformational behavior of haloacetones (Fig. 1), which are good models based on the following facts:[4] (1) The vibrational assignments for haloacetones have already been made. (2) Haloacetones are soluble for various solvents from nonpolar solvents to polar solvents, including water. (3) The rotational axes of haloacetones correspond to one of the rotational axes of polypeptides.

In a previous study[4] we proposed the possibility of the presence of a new molecular species of chloroacetone in water, which is a hydrogen-bonded complex between the *trans* conformer and water molecules, based on the observation of a new Raman band for aqueous solutions. Such a new Raman band was also observed for an aqueous solution of bromoacetone.[5] Quite recently, we reported on the thermodynamics of the conformational equilibria of fluoroacetone in various solvents, including water.[6] The new Raman band for an aqueous solution was also observed, and the *trans′* conformer was characterized thermodynamically.

In this work, we determined thermodynamic quantities (ΔG, ΔH, ΔS, ΔV) for the conformational equilibria of chloroacetone and bromoacetone in various solvents. From these and the previous results for fluoroacetone, we analysed the substituent effect of halogen atoms on the conformational equilibria in water.

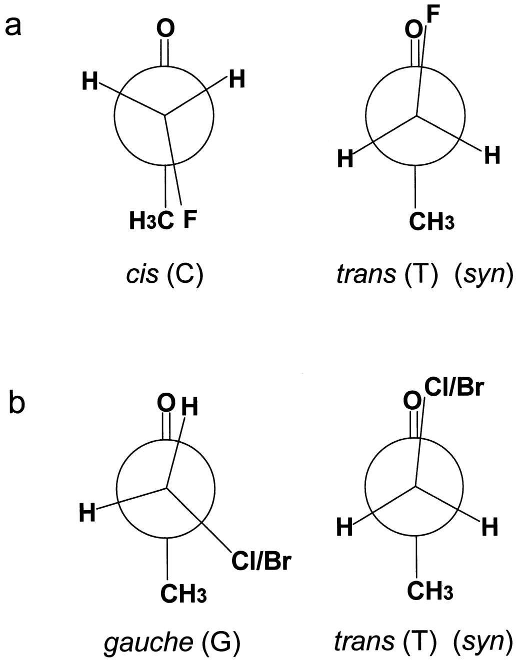

Fig. 1. Conformers of (a) fluoroacetone (the dihedral angles of the C=O and the C–F bonds are 180° for the *cis* conformer and 0° for the *trans* conformer.[1]), (b) chloroacetone (the dihedral angles of the C=O and the C–Cl bonds are 142° for the *gauche* conformer and 0° for the *trans* conformer.[2]) and bromoacetone (the dihedral angles of the C=O and the C–Br bonds are 112° for the *gauche* conformer and 0° for the *trans* conformer.[3]). In previous papers[4,5,6], we called the *trans* conformer '*syn*'.

Experimental

Chloroacetone (95%, Tokyo Kasei Kogyo Co.) was distilled under reduced pressure. Impurities of bromoacetone (90%, Tokyo

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Table 1. Enthalpy Differences between the *Gauche* (*Cis*) and *Trans* Conformers of Haloacetones (Fluoroacetone) in Various Solvents

Solvent	εa)	xb)	ΔH/kJ mol^{-1}			
			G(C) → T	G(C) → T′	T → T′	
Fluoroacetone						
C_2Cl_4	2.27c)	0.05	-2.3 ± 1.5			Ref. 6
THF	7.52d)	0.06	-6.8 ± 1.4			Ref. 6
Neat	24.5e)	1.0	-5.3 ± 0.2			Ref. 6
D_2O	79.8f)	0.04	3.5 ± 0.6	-19.9 ± 1.7	-23.5 ± 1.3	Ref. 6
H_2O	80.2f)	0.04	2.8 ± 0.3	-17.0 ± 1.1	-19.8 ± 1.0	Ref. 6
Chloroacetone						
C_2Cl_4	2.27c)	0.05	-0.7 ± 0.2			this work
THF	7.52d)	0.05	-4.8 ± 0.2			this work
Neat	30.0g)	1.0	-7.5 ± 0.1			this work
CH_3CN	36.6h)	0.05	-7.0 ± 0.2			this work
D_2O	79.8f)	0.02	-6.8 ± 0.3	-25.2 ± 0.9	-18.4 ± 0.9	this work
H_2O	80.2f)	0.02	-6.3 ± 0.2	-23.6 ± 1.6	-17.3 ± 1.5	this work
Bromoacetone						
C_6H_{14}	1.89h)	0.05	-0.7 ± 0.5			this work
$(C_2H_5)_2O$	4.27h)	0.05	-3.6 ± 1.4			this work
THF	7.52d)	0.05	-5.8 ± 1.0			this work
Neat	—	1.0	-6.9 ± 0.1			this work
CH_3CN	36.6h)	0.02	-7.0 ± 1.5			this work
D_2O	79.8f)	0.01	-5.5 ± 0.6	-10.8 ± 0.6	-5.4 ± 0.6	this work
H_2O	80.2f)	0.01	-5.7 ± 0.7	-10.4 ± 1.0	-4.7 ± 0.7	this work

a) Dielectric constant of a solvent. b) Mole fraction of a solute. c) At 30 °C, data from Ref. 8. d) At 22 °C, data from Ref. 8. e) At 38 °C, data from Ref. 9. f) At 20 °C, data from Ref. 10. g) At 19 °C, data from Ref. 11. h) At 20 °C, data from Ref. 8.

Kasei Kogyo Co.) were drained off through a membrane filter. Spectra-grade hexane, cyclohexane, tetrachloroethylene, diethyl ether, tetrahydrofuran (99%, Nacalai Tesque Co.) and acetonitrile (99%, Wako Pure Chemical Industries Co.) were used without further purification. H_2O distilled after ion exchange and deuterium oxide (from CEA) with a purity of 99.9% were used. The concentrations (mole fractions) of the targeted solutions were less than 0.06, as listed in Table 1, so as to avoid the influence of solute-solute interactions.

Raman spectra were recorded using a JRS 400D spectrometer (JEOL Co.) equipped with a cooled HTV-C659 photomultiplier and a photon counting detector (HAMAMATSU TV Co.). Samples were excited with 90° scattering of 514.5 nm radiation from an argon ion laser (Stabilite 2017, Spectra Physics Co.) with a 250–500 mW output. The spectral slit width, the scanning speed, and the number of scannings were 4.2 cm^{-1}, 100 cm^{-1} min^{-1} and 5 to 10, respectively. A glass cell and a hydrostatic optical cell with three sapphire windows[7] were used for temperature and pressure turning measurements, respectively. The temperature of the samples was controlled with an error of ±0.3 °C by thermostated water circulating around the cell. The pressure was estimated using a Heise Bourdon-tube-type gauge with an accuracy of 1 MPa. All of the spectral lines were fitted with Gaussian-Lorentzian mixing functions provided by GRAMS/386 software (Galactic Industries Co.).

Results

Temperature Effect. To determine the enthalpy differences between the conformers of chloroacetone and bromoacetone, we measured the Raman spectra of the C–Cl and the C–Br stretching regions at various temperatures. Typical spectra and assignments have been described elsewhere.[4,5] The enthalpy difference (ΔH) between conformers are given by

$$\Delta H = -R\left(\frac{\partial \ln K}{\partial(1/T)}\right)_p, \qquad (1)$$

where R, K, T, and p have their usual meanings. The Raman intensity from a conformer is essentially proportional to the population of the corresponding conformer. Assuming that the ratio of the scattering cross sections of conformers is independent of the temperature, K can be substituted by the ratio of the integrated intensities.

Figure 2 shows van't Hoff plots for the conformational equilibria in H_2O, which are linear in $1/T$ over the measured temperature range. The slopes in Fig. 2 give ΔH values for the three equilibria in H_2O. The ΔH values are listed in Table 1 together with the relevant data published previously.[6]

Pressure Effect. To analyse the hydration structure of haloacetones volumetrically, we determined the volume differences between the conformers (ΔV) from pressure-turning Raman measurements. The volume difference (ΔV) between conformers is given by

$$\Delta V = -RT\left(\frac{\partial \ln K}{\partial p}\right)_T. \qquad (2)$$

Assuming that the ratio of the scattering cross sections of conformers is independent of pressure, K can be substituted by the ratio of the integrated intensities.

Figure 3 shows typical Raman spectra of the C–Br stretching mode of bromoacetone at various pressures. The conformational bands are well separated from each other. Figure 4

Table 2. Volume Differences between the Conformers of Haloacetones in Various Solvents at 20 °C

	Solvent	x	ΔV/cm^3 mol^{-1}		
			G(C) → T	G(C) → T′	T → T′
Fluoroacetone	C_2Cl_4	0.04	−2.4 ± 0.8		
	D_2O	0.04	5.4 ± 0.3[a)]	−8.3 ± 0.2[a)]	−13.7 ± 0.3[a)]
	H_2O	0.04	5.1 ± 0.2[a)]	−6.0 ± 0.6[a)]	−11.0 ± 0.4[a)]
Chloroacetone	CS_2	0.05	−1.6 ± 0.1[b)]		
	D_2O	0.02	0.5 ± 0.4	−7.4 ± 0.7	−7.6 ± 0.5
	H_2O	0.02	−0.9 ± 0.4	−6.1 ± 0.8	−5.2 ± 0.8
Bromoacetone	C_6H_{14}	0.05	−1.5 ± 0.3		
	D_2O	0.01	−1.5 ± 0.7	−6.3 ± 0.5	−4.8 ± 0.5
	H_2O	0.01	−1.8 ± 0.5	−5.7 ± 0.6	−3.9 ± 0.5

a) Data from Ref. 6. b) Datum from Ref. 12.

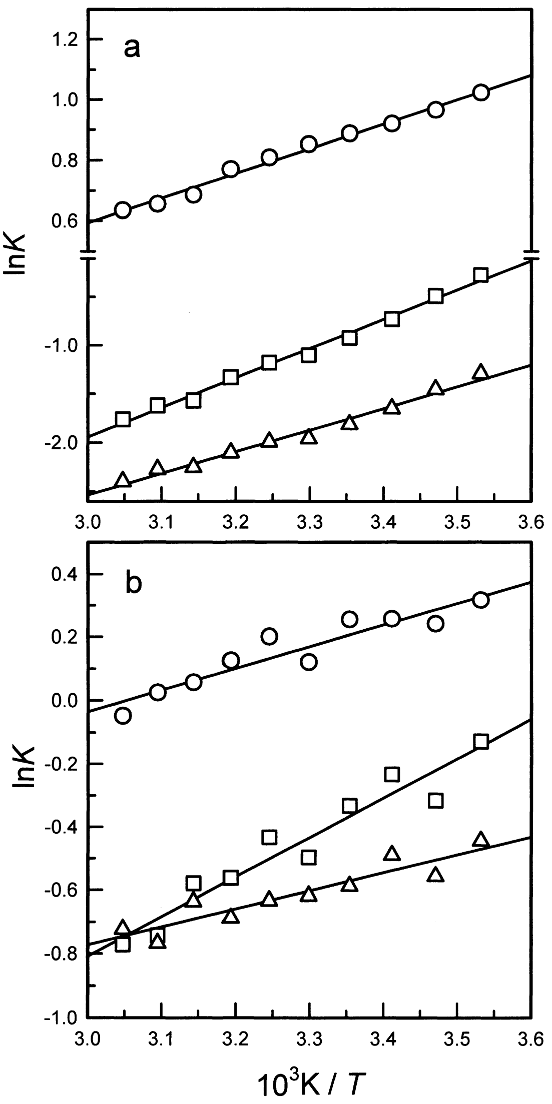

Fig. 2. van’t Hoff plots for the conformational equilibria of (a) chloroacetone and (b) bromoacetone in H_2O: $K = I_T/I_G$ (○), $I_{T'}/I_G$ (□), $I_{T'}/I_T$ (△).

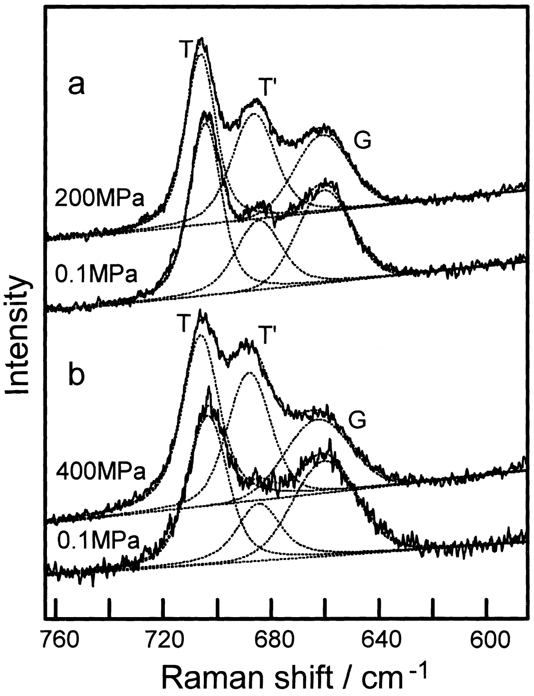

Fig. 3. Raman spectra of the C–Br stretching region of bromoacetone in (a) D_2O and (b) H_2O at various pressures.

shows the pressure dependence of the ratios of the integrated intensities between the conformation bands for chloroacetone and bromoacetone in H_2O, indicating linear relations. The slopes of the lines give the volume difference between the conformers in H_2O, which are summarized in Table 2, together with the relevant data published previously.[6]

Discussion

Thermodynamics for the Formation of the *Trans′* Conformer. The negative values of $\Delta V_{\mathrm{T}\to\mathrm{T}'}$ agree with a general acceptance that the hydrogen-bond formation contributes to a decrease in the volume of the system. Moreover, a smaller value for D_2O than H_2O (Table 2) agrees with many reports that the hydrogen-bond enthalpy of D_2O is larger than that of H_2O.[13,14,15] These results support the assignment for the *trans′* band.[4,5,6]

Recently, we reported that the number of water molecules binding to the fluorine atom of the *trans′* conformer of fluoroacetone is about 2 at 20 °C, and further that $\Delta V_{\mathrm{T}\to\mathrm{T}'} = -11.0$ cm^3 mol^{-1} in H_2O and -13.7 cm^3 mol^{-1} in D_2O.[6] The present

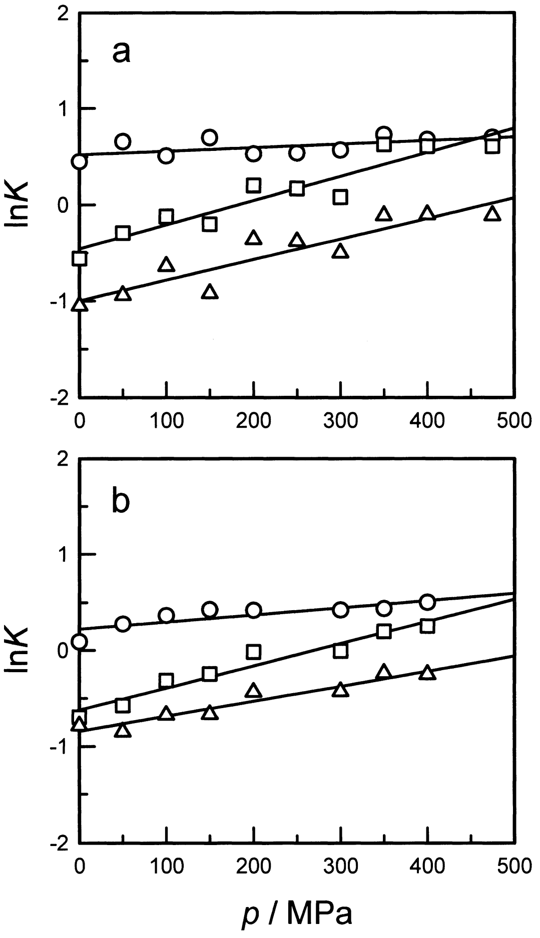

Fig. 4. Pressure dependence of ln$K$ for the conformational equilibria of (a) chloroacetone and (b) bromoacetone in H_2O: $K = I_T/I_G$ (○), $I_{T'}/I_G$ (□), $I_{T'}/I_T$ (△).

values for chloroacetone and bromoacetone are approximately half of these, and are within the range of a volume difference with the formation of a hydrogen-bond complex reported so far.[16] Thus, the number of the binding H_2O molecules of the *trans′* conformer of chloro- and bromoacetones seems to be about 1.

From Table 1, we obtain an order of magnitude of $\Delta H_{T\to T'}$: ($\Delta H_{T\to T'}$ for fluoroacetone) < ($\Delta H_{T\to T'}$ for chloroacetone) < ($\Delta H_{T\to T'}$ for bromoacetone). This agrees qualitatively with previous works[17,18] that the intermolecular hydrogen bond enthalpy between phenol and a cyclohexyl halide increases in proportional to the electronegativity of halogen atoms (Br: 2.8, Cl: 3.0, F: 4.0).[19]

***Cis* ⇆ *Trans*, *Gauche* ⇆ *Trans* Equilibria in Various Solvents.** In this section, we discuss the solvent effect on the thermodynamics for the *cis* ⇆ *trans* equilibrium of fluoroacetone and the *gauche* ⇆ *trans* equilibria of other haloacetones in terms of the dielectric continuum model.[20] From a comparison of the experimental and theoretical results, we elucidated the relationship between the conformation and hydration structure.

ΔG, ΔH, ΔS: The change in the conformational free energy with the solvent change from solvent **1** to solvent **2**, $\Delta\Delta G_{G(C)\to T}$ (1 → 2) is given by

$$\Delta\Delta G_{G(C)\to T}\ (1 \to 2) = RT\left[\ln\frac{I_T^{solv1}}{I_{G(C)}^{solv1}} - \ln\frac{I_T^{solv2}}{I_{G(C)}^{solv2}} + \ln\left(\frac{\sigma_{G(C)}^{solv1}}{\sigma_T^{solv1}} \Big/ \frac{\sigma_{G(C)}^{solv2}}{\sigma_T^{solv2}}\right)\right]. \qquad (11)$$

Assuming that the ratio of the scattering cross sections between the conformers ($\sigma_{G(C)}/\sigma_T$) is independent of solvent, the above equation is replaced by

$$\Delta\Delta G_{G(C)\to T} = RT\left(\ln\frac{I_T^{solv1}}{I_{G(C)}^{solv1}} - \ln\frac{I_T^{solv2}}{I_{G(C)}^{solv2}}\right). \qquad (12)$$

The corresponding enthalpy ($\Delta\Delta H_{G(C)\to T}$) is calculated from the experimental values in Table 1. Thus, $T\Delta\Delta S_{G(C)\to T}$ is obtained from

$$T\Delta\Delta S_{G(C)\to T} = \Delta\Delta H_{G(C)\to T} - \Delta\Delta G_{G(C)\to T}. \qquad (13)$$

The obtained $\Delta\Delta G_{G(C)\to T}$, $\Delta\Delta H_{G(C)\to T}$ and $T\Delta\Delta S_{G(C)\to T}$ values for all of the haloacetones are summarized in Table 3.

For a comparison, we calculated the corresponding quantities based on a dielectric continuum model. According to a continuum model including a quadrupole term,[20] the solvation free energy difference between conformers (ΔG^{elec}) is given by

$$\Delta G^{elec} = -N_A\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right)\left(\frac{1}{1 - \alpha f}\right)\left(\frac{\mu_T^2 - \mu_{G(C)}^2}{a^3}\right) - \frac{3}{2}N_A\left(\frac{\varepsilon - 1}{3\varepsilon + 2}\right)\left(\frac{\eta_T^2 - \eta_{G(C)}^2}{a^5}\right), \qquad (14)$$

where N_A is Avogadro's constant, ε is the dielectric constant of the solvent, α is the molecular polarizability of solute, f is the reaction factor $\{2(\varepsilon - 1)/a^3(2\varepsilon + 1)\}$, a is the radius of the solute cavity, and μ and η are, respectively, the dipole and the quadrupole moments of a conformer. The product αf is expressed as

$$\alpha f = \left(\frac{n^2 - 1}{n^2 + 2}\right)\left\{\frac{2(\varepsilon - 1)}{2\varepsilon + 1}\right\}, \qquad (15)$$

where n is the refractive index of a solute. Moreover, the conformational entropy is given by

$$\Delta S^{elec} = \frac{3N_A\varepsilon}{(2\varepsilon + 1)^2}\left(\frac{\partial \ln\varepsilon}{\partial T}\right)_p\left(\frac{1}{1 - \alpha f}\right)^2\left(\frac{\mu_T^2 - \mu_{G(C)}^2}{a^3}\right) + \frac{15N_A\varepsilon}{2(3\varepsilon + 2)^2}\left(\frac{\partial \ln\varepsilon}{\partial T}\right)_p\left(\frac{\eta_T^2 - \eta_{G(C)}^2}{a^5}\right), \qquad (16)$$

assuming that the dipole moment and the cavity radius are independent of the temperature. Whether the size of the cavity is independent of temperature and/or pressure is a subject of debate. Based on classical electrostatics, the shape of the cavity is defined by the boundary condition. It should be defined by the molecular orbital in terms of quantum theory.[21] In the temperature and pressure ranges of the present experiment, the cavity volume should be practically constant. Indeed, Raman studies[22,23] of the pressure effect on conformational equilibrium support that the cavity volume is independent of the pressure. Hence, changes in the conformational free energy ($\Delta\Delta G^{elec}$) and the conformational entropy ($\Delta\Delta S^{elec}$) were calculated from Eqs. 14 and 16, respectively.

Table 3. Changes in the Thermodynamic Differences (kJ mol^{-1}) between *Gauche (Cis)* and *Trans* Conformers of Each Haloacetone with Solvent Changes at 20 °C

Solvent change	$\Delta\Delta G$	$\Delta\Delta G^{elec}$	$\Delta\Delta H$	$\Delta\Delta H^{elec}$	$T\Delta\Delta S$	$T\Delta\Delta S^{elec}$
Fluoroacetone						
$C_2Cl_4 \rightarrow$ THF	-3.0 ± 2.9[a]	-0.8	-4.5 ± 2.1[a]	-1.8	-1.5 ± 3.5[a]	-1.0
$C_2Cl_4 \rightarrow$ Neat	-5.2 ± 2.1[a]	-1.6	-3.0 ± 1.5[a]	—	2.2 ± 2.6[a]	
$C_2Cl_4 \rightarrow D_2O$	-5.5 ± 2.2[a]	-1.9	5.8 ± 1.6[a]	—	11.3 ± 2.7[a]	—
$C_2Cl_4 \rightarrow H_2O$	-5.6 ± 2.1[a]	-1.9	5.1 ± 1.5[a]	-2.2	10.7 ± 2.6[a]	-0.3
Chloroacetone						
$C_2Cl_4 \rightarrow$ THF	-2.6 ± 0.4	-2.5	-4.0 ± 0.3	-4.1	-1.4 ± 0.5	-1.6
$C_2Cl_4 \rightarrow$ Neat	-3.9 ± 0.3	-4.2	-6.8 ± 0.2	—	-2.8 ± 0.3	—
$C_2Cl_4 \rightarrow CH_3CN$	-4.4 ± 0.4	-4.3	-6.2 ± 0.3	-4.9	-1.8 ± 0.4	-0.5
$C_2Cl_4 \rightarrow D_2O$	-5.2 ± 0.5	-4.7	-6.0 ± 0.3	—	-0.8 ± 0.6	—
$C_2Cl_4 \rightarrow H_2O$	-4.9 ± 0.4	-4.7	-5.5 ± 0.3	-4.5	-0.6 ± 0.5	0.1
Bromoacetone						
$C_6H_{14} \rightarrow (C_2H_5)_2O$	-0.9 ± 2.0	-4.1	-2.9 ± 1.4	-6.9	-2.0 ± 2.5	-2.7
$C_6H_{14} \rightarrow$ THF	-2.8 ± 1.6	-6.3	-5.1 ± 1.2	-8.8	-2.3 ± 2.0	-2.5
$C_6H_{14} \rightarrow$ Neat	-4.0 ± 0.7	—	-6.2 ± 0.5	—	-2.2 ± 0.9	—
$C_6H_{14} \rightarrow CH_3CN$	-5.1 ± 2.2	-9.3	-6.3 ± 1.6	-9.7	-1.2 ± 2.7	-0.5
$C_6H_{14} \rightarrow D_2O$	-6.2 ± 1.1	-9.7	-4.8 ± 0.8	—	1.4 ± 1.3	—
$C_6H_{14} \rightarrow H_2O$	-6.2 ± 1.2	-9.7	-5.0 ± 0.9	-9.2	1.2 ± 1.5	0.5

a) Data from Ref. 6.

Table 4. Molecular Parameters Used for the Thermodynamic Calculations Based on the Continuum Model

Solute		$10^{18}\mu$/esu cm[a]	$10^{52}\eta^2$/esu^2 cm^4 [a]	$10^8 a$/cm[b]	n[c]
Fluoroacetone	*cis*	1.408	175.1	2.547	1.370
	trans	4.625	14.9		
Chloroacetone	*gauche*	1.833	172.9	2.659	1.433
	trans	4.552	31.7		
Bromoacetone	*gauche*	2.380	186.8	2.709	1.471
	trans	4.444	107.9		

a) Calculated by MP2/6-31G* ab initio calculations [Gaussian 94 (Gaussian Co.)]. b) Cavity radius: we employed the value for the radius of a sphere which have the same van der Waals volume of the corresponding molecule. c) Refractive index at 20 °C measured by a refractometer (Optical works Co.).

Table 5. Temperature and Pressure Dependence of the Dielectric Constants of Various Solvents

Solvent	$10^2(\partial\varepsilon/\partial T)_p$/K^{-1}	$10^{11}(\partial\ln\varepsilon/\partial p)_T$/dyn^{-1} cm^2
C_6H_{14}	-0.13[a]	4.01[c]
C_2Cl_4	-0.20[b]	7.84[d]
CS_2	—	5.45[c]
$(C_2H_5)_2O$	-1.25[a]	—
THF	-0.03[a]	—
CH_3CN	-0.23[a]	—
H_2O	-0.36[a]	4.36[e]

a) Data from Ref. 24. b) Datum for carbon tetrachloride from Ref. 24. c) At 20 °C, data from Ref. 25. d) Datum for carbon tetrachloride from Ref. 25. e) At 20 °C, datum from Ref. 10.

The change in the conformational enthalpy is given by

$$\Delta\Delta H^{elec} = \Delta\Delta G^{elec} + T\Delta\Delta S^{elec}. \tag{17}$$

By employing the parameters listed in Tables 4 and 5, we calculated $\Delta\Delta G^{elec}$, $T\Delta\Delta S^{elec}$, $\Delta\Delta H^{elec}$ according to Eqs. 14, 15, 16, and 17. These values are included in Table 3. It was impossible to calculate some thermodynamic values due to no available data of the dielectric constants and/or their temperature dependence of some solvents.

The calculated and observed $\Delta\Delta G$ values approximately agree with each other. Particularly, as for chloroacetone, the agreements are excellent. The observed $\Delta\Delta H$ and $T\Delta\Delta S$ values for chloroacetone and bromoacetone also qualitatively agree with the corresponding calculated values. As for fluoroacetone, however, even the signs of $\Delta\Delta H^{elec}(C_2Cl_4 \rightarrow H_2O)$ and $T\Delta\Delta S^{elec}(C_2Cl_4 \rightarrow H_2O)$ are different from those of $\Delta\Delta H(C_2Cl_4 \rightarrow H_2O)$ and $T\Delta\Delta S(C_2Cl_4 \rightarrow H_2O)$. Such a failure of the continuum model should be attributed to the hydration effect on the thermodynamics. The *trans* conformer in water is more (less) favorable in terms of entropy (enthalpy) than the *cis* conformer. That is, the hydration structure of the *cis* conformer of fluoroacetone would be more ordered than that of the *trans* conformer.

ΔV: In a nonpolar solvent, the volume difference between the conformers (ΔV) is expressed by the summation of the vol-

Table 6. Experimental and Calculated Volume Differences ($cm^3\ mol^{-1}$) between Conformers of Haloacetones in Nonpolar Solvents and H_2O

	Solvent	$\Delta V_{G(C)\rightarrow T}$	$\Delta V^{elec}_{G(C)\rightarrow T}$ [a)]	$\Delta V^{local}_{G(C)\rightarrow T}$ [b)]
Fluoroacetone	C_2Cl_4	-2.4 ± 0.8	0.2	-2.6
	H_2O	5.1 ± 0.2 [c)]	-0.1	5.2
Chloroacetone	CS_2	-1.6 ± 0.1 [d)]	-1.1	-0.5
	H_2O	-0.9 ± 0.4	-0.1	-0.8
Bromoacetone	C_6H_{14}	-1.5 ± 0.3	-2.2	0.7
	H_2O	-1.8 ± 0.5	-0.2	-1.6

a) Calculated from Eq. 19. b) $\Delta V^{local}_{G(C)\rightarrow T} = \Delta V_{G(C)\rightarrow T} - \Delta V^{elec}_{G(C)\rightarrow T}$. c) Datum from Ref. 6. d) Datum from Ref. 12.

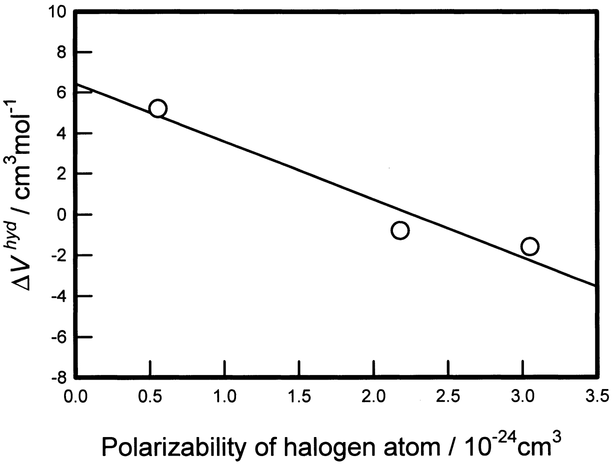

Fig. 5. The relationship between ΔV^{hyd} for haloacetones and the polarizabilities of halogen atoms.

ume differences caused by the electrostatic effect (ΔV^{elec}) and the local solute-solvent interaction (ΔV^{local}).[26] Then, we apply the equation

$$\Delta V_{G(C)\rightarrow T} = \Delta V^{elec}_{G(C)\rightarrow T} + \Delta V^{local}_{G(C)\rightarrow T} \tag{18}$$

for haloacetones in a nonpolar solvent. The pressure derivative of Eq. 14 leads to

$$\begin{aligned}\Delta V^{elec}_{G(C)\rightarrow T} = &-\frac{3\varepsilon N_A}{(2\varepsilon + 1)^2}\left(\frac{\partial \ln\varepsilon}{\partial p}\right)_T\left(\frac{\mu_T^2 - \mu_{G(C)}^2}{a^3}\right)\left(\frac{1}{1-\alpha f}\right)^2 \\ &- \frac{15\varepsilon N_A}{2(3\varepsilon + 2)^2}\left(\frac{\partial \ln\varepsilon}{\partial p}\right)_T\left(\frac{\eta_T^2 - \eta_{G(T)}^2}{a^5}\right).\end{aligned} \tag{19}$$

In Table 6 we summarize the values of $\Delta V^{elec}_{G(C)\rightarrow T}$ calculated using the paremeters in Tables 4 and 5, and the values of $\Delta V^{local}_{G(C)\rightarrow T}$ obtained by subtracting $\Delta V^{elec}_{G(C)\rightarrow T}$ from the experimental values ($\Delta V_{G(C)\rightarrow T}$). In a nonpolar solvent, $\Delta V^{local}_{G(C)\rightarrow T}$ is attributed to the molecular packing effect due to the repulsive intermolecular interactions, that is, $\Delta V^{local}_{G(C)\rightarrow T} = \Delta V^{p}_{G(C)\rightarrow T}$.[26,27]

According to a statistical mechanics calculation of butane in nonpolar solvents,[27] the volume difference between the conformers caused by the packing effect is enhanced with increasing radius of the solvent molecule. In the targeted systems, if the packing effect is dominant among the local contributions, there should be the following relationships: $\Delta V^{local}_{G(C)\rightarrow T}$ (in C_2Cl_4) < $\Delta V^{local}_{C\rightarrow T}$ (in H_2O) < 0 for fluoroacetone, $\Delta V^{local}_{G\rightarrow T}$(in CS_2) < $\Delta V^{local}_{G\rightarrow T}$(in H_2O) < 0 for chloroacetone and 0 < $\Delta V^{local}_{G\rightarrow T}$(in H_2O) < $\Delta V^{local}_{G\rightarrow T}$(in C_6H_{14}) for bromoacetone. In fact, such relationships were obviously not seen for fluoroacetone and bromoacetone. Thus, the packing effect is not dominant among the local contribution in aqueous systems. The hydration effect should be taken into consideration. In previous studies[4,5] we observed a low-frequency shift of the C–halogen stretching mode of the *trans* form of haloacetones when changing the solvent from nonpolar solvents to water. Therefore, the present hydration effect is expected not to be hydrophilic, but hydrophobic-like. We further discuss the hydration effect based on volume changes.

Hence, $\Delta V^{local}_{G(C)\rightarrow T}$ in an aqueous solution is given by

$$\Delta V^{local}_{G(C)\rightarrow T} = \Delta V^{p}_{G(C)\rightarrow T} + \Delta V^{hyd}_{G(C)\rightarrow T} \tag{20}$$

The first term is the contribution of a packing effect when the H_2O molecule is assumed to be nonpolar. The second term is the contribution of a hydration effect when we give an electric charge on the H_2O molecule. To discuss the substitution effect on hydration, we then calculate the values of $\Delta V^{hyd}_{G(C)\rightarrow T}$ using the values in Table 6. Considering $\Delta V^{local}_{G(C)\rightarrow T}$ (in C_2Cl_4, CS_2, and C_6H_{14}) = $\Delta V^{p}_{G(C)\rightarrow T}$ (in C_2Cl_4, CS_2, and C_6H_{14}) and $|\Delta V^{p}_{G(C)\rightarrow T}$ (in H_2O)$|$ < $|\Delta V^{p}_{G(C)\rightarrow T}$ (in C_2Cl_4, CS_2, and C_6H_{14})$|$, the $\Delta V^{p}_{G(C)\rightarrow T}$ (in H_2O) values are expected to be -2.6 to 0 $cm^3\ mol^{-1}$ for fluoroacetone and about 0 $cm^3\ mol^{-1}$ for other haloacetones. Therefore, the $\Delta V^{hyd}_{G(C)\rightarrow T}$ values (= $\Delta V^{local}_{G(C)\rightarrow T}$ (in H_2O) − $\Delta V^{p}_{G(C)\rightarrow T}$ (in H_2O)) are around 6.5, -0.8 and -1.6 $cm^3\ mol^{-1}$ for fluoroacetone, chloroacetone and bromoacetone, respectively.

Figure 5 shows the relationship between the ΔV^{hyd} values of haloacetones and the polarizabilities of the halogen atoms. This plot shows that the contribution from the hydration effect correlates with the polarizability of the halogen atom. From the results that $T\Delta\Delta S$ ($C_2Cl_4 \rightarrow H_2O$) and $\Delta V^{hyd}_{C\rightarrow T}$ for fluoroacetone are large in positive, we can say that the structural order of hydration around the *cis* conformer of fluoroacetone is higher compared with that around the *trans* conformer. Because the polarizability of fluorine atom is small (F: 0.56×10^{-24} cm^3, Cl: 2.18×10^{-24} cm^3, Br: 3.05×10^{-24} cm^3 [28]), it seems impossible that the fluorine atom attractively interacts with water through a dispersive force. Therefore, the hydration around the fluorine atom of fluoroacetone, except for the *trans′* conformer, would be hydrophobic. Since the hydrophobic fluorine and the hydrophilic oxygen atoms are away from each other in the *cis* form (Fig. 1), there is no overlap between the two different hydrations. This can be the main cause of the more ordered and compact hydration of the *cis* conformer.

On the other hand, the conformational thermodynamics (G, H, S, V) of chloroacetone and bromoacetone seem to be in better agreement with the dielectric continuum model. Water in a hydrophobic shell around the chlorine and the bromine atoms having large polarizabilities can attractively interact with these atoms. Thus, hydrophobic hydrations around the halogen atoms of chloroacetone and of bromoacetone should not be as tight as the hydration around the fluorine atom of fluoroacetone. In the *trans* conformers, the hydration shells around the halogen atoms of chloroacetone and bromoacetone do not significantly interfere with the hydration shell around an oxygen atom. Eventually, the hydration structures around chloroacetone and bromoacetone are not significantly influenced by a conformational change compared with fluoroacetone.

In the present work we investigated the effect of a solvent and halogen substitution on the conformational equilibria of haloacetones. We obtained the detailed thermodynamics (G, H, S, V) for the conformational equilibria via extensive temperature and pressure tuning Raman measurements. The hydrogen bonds between the *trans* form and water (*trans′* conformer) were observed commonly for haloacetones and characterized by thermodynamic quantities. The hydration change by a conformational change of G(C) to T was also characterized in details based on thermodynamic quantities. It was found that the magnitude of the change correlates with the polarizability of the halogen atom. The present work showed that the conformational behavior of haloacetones in water is not simple (not explained by a continuum model) due to the hydration effect. In other words, the conformation of a solute significantly affects the hydration thermodynamics. The hydration of a biomolecule, such as a protein, is an important factor for the structural stability of the molecule. This work implies that taking account of the conformational effect on hydration is of importance for understanding the structural stability.

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