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An enthalpic scale of hydrogen-bond basicity, part 1: halogenoalkanes

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ABSTRACT: Hydrogen bond enthalpies $\Delta H°$ for the interaction of 4-fluorophenol with 18 fluoro-, chloro-, bromo-, and iodo-alkanes in CCl_4 solution have been determined through the temperature variation of hydrogen-bond equilibrium constants. A statistical analysis of the $\Delta H°$–$\Delta S°$ correlation shows that this extrathermodynamic relationship is valid for the family of halogenoalkanes. The enthalpic data are also used to test the correlation of $\Delta H°$ *versus* $\Delta\nu$(OH), the IR frequency shifts of the OH band of 4-fluorophenol caused by the hydrogen bonding (the Badger–Bauer relationship). This relationship is family dependent, and, for fluoroalkanes and iodoalkanes, does not pass through the origin. These findings allow a safer use of the Badger–Bauer relationship to predict hydrogen-bond enthalpies accurately. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: hydrogen-bond enthalpy; halogenoalkanes; basicity; isoequilibrium relationship; Badger–Bauer relationship

INTRODUCTION

Despite the importance of the hydrogen bond in chemistry,[1–3] physics,[1] and biology,[4] there is a serious dearth of reliable hydrogen-bond enthalpies. Discrepancies amounting to 5–10 kJ mol^{-1} are often found[3] between the results obtained by different workers studying the same system by the same or different methods. For example, the results of 16 determinations[3] of the enthalpy of complexation of the phenol–pyridine system vary from −20.9 to −31.8 kJ mol^{-1}. In view of the fact that most hydrogen-bond enthalpies[3] for neutral hydrogen-bond donors and acceptors fall between −10 and −40 kJ mol^{-1}, these discrepancies seriously reduce the usefulness of such measurements. The difficulties of finding good data for weak organic bases (hydrogen-bond acceptors) are even more critical. Among these, halogenoalkanes have such reduced basic properties that it was stated in the literature that ‘fluorine atoms attached to carbon do not have significant power to act as proton acceptors in the formation of hydrogen bonds’,[5] ‘evidence for the formation of intermolecular hydrogen bonds involving halogen atoms seems to be very slight’,[6] or ‘covalently bound fluorine hardly ever acts as a hydrogen-bond acceptor’.[7]

We have recently[8] provided a contrasting view to these conclusions by determining the Gibbs energy for the complexation of a reference hydrogen-bond donor, 4-fluorophenol, with halogenoalkanes. These Gibbs energies (on the mole fraction scale) extend from −1.79 kJ mol^{-1} (1,1,1-trichloroethane) to −7.55 kJ mol^{-1} (1-fluoroadamantane). Significant shifts upon complexations were also found for the OH stretching vibration of 4-fluorophenol. These $\Delta\nu$(OH) shifts range from 13 cm^{-1} (1,1,1-trichloroethane) to 101 cm^{-1} (1-iodoadamantane).

The primary aim of this work is to determine the enthalpy of complexation of 18 fluoro-, chloro-, bromo- and iodo-alkanes with 4-fluorophenol in order to construct an enthalpic scale of hydrogen-bond basicity (basicity towards hydrogen-bond donors). Subsequent articles will be devoted to nitrogen, oxygen, and sulfur bases. A few studies[3,9–11] on the enthalpies of hydrogen bonding to halogenoalkanes have been reported, but they were not carried out in a systematic manner. Literature data are (i) scarce, since only cyclohexyl,[9,11] *n*-heptyl,[10] and *n*-butyl halides[11] have been studied, and (ii) inhomogeneous, because they refer to various hydrogen-bond donors (phenol,[9,10] 4-fluorophenol[11] or 1-butanol[11]) and various solvents (CCl_4,[9,11] C_2Cl_4,[10] or pure base[11]). In contrast with these results, our data will be homogeneous (4-fluorophenol and CCl_4 as standard donor and solvent respectively) and will cover a wide basicity range. For this purpose we have selected halogenoalkanes substituted with groups spanning a wide range of electronic effects, from 1-adamantyl, which

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enhances basicity through a high polarizability effect, to 1-halogenopropyl, which decreases basicity through a field-inductive electron-withdrawing effect.

We shall outline the IR procedure for obtaining accurate enthalpy data from the temperature dependence of complexation constants. Reliable enthalpy values are necessary in order for comparison with quantum-chemical enthalpy calculations, but also for testing such extrathermodynamic relationships as the isoequilibrium (enthalpy–entropy) relationship[12] or the Badger–Bauer[1–3] correlation of the hydrogen-bond enthalpy with the IR shift.

Opinion is divided about the matter whether the enthalpy or the Gibbs energy is the better parameter to employ for measuring basicity.[13] This dilemma can be solved by the existence of an extrathermodynamic relationship between enthalpy and entropy. In 1960, Pimentel and McClellan[1] proposed a monotonic relationship between ΔH° and ΔS° for hydrogen-bond formation on the basis that a 'higher value of $-\Delta H$ implies stronger bonding, with a more restricted configuration in the complex, hence greater order, leading to a larger value of $-\Delta S$'. However, in 1974, the reliable hydrogen-bonding data of Arnett *et al.*[14] indicated that 'in general, a straight line correlation between ΔS° and ΔH° does not hold, although a trend is clear'.

The enthalpy–IR-shift relationship has also been supported by some workers[15–25] and challenged by many others.[9–11,14,26–32]

The second aim of this work is to assess the Badger–Bauer and isoequilibrium relationships in the family(ies) of halogenoalkanes. This family should be instructive, since it covers four periods of the periodic table.

EXPERIMENTAL

Chemicals and spectra

Tetrachloromethane, 4-fluorophenol and halogenoalkanes were purified as described elsewhere.[8] The FTIR spectrometer, the cell, and the method of measuring the IR wavenumber shifts, $\Delta\nu(\mathrm{OH})$, are also described in Ref. 8.

Determination of enthalpy

The formation of a 1:1 complex from 4-fluorophenol and halogenoalkanes RX can be represented by the equilibrium Eqn. 1.

$$\mathrm{FC_6H_4OH + XR \rightleftharpoons FC_6H_4OH \cdots XR} \qquad (1)$$

If C_c, C_a, and C_b are the equilibrium concentrations, on the molar scale, of the complex, the acid 4-fluorophenol, and the base RX respectively, and if C_a° and C_b° are the initial concentrations, then the equilibrium constant is given by Eqn. 2.

$$\begin{aligned} K_\mathrm{c}/\mathrm{dm^3\,mol^{-1}} &= C_\mathrm{c}/C_\mathrm{a}C_\mathrm{b} \\ &= (C_\mathrm{a}^\circ - C_\mathrm{a})/C_\mathrm{a}(C_\mathrm{b}^\circ - C_\mathrm{a}^\circ + C_\mathrm{a}) \end{aligned} \qquad (2)$$

$$C_\mathrm{a} = A/\varepsilon\ell \qquad (3)$$

C_a is obtained [Eqn. 3] from the absorbance A of the free OH band of 4-fluorophenol at 3614 $\mathrm{cm^{-1}}$, the absorption coefficient ε (238 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$), and the pathlength (1 cm). C_a° and C_b° are obtained by weighing. C_a° is kept below 5×10^{-3} $\mathrm{mol\,dm^{-3}}$ in order to neglect the self-association of 4-fluorophenol. This concentration requires a 1 cm pathlength cell to give a good signal. C_b° is adjusted so that the complexation of 4-fluorophenol lies in the range 15–20%. The solutions are prepared in a glove box under dry atmosphere at room temperature. A density correction is made on the concentrations C_a° and C_b° in order to take into account the difference of temperature between the room and the cell. A new absorption coefficient ε is calculated in each experiment in order to check the concentration C_a°. A small variation in the limits of 238 ± 4 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ is allowed. This compensates for different variables in the experiment, such as the position of the cell in the spectrometer or different acquisition parameters of the interferogram. When ε is found outside this range, a weighing error on C_a° is suspected and a new stock solution of 4-fluorophenol is prepared. Finally, a small absorbance correction must be made to take into account a small overlap of the free OH band and the broad OH band of the complex. We corrected for this overlap by using the Curve Fit Bruker software, which enables overlapping bands to be mathematically resolved into their Gauss–Lorentz components.

Very precise enthalpy measurements are obtained by following the absorbance of a *single solution* as a function of temperature. In a typical measurement, the spectra of a solution containing *ca* 3×10^{-3} $\mathrm{mol\,dm^{-3}}$ of 4-fluorophenol and a halogenoalkane concentration adjusted as described before are generally recorded at five temperatures between -5 and $+45$ °C. The thermal stability of the solution is checked by comparing the final and the initial spectra at 25 °C. The temperature of the measuring quartz cell is controlled to ± 0.1 °C by means of a Peltier thermoelectric device. The temperature of the solution is checked by a thermocouple inserted in the cell centre during the spectral record of a reference solution containing only $\mathrm{CCl_4}$ and halogenoalkanes. The method requires knowledge of the temperature dependence of the absorption coefficient. ε falls off linearly in the -5 to $+55$ °C range with increasing temperature t/°C according to Eqn. 4:

$$\varepsilon(t) = \varepsilon(25) - 0.624733(t - 25) \qquad (4)$$

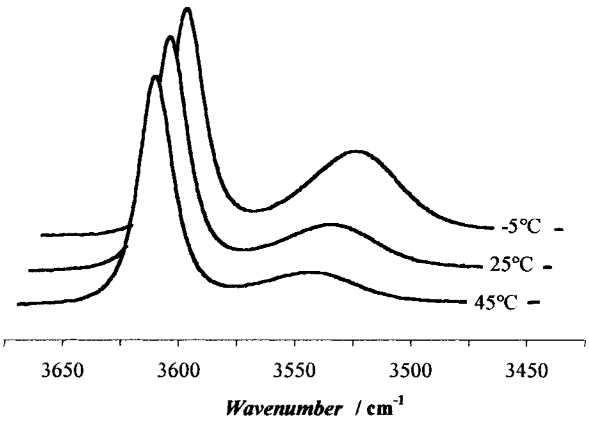

Figure 1. IR determination of the enthalpy for hydrogen bonding of 1-fluoroadamantane to 4-fluorophenol in CCl_4. The absorbance of the OH band of free 4-fluorophenol at 3614 cm^{-1} decreases with decreasing temperature to the benefit of the OH band of the complex at 3544 cm^{-1}

Figure 1 shows the IR spectra recorded for the 4-fluorophenol–1-fluoroadamantane complex. The absorbance and concentration data and the calculation of complexation constants at the various temperatures are reported in Table 1. The enthalpy ΔH_c° is obtained from the slope of a ln K_c *versus* $1/T$ van't Hoff plot:

$$\ln K_c = -\frac{\Delta H_c^\circ}{R}\frac{1}{T} + \frac{\Delta S_c^\circ}{R} \tag{5}$$

Over the 50 °C temperature range employed, no evidence for a change in ΔH_c° with temperature was found. It should be noted that the experiment is controlled in three ways. Firstly, the accuracy of the 4-fluorophenol stock solution concentration C_a° is tested by a calculation of ε, which must fall within the limits 238 ± 4 $dm^3\ mol^{-1}\ cm^{-1}$. Secondly, the equilibrium constant calculated at 25 °C must match the value found in our previous work.[8] In the latter work, K_c was the average of five determinations in which the halogenoalkane concentration was varied in order to complex various quantities of 4-fluorophenol (*ca* 15, 20, 30, 35, and 45%). A new stock solution of halogenoalkane is made if the two K_c values obtained from the concentration and the temperature variation differ by more than 10%. Thirdly, the least-squares treatment of the van't Hoff plot must give a squared correlation coefficient greater than 0.9990.

Calculations of entropy

The entropy can be calculated from the intercept of the van't Hoff plot [Eqn. 5]. It can also be obtained [Eqn. 6] from the enthalpy of the single solution experiment and the Gibbs energy, calculated [Eqn. 7] from $K_{c,298}$, which is obtained as the mean of five equilibrium constant determinations with various halogenoalkane concentrations. The two methods give results that are in excellent agreement.

$$\Delta S_{c,298}^\circ = (\Delta H_c^\circ - \Delta G_{c,298}^\circ)/298.15 \tag{6}$$

$$\Delta G_{c,298}^\circ = 298.15 R \ln K_{c,298} \tag{7}$$

Standard states

The enthalpies, entropies, and Gibbs energies of Eqns (5)–(7) are calculated on the molar concentration scale, since the K_c unit is $dm^3\ mol^{-1}$ [Eqn. 2]. Hepler[33] has shown that this ΔH_c° value relative to molarity is not the correct 'standard-state infinite dilution' ΔH°. The thermodynamically correct value must be calculated from K_x relative to mole fraction and is related to ΔH_c° by Eqn. 8

$$\Delta H^\circ = \Delta H_c^\circ - \alpha R T^2 \tag{8}$$

where α is the coefficient of thermal expansion of the solvent. For CCl_4 at 298 K the correction term amounts to 0.9 kJ mol^{-1}. K_x values lead to standard Gibbs energies $\Delta G_x^\circ = -RT \ln K_x$ and entropies ΔS_x° that are different

Table 1. Determination of the complexation enthalpy for hydrogen bonding of fluoroadamantane to 4-fluorophenol in CCl_4[a]

t/°C	−4.8	25.0	44.6
Absorbance A	0.3334	0.3430	0.3342
Temperature-corrected concentrations and absorption coefficient			
C_a°	1.76	1.70	1.66
C_b°	102.42	98.84	96.47
ε/$dm^3\ mol^{-1}\ cm^{-1}$	261.63	242.55	229.92
$C_a = A/\epsilon\ l$	1.27	1.41	1.45
$C_c = C_a^\circ - C_a$	0.49	0.28	0.20
$C_b = C_b^\circ - C_c$	101.94	98.56	96.27
K_c/$dm^3\ mol^{-1}$	3.74	2.04	1.46
$-\Delta H_c^\circ = 13.52$ kJ mol^{-1}		$-\Delta S_c^\circ = 39.4$ J K^{-1} mol^{-1}	

[a] All concentrations in mmol dm^{-3}.

Table 2. Thermodynamic functions ΔG, ΔH (kJ mol^{-1}), and ΔS(J K^{-1} mol^{-1}) and IR shifts (cm^{-1}) for hydrogen bonding of halogenoalkanes to 4-fluorophenol in CCl_4

	$-\Delta H^{\circ}$[a]	$-\Delta S^{\circ}_{x,298}$[a]	$-\Delta G^{\circ}_{x,298}$[b]	$\Delta\nu(OH)$[c]
Fluoroalkanes				
1-fluoroadamantane	14.43	23.1	7.55	70
fluorocyclohexane	12.65	21.1	6.29	58.7
1-fluoropentane	10.47	15.8	5.44	44
1,3-difluoropropane	9.71	12.1 (17.9)[d]	5.95 (4.23)[d]	31.6
Chloroalkanes				
1-chloroadamantane	10.17	18.0	4.81	85
chlorocyclohexane	8.81	15.1	4.24	76.9
1-chloropentane	6.96	10.4	3.61	63
1,5-dichloropentane	6.41	3.8 (9.6)[d]	5.27 (3.55)[d]	58.5
1,3-dichloropropane	5.82	4.6 (10.4)[d]	4.53 (2.81)[d]	48
Bromoalkanes				
1-bromoadamantane	9.68	16.5	4.53	97
bromocyclohexane	7.46	10.2	4.30	88
1-bromopentane	7.15	11.2	3.73	75.8
1,3-dibromopropane	5.29	2.2 (8)[d]	4.47 (2.75)[d]	58.7
Iodoalkanes				
1-iodoadamantane	8.52	13.4	4.70	102
2-iodo-2-methylpropane	6.74	9.6	3.90	95
iodocyclohexane	6.24	7.6	3.90	91.5
1-iodopentane	5.25	5.1	3.72	79
1,3-diiodopropane	4.96	1.2 (7)[d]	4.53 (2.81)[d]	66

[a] Calculated from Eqn. 5.

[b] $\Delta G^{\circ}_{x,298} = -RT \ln K_{x,298}$.

[c] Ref. 8.

[d] Statistically corrected.

from ΔG°_{c} and ΔS°_{c}:

$$\Delta G^{\circ}_{x}/\text{kJ mol}^{-1} = \Delta G^{\circ}_{c} - 5.8 \qquad (9)$$

$$\Delta S^{\circ}_{x}/\text{J K}^{-1}\ \text{mol}^{-1} = \Delta S^{\circ}_{c} + 16.3 \qquad (10)$$

Statistical treatment of data

In the single solution method, the precision of the results (due to random error) is certainly overestimated if taken from the error limits of the slope and intercept in the regression analysis of the van't Hoff plot. An illustration is given by the 4-fluorophenol–fluorocyclohexane complex. A first experiment gives $-\Delta H^{\circ}_{c} = 12.04 \pm 0.20$ kJ mol^{-1} and $-\Delta S^{\circ}_{c} = 38.48 \pm 0.67$ J K^{-1} mol^{-1}. The precision is certainly worse than 0.2 kJ mol^{-1} for enthalpy and 0.7 J K^{-1} mol^{-1} for entropy. Indeed, a second experiment leads to $-\Delta H^{\circ}_{c} = 11.43 \pm 0.14$ kJ mol^{-1} and $-\Delta S^{\circ}_{c} = 36.24 \pm 0.48$ J K^{-1} mol^{-1}. The arithmetic means from these two measurements have standard deviations of 0.3 kJ mol^{-1} and 1.1 J K^{-1} mol^{-1}, which seem more realistic estimates of the precision. The correctness of the results is still more difficult to estimate because of the systematic and the gross error. It is interesting to compare our van't Hoff complexation enthalpies of 8.81 kJ mol^{-1}, 7.46 kJ mol^{-1}, and 6.24 kJ mol^{-1} for the complexes of 4-fluorophenol with chloro-, bromo-, and iodo-cyclohexane respectively with the results obtained by Arnett *et al.*[11] from their pure base calorimetric method: 8.87 kJ mol^{-1}, 8.13 kJ mol^{-1}, and 6.11 kJ mol^{-1} respectively. For the chloro- and iodo-cyclohexane, the results differ by 0.06 kJ mol^{-1} and 0.13 kJ mol^{-1} respectively, probably by chance. The difference of 0.67 kJ mol^{-1} for the bromocyclohexane seems a more realistic estimate of the correctness of our hydrogen-bond enthalpies.

RESULTS

Table 2 presents the Gibbs energies $\Delta G^{\circ}_{x,298}$, the enthalpies ΔH°, and the entropies $\Delta S^{\circ}_{x,298}$ for the complexation of 18 halogenoalkanes with 4-fluorophenol in CCl_4. Statistical corrections of $-RT \ln 2$ and $-R \ln 2$ are applied, respectively, to the Gibbs energies and entropies of dihalogenoalkanes. For the IR shifts $\Delta\nu$(OH) of the 3614 cm^{-1} band of 4-fluorophenol, we use the data measured in a previous study.[8] This IR spectroscopic scale of hydrogen-bond basicity is illustrated in Fig. 2. The agreement of these data with the results of West *et al.*,[9] obtained by a near-IR method,[27] for the complexes of phenol with four halogenoalkanes can be appreciated by the correlation coefficient r, the standard error of the estimate s, the Fisher test F, the slope greater than unity (4-fluorophenol is a better hydrogen-bond donor than

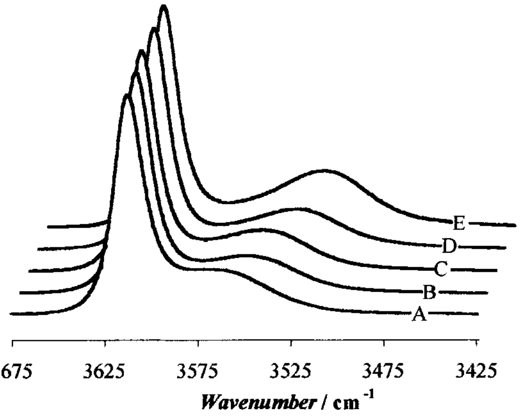

Figure 2. IR shifts of the OH band of 4-fluorophenol for the 4-fluorophenol–chloroalkanes complexes: (A) 1,3-dichloropropane; (B) 1,5-dichloropentane; (C) 1-chloropentane; (D) chlorocyclohexane; (E) 1-chloroadamantane

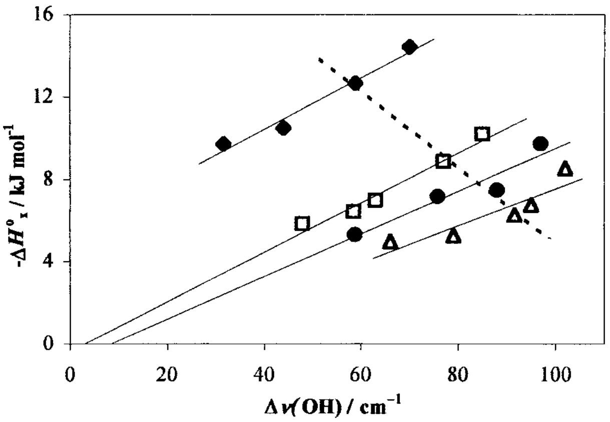

Figure 3. Plot of the ΔH° *versus* $\Delta\nu$(OH) for the complexes of 4-fluorophenol with (◆) fluoroalkanes, (□) chloroalkanes, (●) bromoalkanes, and (△) iodoalkanes. The dashed line corresponds to the hypothetical family of halogenocyclohexanes

phenol), and the intercept close to zero, of Eqn. (11):

$$\Delta H^\circ(\mathrm{FC_6H_4OH, cHexX}) = 1.12(\pm 0.07)\Delta H^\circ(\mathrm{C_6H_5OH, cHexX}) + 0.6(\pm 0.6) \quad (11)$$

$$n = 4 \qquad r = 0.997 \qquad s = 0.28\,\mathrm{kJ\ mol^{-1}} \qquad F = 295$$

DISCUSSION

Validity of frequency shifts–enthalpy correlations

There has been a continuing controversy in the literature[15–32] concerning the validity of the Badger–Bauer relationship between $-\Delta H^\circ$ and $\Delta\nu$(OH), the shift of the OH stretching mode upon hydrogen-bond formation. The present data furnish an interesting test of the relationship, because (i) accurate enthalpies and IR shifts have been measured, (ii) the data pertain to weak hydrogen-bond acceptors, which should allow one to study the domain near the intercept, (iii) the data refer to four different hydrogen-bond acceptor atomic sites spreading over four periods of the periodic table, and (iv) the basicity of each site is varied as widely as chemistry allows, from the 1-halogenoadamantanes to the 1,3-dihalogenopropanes.

The plot of $-\Delta H^\circ$ versus $\Delta\nu$(OH) shows (Fig. 3) that there is no connection between ΔH° and $\Delta\nu$(OH) for halogenoalkanes ($n = 18$, $r = 0.09$).

Each halogen atom draws its own line in the ΔH°–$\Delta\nu$(OH) plane (full lines of Fig. 3). In other words, the Badger–Bauer relationship exists, but only as a family-dependent relationship. Here, a family is defined by a common hydrogen-bond acceptor atomic site. If one tries to define an RX family by a common group R and various halogens X, one observes (dashed line of Fig. 3) that $-\Delta H^\circ$ decreases in the order F > Cl > Br > I, the reverse of the IR-shift order. This inverse Badger–Bauer relationship does not seem to have received a theoretical interpretation since it was first observed in 1962.[9]

The comparison of Eqns (12)–(15) for fluoro-, chloro-, bromo-, and iodo-alkanes

$$-\Delta H^\circ(\mathrm{FC_6H_4OH, RF}) = 0.13(\pm 0.02)\Delta\nu(\mathrm{OH\cdots F}) + 5.4(\pm 0.8) \quad (12)$$

$$n = 4 \qquad r = 0.986 \qquad s = 0.44\,\mathrm{kJ\ mol^{-1}} \qquad F = 68$$

$$-\Delta H^\circ(\mathrm{FC_6H_4OH, RCl}) = 0.12(\pm 0.01)\Delta\nu(\mathrm{OH\cdots Cl}) - 0.4(\pm 0.8) \quad (13)$$

$$n = 5 \qquad r = 0.984 \qquad s = 0.37\,\mathrm{kJ\ mol^{-1}} \qquad F = 94$$

$$-\Delta H^\circ(\mathrm{FC_6H_4OH, RBr}) = 0.10(\pm 0.02)\Delta\nu(\mathrm{OH\cdots Br}) - 0.9(\pm 1.9) \quad (14)$$

$$n = 4 \qquad r = 0.952 \qquad s = 0.68\,\mathrm{kJ\ mol^{-1}} \qquad F = 19$$

$$-\Delta H^\circ(\mathrm{FC_6H_4OH, RI}) = 0.09(\pm 0.02)\Delta\nu(\mathrm{OH\cdots I}) - 1.45(\pm 2.1) \quad (15)$$

$$n = 5 \qquad r = 0.906 \qquad s = 0.69\,\mathrm{kJ\ mol^{-1}} \qquad F = 14$$

shows that only the chloro- and bromo-alkanes can be considered to pass through the origin [the poor quality of Eqn. (15) prevents any conclusion for iodoalkanes]. Thus, the Badger–Bauer relationships in Eqns (13) and (14) constitute a satisfactory method for providing reliable $\Delta H°$ data for any chloro- and bromo-alkane from an easily measured IR spectroscopic shift, over the entire basicity range from CCl_4 [$\Delta\nu(OH) = 0\,cm^{-1}$] to 1-chloroadamantane [$\Delta\nu(OH) = 85\,cm^{-1}$]. On the contrary, the prediction of $\Delta H°$ in the fluoroalkane and iodoalkane family seems limited to the experimental range of frequency shifts. For frequency shifts outside this region, we know nothing about the extrapolation that is allowed.

Isoequilibrium relationships

A linear dependence of enthalpy and entropy within a series of related reactions has the form of Eqn. 16:

$$\Delta H° = \beta \Delta S° + \text{constant} \qquad (16)$$

This apparently simple equation hides difficult statistical problems, since both $\Delta H°$ and $\Delta S°$ are loaded with correlated errors. Since $\Delta H°$ and $\Delta S°$ are obtained from the linear regression in Eqn. 5, any experimental error that makes $\Delta H°$ greater also makes $\Delta S°$ greater. Therefore, their correlation cannot be pursued for fear of merely generating error contours from two sets of numbers ($\Delta H°$ and $\Delta S°$) extracted from the treatment of the same set of experimental data.

Exner and Beranek[12,34,35] have achieved a statistically correct solution by returning to the original experimental quantities. By substituting $\Delta S°$ from Eqn. 16 into Eqn. 5 one obtains:

$$\ln K = (\Delta H°/R)(\beta^{-1} - T^{-1}) + \text{ constant} \qquad (17)$$

In the coordinates ln K and T^{-1}, Eqn. 17 represents a family of straight lines with different slopes ($-\Delta H°/R$) intersecting at one point at $T = \beta$ (the isoequilibrium temperature). A linear dependence in the coordinates $\Delta H°$ and $\Delta S°$ is thus mathematically, but not statistically, strictly equivalent to the constraint of a common point of intersection in the coordinates ln K and T^{-1}.

Exner and Beranek have solved algebraically (in a special case)[34] and by successive approximations (in the general case)[35] the mathematical problem of several regression lines with one point of intersection. Recently, Ouvrard *et al.*[36] wrote a program[37] that can test several hypotheses: whether the lines are parallel ($\beta^{-1} = \infty$, isoenthalpic reactions), intersect at $\beta^{-1} = 0$ (isoentropic reactions), or intersect at any other β^{-1} value (isoequilibrium relationship). The program also estimates from the Ψ Exner test[38] whether the isoequilibrium relationship is acceptable as an experimental relationship of an approximate validity.

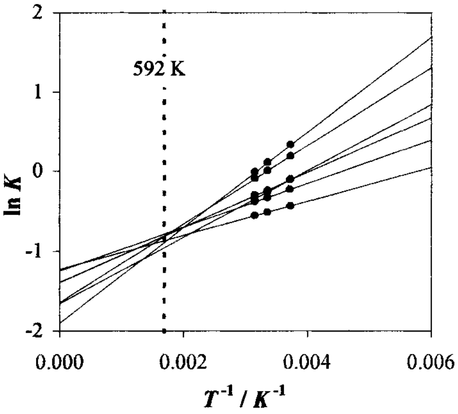

Figure 4. Isoequilibrium relationship [Eqn. 17] for the hydrogen bonding of 4-fluorophenol to halogenoalkanes in CCl_4. For the sake of clarity only six van't Hoff plots are shown (fluorocyclohexane, fluoropentane, chlorocyclohexane, bromocyclohexane, iodocyclohexane, 1,3-diiodopropane)

In the field of hydrogen-bond complexation we are not aware of any correct statistical treatment of the extra-thermodynamical Eqn. 16, although this relationship has often been anticipated[3] on the basis of wrong statistics. For the hydrogen bonding of 4-fluorophenol to halogenoalkanes in CCl_4 [Eqn. 1], Fig. 4 shows that the van't Hoff plots intersect approximately at one point. The isoequilibrium relationship is accepted as an approximate relationship ($\Psi = 0.084$). The isoequilibrium temperature ($\beta = 592$ K) is determined with some uncertainty, but the confidence interval (529–701 K) does not include the isoentropic relationship.

Attempts to divide the family of halogenoalkanes into four sub-families (RF, RCl, RBr, and RI) lead to isoequilibrium relationships with confidence intervals for the isoequilibrium temperature including the isoentropic relationship. However, the structural variation and the data number inside each sub-family are too restricted[†] to allow safe conclusions on the isoentropic behaviour. In particular, we are unable to prove that the isoentropic values (J $K^{-1}\,mol^{-1}$) for the chloroalkanes (−12), bromoalkanes (−11), and iodoalkanes (−9) are different, taking into account the experimental uncertainty.

CONCLUSIONS

(1) We have constructed, from the complexation of halogenoalkanes by 4-fluorophenol in CCl_4, a reliable enthalpic scale of hydrogen-bond basicity for halogenoalkanes spanning from $-14.4\,kJ\,mol^{-1}$ (1-fluoroadamantane) to $-4.96\,kJ\,mol^{-1}$ (1,3-diiodopropane).

[†] We cannot introduce more powerful substituents for varying the basicity more widely, because they introduce a new hydrogen-bonding site. This is for example the case of $RC{\equiv}CX$, C_6H_5X, $RCH{=}CHX$ (π site), or $X'(CH_2)_nX$ (second halogen site).

(2) For this series of reactions, we have established the validity of the isoequilibrium relationship (ΔH° *versus* ΔS°) by a statistically correct procedure.
(3) We have shown the validity of the Badger–Bauer relationship [ΔH° *versus* $\Delta\nu$(OH)] as a family-dependent relationship. Reliable hydrogen-bond enthalpies can be calculated from IR shifts either on the whole basicity range, for RCl and RBr, or on a restricted range, for RF and RI, depending on whether the Badger–Bauer line passes through the origin or not.

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