FARADAY

Hydrogen bonding

Part 44† Thermodynamics of complexation of 3,5-dichlorophenol with ketones and ethers in cyclohexane: the Badger–Bauer relationship

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Equilibrium constants for 1 : 1 hydrogen bond complexation between 3,5-dichlorophenol (DCP) and 17 ketones and 12 ethers in cyclohexane solution have been obtained by an FTIR method that takes into account both dimerization of the acid and formation of 2 : 1 complexes. Enthalpies of complexation for the same ketones and ethers have been determined by a calorimetric method, leading to values of log K, ΔG°, ΔH° and ΔS° for 1 : 1 complexation in the 29 systems, as well as log K_2 for the 2 : 1 complexation between 2 mol of acid and 1 mol of base. For the ketone systems there is very little variation in the three thermodynamic parameters with alkyl substitution, but for the ethers there are systematic variations depending on the alkyl substituent or if the ethers are cyclic.

Values of the OH stretching frequency in the DCP complexes with the ketones and ethers in cyclohexane have been obtained. The band shapes for the DCP–ketone complexes are very asymmetric, possibly due to the presence of stereoisomeric complexes, but the ν_{OH} band for DCP–ether complexes is symmetric and very suitable for the evaluation of any relationship between ν_{OH} and ΔH°. It is found that for the complexation of DCP with the 12 aliphatic ethers in cyclohexane, there is almost no connection between the calorimetrically determined ΔH° values and values of $\Delta\nu_{OH}$.

In 1937, Badger and Bauer[1] studied the self-association of a number of compounds and suggested that there was a relationship between $\Delta\nu_{OH}$ for self-association and the energy of self-association. The latter was found by indirect methods such as a comparison of the enthalpy of vaporization of alcohols with that of alkanes. In a subsequent paper, the energies of hydrogen bond formation for 2-chlorophenol and 2-chloroethanol were obtained from differences in energy of the two molecular configurations, in one of which there is an intramolecular hydrogen bond.[2] However, the plot of $\Delta\nu_{OH}$ *vs.* hydrogen bond energy was shown as a curve, and not as a straight line.[2] Over the years, these observations of Badger and Bauer have been elevated into what appears to be a physicochemical rule. By 1971, Vinogradov and Linnell[3] could state that 'A direct relationship between the shift in the IR stretching frequency $\Delta\nu$ caused by hydrogen bonding and the magnitude of $-\Delta H^\circ$ was first suggested by Badger and Bauer', and Joesten and Schaad[4] used a similar expression, even though Badger and Bauer[1,2] nowhere mention $-\Delta H^\circ$, and even though their observations were confined to self-association and to intramolecular hydrogen bonds.

The use of the term 'Badger–Bauer relationship' is now so widespread, that we shall use this expression, not in the original sense,[1,2] but defined as a relationship between $\Delta\nu_{OH}$ for a given acid in a series of hydrogen bond complexes with various bases, and ΔH° for the complexation of the acid with the bases, both in the same given solvent. The definition can also include the case of a series of OH acids with a given base, and might possibly be extended to relationships between $\Delta\nu$ for C=O shifts and ΔH° values. Used in these terms, the Badger–Bauer relationship has been supported by several workers,[5–12] but challenged by others,[13–16] some of whom maintain that the relationship is family dependent.[14–16] In a detailed study, Joesten and Schaad[4] found that the Badger–Bauer relationship sometimes held reasonably well, but sometimes only very roughly. Kasende and Zeegers-Huyskens[17,18] observed a linear relationship between $\Delta\nu_{OH}$ and ΔH° for a series of phenols against a given base, although different lines were obtained when the base was varied, a clear example of family dependent relationships. Similar observations were made by Rao *et al.*[19] in an earlier detailed study. More recently, Goralski[20] found an approximate Badger–Bauer relationship for the complexation of cholesterol with a series of bases, and suggested that the relationship could be used to estimate further ΔH° values. However, inspection of the $\Delta\nu_{OH}$ *vs.* ΔH° plot shows a small but significant family dependent relationship. Borisenko *et al.*[21] have shown that the Badger–Bauer relationship fails for a series of NH acids against a given base. On the other hand, Deng *et al.*[22] have actually used a Badger–Bauer relationship to estimate enthalpies of interaction from frequency shifts.

One difficulty in assessing the Badger–Bauer relationship is that some of the enthalpy data have been obtained through the temperature variation of hydrogen bond equilibrium constants, the so-called van't Hoff method. This requires not only very accurate equilibrium constants, but also accurate temperature measurements as well, and it is doubtful if many reported van't Hoff ΔH° values have errors of less than 0.5 kcal mol^{-1}. A major aim of the present work was to determine thermodynamic parameters for hydrogen bond complexation, using FTIR methods to obtain equilibrium constants, and calorimetry to obtain ΔH° values. With accurately measured ΔH° values, it should be possible to evaluate the Badger–Bauer relationship thoroughly. Since we would be in possession of ΔH°, ΔG° and ΔS° values for hydrogen bond

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complexation, we could also study constitutional effects on these thermodynamic parameters.

The choice of acid, bases, and solvent may be quite critical, and our selection was made as follows. First we chose cyclohexane as a solvent because this precludes any specific solute–solvent interactions. In addition, if various alkyl substituents are introduced into the base, the relative permittivity in the vicinity of the base functional group will not alter. Secondly, it was necessary to choose an OH acid, and we selected 3,5-dichlorophenol (DCP) because it is a solid, easy to handle, and because with our selection of bases it would yield equilibrium constants of the order of 10^2, a convenient and practical value. Thirdly, we chose a series of aliphatic ketones and aliphatic ethers as the bases. Only aliphatic hydrocarbon substituents were allowed, so as to maintain a constant relative permittivity around the base functional group.

Materials and methods

Chemicals

Cyclohexane was BDH Analar grade; DCP was the best available commercial grade (Aldrich). The various bases used were either the best available commercial grades, or were from the ICI compound collection.

FTIR studies

All IR measurements were carried out on a Digilab FTS-20E Fourier transform spectrophotometer. Spectra were recorded at a resolution of 4 cm^{-1} and collected over 600 scans, unless otherwise stated. A 1 mm cell with calcium fluoride windows was used, and was placed in a water-jacketed cell holder (Specac) thermostated at 298 K to within 0.5 K using an LKB Multitemp water circulator. At least 10 min was allowed for the temperature to equilibrate, and the instrument was continually purged with dry nitrogen to remove traces of water and carbon dioxide.

Calorimetric studies

The apparatus used was a modified Hart Scientific 5021 isoperibol titration calorimeter fitted with a burette of capacity 2.5 ml driven by a reversible stepper motor. The burette delivery rate could be varied from 0.01 to 999 steps per second, and the delivery time could be controlled either manually or automatically from a Tronac CCP 930 calorimeter computer programmer. The titrant outlet was fitted with a pinched syringe needle in order to reduce the outlet area. This modification was very important when working with non-aqueous solvents as otherwise premature mixing of reactants took place. The calorimeter was contained in a constant temperature bath of 40 l capacity, fitted with a motor driven stirrer, an auxiliary cooling system with a temperature 5–10 K below the set point, and an electronic thermostat. Under normal conditions the bath temperature could be maintained at 298.15 K with a deviation of 0.003 K over a period of 24 h. A Tronac CCP 930 calorimeter computer programmer complete with a Texas Instruments Silent 700 data terminal was interfaced to the burette motor, the electronic console and a digital voltmeter. This enabled programmed control of both the burette delivery rate and the calibration heating time, together with programmed data processing of a thermogam. The burette was calibrated by weighing water delivered, and a delivery rate of 6.61 μl s^{-1} and a step volume of 0.1322 μl were found. The calibration constant was found for both 50.0 ml water and 50.0 ml cyclohexane in the vessel, and was constant to 0.6% with water, and to 0.5% with cyclohexane.

As a check, the heat of ionization of tris(hydroxymethyl)aminomethane (THAM) was obtained by incremental addition of a 0.2512 M aqueous solution of THAM to 50.0 ml of aqueous HCl. After correction for heat of dilution and the heat of hydrolysis of THAM, the heat of ionization was found to be -11.39 ± 0.06 kcal mol^{-1} over 16 additions. This compares well with the value reported by Ojelund and Wadso[23] of -11.35 ± 0.01 kcal mol^{-1} at the same ionic strength.

The heat of ionization of water was also obtained, through the incremental addition of aqueous perchloric acid to aqueous sodium hydroxide. Over 16 additions a value of 13.40 ± 0.10 kcal mol^{-1} was found, in good agreement with reported values of 13.336,[24] 13.335[25] and 13.331 kcal mol^{-1}.[26]

Determination of equilibrium constants by FTIR

A calibration was first carried out of the absorbance, A, of the OH fundamental stretching vibration of DCP at 3609 cm^{-1}. The DCP concentration, a_0, was varied between 0.001 M and 0.02 M using 15 separately made-up solutions. A linear regression analysis was carried out on eqn. (1), where ε = (molar absorption coefficient) × [cell path length (1 mm)].

$$A = \varepsilon a_0 + c \quad (1)$$

There was a definite trend in both the slope and intercept, so that eqn. (1) was not strictly obeyed. We concluded that although the maximum DCP concentration was only 21 mM, there was still some self-association of the phenol that had to be taken into account. The dimerization constant, K_d, is given by,

$$K_d = d/a^2 \quad (2)$$

where d and a are the dimer and monomer concentrations, the former being given by,

$$d = (a_0 - a)/2 = (A_0 - A)/2\varepsilon \quad (3)$$

However, if DCP forms a linear dimer, rather than a cyclic dimer, the terminal OH of the dimer will be almost equivalent to the OH of the monomer. The measured value of $(A_0 - A)$ for the linear dimer will then be only half that for a cyclic dimer, and eqn. (3) is more correctly written as,

$$d = (A_0 - A)/\varepsilon \quad (4)$$

The same argument leads to

$$a^2 = (A/\varepsilon - d)^2 \quad (5)$$

For dilute solutions $A/\varepsilon \gg d$, and eqn. (2), (4) and (5) then generate a quadratic in A/ε,

$$K_d(A/\varepsilon)^2 + (A/\varepsilon) - a_0 = 0 \quad (6)$$

which with incorporation of a possible intercept (c) leads to

$$A = \varepsilon\{[-1 + (1 + 4K_d a_0)^{1/2}]/2K_d\} + c \quad (7)$$

We then fitted our data to eqn. (7), with the results shown in Table 1. Unlike the linear model, the non-linear fitting curve passes through the origin, within the given standard error. The dimerization constant of 2.27 l mol^{-1}, when statistically corrected to 1.14 l mol^{-1}, compares favorably with the association of DCP with the model compound 3,5-dichloroanisole, *viz.* 1.2 l mol^{-1} as found in this work.

We can now take account of DCP dimerization to obtain an expression for the equilibrium constant for a 1 : 1 DCP–

Table 1 Non-linear fitting of absorbance–concentration data

parameter	estimate	error	95% confidence interval
K_d	2.27 l mol^{-1}	0.45	1.28–3.25
ε	31.32 l mol^{-1}	0.27	30.73–31.91
c	0.0007	0.0011	−0.0018–0.0032

base complex, reaction (I), as the expression in eqn. (8) where b_0 is the initial base concentration.

$$\text{DCP} + \text{base} \overset{K}{\rightleftharpoons} \text{DCP}\cdots\text{base} \qquad \text{(I)}$$

Note that the terms in K_d in eqn. (8) simply allow for the non-linearity of the absorbance–concentration data.

$$K = \frac{a_0 - A/\varepsilon - K_d(A/\varepsilon)^2}{[A/\varepsilon - K_d(A/\varepsilon)^2] \times [b_0 - a_0 + A/\varepsilon + K_d(A/\varepsilon)^2]} \qquad (8)$$

A titration experiment was conducted for the complexation of DCP with cyclohexanone; solutions were made up with various cyclohexanone initial concentrations and the same initial concentration of DCP. Six solutions were studied, and K values were calculated through eqn. (8); the value of K did not remain constant, but decreased as the fraction of complexed DCP increased. The most likely explanation is the formation of a 2 : 1 complex as well as the 1 : 1 complex. There are two possible forms of a 2 : 1 complex, see Fig. 1, for a ketone base.

The C=O band of cyclohexanone was monitored in the presence of increasing concentrations of DCP; the first 1 : 1 bound band at 1706 cm^{-1} gradually broadened and shifted to 1701 cm^{-1} indicating the presence of a type II complex. A very small concentration of a type I complex could just be detected at 1678 cm^{-1}. With the sterically hindered ketone, di-*tert*-butylketone, only the 1 : 1 bound band and the type II complex band could be detected.

We have, therefore, to take into account not only the non-linear absorbance–concentration data due to DCP dimerization, but also the formation of 1 : 1 and 2 : 1 type II complexes. Titration experiments usually take the form of a constant initial concentration of acid, and a succession of increased initial concentrations of base, see, for example Table 2. In this procedure, the excess of base over acid towards the end of the titration prevents appreciable formation of 2 : 1 complexes. If a reverse titration is carried out with different initial concentrations of acid, and a fixed initial concentration of base, 2 : 1 complexes will become more favoured towards the end of the titration. At first sight, this seems not to be the correct titration mode in order to obtain 1 : 1 complexation constants. However, it has a considerable advantage in that the procedure is very sensitive to the value of the second equilibrium constant, K_2, and it is much easier to check for 2 : 1 complexes than with the normal mode of titration. This can be seen, Table 3, from a reverse titration of DCP with cyclohexanone, using the non-linear absorbance–concentration fit, but assuming only a 1 : 1 complex. The apparent equilibrium constant increases by a factor of two throughout the titration,

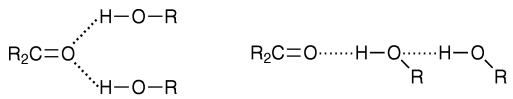

Fig. 1 Possible 2 : 1 complexes of DCP with ketones

Table 2 Spectroscopic titration of DCP with cyclohexanone in cyclohexane at 298 K

a_0/mM	b_0/mM	$A \times 100$	K/l mol^{-1}
10.09	0.00	30.98	—
10.09	3.54	23.92	253
10.09	7.08	18.83	218
10.09	14.16	12.17	201
10.09	21.24	8.60	193
10.09	28.32	6.56	188

Table 3 Reverse spectroscopic titration of DCP with cyclohexanone in cyclohexane, at 298 K, assuming only a 1 : 1 complex

a_0/mM	b_0/mM	$A \times 100$	K/l mol^{-1}
3.08	5.91	5.27	184
6.17	5.91	11.46	199
9.25	5.91	18.42	216
12.34	5.91	25.56	267
15.42	5.91	33.38	308
18.50	5.91	41.47	361

so that the reverse titration is a powerful method for determining the model to be used. We therefore use a model that involves both 1 : 1 and 2 : 1 complexation, reaction (II), as well as the non-linear absorbance–concentration fit.

$$\text{DCP} + \text{DCP}\cdots\text{base} \overset{K_2}{\rightleftharpoons} \text{DCP}\cdots\text{DCP}\cdots\text{base} \qquad \text{(II)}$$

Previous workers have solved the problem of 1 : 1 and 2 : 1 complexation in a number of ways. Neel *et al.*[27] introduced an iterative graphical method, which is laborious but which has been used quite successfully. A much easier method was applied by Zeegers-Huyskens and co-workers[28] who first calculated an apparent equilibrium constant, K_{app}, assuming only a 1 : 1 complex, and then related K_{app} to K, K_2 and the free acid concentration. Although relatively quick, the method has two main disadvantages: (i) the points which have the greatest experimental error are those that have the greatest weight in the calculation of K and K_2, and (ii) it is difficult to evaluate the errors in K and K_2.

In our method we obtain an expression of the type $K = f(K_2)$ as follows. At equilibrium, let the concentration of monomer DCP be a, that of the 1 : 1 complex be x, that of the 2 : 1 complex be y and that of the dimer DCP be z. Then,

$$a_0 = a + x + 2y + z \qquad (9)$$

$$b_0 = b + x + y \qquad (10)$$

$$K = x/ab \qquad (11)$$

$$K_2 = y/ax \qquad (12)$$

and K is given by the expression,

$$K = \frac{(a_0 - a - 2z)}{a[b_0(1 + 2aK_2) - (a_0 - a - 2z)(1 + 2aK_2)]} \qquad (13)$$

If the identities $(a + z) = A/\varepsilon$ and $z = K_d(A/\varepsilon)^2$ are substituted into eqn. (13), the function $K = f(K_2)$ contains only terms which are experimentally obtainable. The final stage is non-linear fitting of the data to the equation $f(K_2) - K = 0$, thereby generating the optimum values of the adjustable parameters K and K_2. Except for a study of complexes of acetic acid and amines,[29] this seems to be the first method of analysis that takes into account both acid self-association and 2 : 1 complex formation in the measurement of 1 : 1 equilibrium constants. In Table 4 are summarized the results of four independent reverse titration experiments; there is excellent reproducibility of both K and K_2.

Determination of ΔH for complexation by calorimetry

The titration curve for 1 : 1 complexation is described by the equation,

$$Q = \Delta HV/2\{(a_0 + b_0 + 1/K) - [(a_0 + b_0 + 1/K)^2 - 4a_0 b_0]^{1/2}\} \qquad (14)$$

where Q is the heat due to hydrogen bonding and V is the total volume of the calorimeter vessel contents in litres. The

Table 4 Results of the reverse titration procedure for the DCP–cyclohexanone association in cyclohexane, at 298 K, assuming both 1 : 1 and 2 : 1 complexation

expt.	K/l mol^{-1}	σ	95% confidence interval		K_2/l mol^{-1}	σ	95% confidence interval	
(i)	176.5	4.9	163.0	190.1	13.2	1.2	10.0	16.4
(ii)	172.1	2.7	164.7	179.5	13.0	0.7	11.1	14.9
(iii)	182.5	3.4	173.1	192.0	14.3	0.8	12.0	16.6
(iv)	184.6	4.4	172.4	196.8	10.4	0.9	7.8	13.0
mean	178.9	—	—	—	12.7	—	—	—

various quantities in eqn. (14) are evaluated as,

$$Q = \sum_{i=1}^{i=n} q_i^{HB} \quad (15)$$

$$V = 0.05 + \sum_{i=1}^{i=n} v_i \quad (16)$$

$$a_0 = 0.05[\text{DCP}]/V \quad (17)$$

$$b_0 = \sum_{i=1}^{i=n} v_i[\text{base}]/V \quad (18)$$

where q_i^{HB} is the titration run heat less an equivalent dilution run heat, v_i is the volume of the ith increment, [DCP] is the initial concentration of DCP in the vessel, and [base] is the titrant base concentration. Values of ΔH and K are then evaluated by fitting the titration data, eqn. (15)–(18), to eqn. (14). We found that there was a distinct trend in both ΔH and K as the titration progresses. Experiments with other bases also show this effect, which, from our spectroscopic work, seems to be due to 2 : 1 complexation as well as 1 : 1 complexation. If this so, a single titration experiment must be analysed in such a way as to yield no less than four parameters, *viz.* K, K_2, ΔH and ΔH_2. This is simply not practical, and so we were forced to develop an alternative calorimetric procedure.

If a relatively dilute solution of DCP is added to a more concentrated solution of the base in the calorimeter vessel, the formation of 2 : 1 complexes (2 mol of acid and 1 mol of base) will be avoided, and the titration heat will be due only to the formation of the 1 : 1 complex (after correcting for the dilution run). We refer to this procedure as the excess base method. However, since the concentration of base is actually no more than around 0.2 M, the results will still refer to cyclohexane solution. Although most of the DCP will be in the complexed form during the titration, a small quantity will be present as the free acid. The spectroscopically determined K value is used to correct for this, as follows. For each addition of DCP,

$$\Delta H = Q/Nf \quad (19)$$

where N is the total number of mol of DCP added during the addition, and f is the fraction of DCP that is actually complexed. For each of the triplicate additions in a single run, N is constant and is given by

$$N = 6.61 \times 10^{-4}[\text{DCP}] \quad (20)$$

where [DCP] is the concentration of DCP in the burette. At any point during the run, the total fraction of DCP complexed, f^T, may be calculated from the equation,

$$f^T = \{(a_0 + b_0 + 1/K) - [(a_0 + b_0 + 1/K)^2 - 4a_0 b_0]^{1/2}\}/2a_0 \quad (21)$$

where a_0 is the total concentration of DCP in the vessel. Then if the total fraction of DCP complexed after i additions is f_i^T, it follows that the fraction complexed during the ith addition, f_i, is given by

$$f_i = if_i^T - (i-1)f_{i-1}^T \quad (22)$$

ΔH is finally calculated for each addition by substituting the appropriate value of f into eqn. (19). It should be noted that K in eqn. (21) is used only as a minor correction factor, so that ΔH is calculated effectively independently of K.

Four independent experiments were carried out, in each of which three additions of DCP were made to an excess of cyclohexanone, leading to a value of ΔH° of -7.21 ± 0.09 kcal mol^{-1}. These results have been obtained using $K = 178.9$ l mol^{-1}, but they are insensitive to the exact value of K used; the calculated ΔH° value is essentially constant (to within 0.03 kcal mol^{-1}) over a range of K values from 160 to 200 l mol^{-1}. The f values are *ca.* 0.97, so that the K value is only used to correct for a small fraction of uncomplexed DCP; hence ΔH° and ΔG° are essentially independent quantities.

Results and Discussion

Thermodynamics of hydrogen bond complexation

The FTIR method described above was used to obtain values of K and K_2 for the complexation of DCP with 17 aliphatic ketones and 12 aliphatic ethers in cyclohexane at 298 K. Results are summarized in Tables 5 and 6.

The K values for the ketones show only a small steric effect of two secondary or two tertiary alkyl groups: cyclohexanone (179), Me_2CO (119), Et_2CO (100), n-Pr_2CO (106), n-Bu_2CO (112), n-Hexyl$_2$CO (124), i-Pr_2CO (100) and t-Bu_2CO (64). This is to be expected because the R_1 and R_2 alkyl groups in the ketones are some way away from the C=O···HO hydrogen bond. In agreement with this is the lack of any significant steric effect of a single secondary or single tertiary group. The K_2 values are all very nearly the same, from 10 to 16, as would be expected for type II complexes but not for type I complexes, Fig. 1.

Massat *et al.*[30] have determined K values for the complexation of 9 phenols with 23 aliphatic ketones at 301 K, but in

Table 5 Values of K and K_2 for complexation of DCP with ketones, R^1COR^2, in cyclohexane at 298 K

R^1	R^2	K/l mol^{-1}	σ	K_2/l mol^{-1}	σ
Me	Me	119.3	3.0	14.3	1.2
Me	Et	111.7	5.1	12.2	2.2
Me	*n*-Pr	118.7	3.0	11.6	1.2
Me	*i*-Pr	111.8	0.8	12.0	0.3
Me	*n*-Bu	117.6	5.0	16.4	2.1
Me	*i*-Bu	109.8	1.4	14.4	0.7
Me	*t*-Bu	108.5	2.9	10.8	1.2
Me	*n*-Hept	117.1	4.0	15.3	1.7
Et	Et	100.4	2.6	13.9	1.3
Et	*n*-Bu	110.3	1.4	9.8	0.5
n-Pr	*n*-Pr	106.2	1.5	11.0	0.6
i-Pr	*i*-Pr	99.7	2.6	12.9	1.3
n-Bu	*n*-Bu	112.4	1.4	14.7	0.6
t-Bu	*t*-Bu	64.5	1.0	10.4	0.8
n-Hex	*n*-Hex	124.2	3.4	15.2	1.7
cyclopentanone		163.5	2.3	12.6	0.6
cyclohexanone[a]		178.9	—	12.7	—

[a] From Table 4.

Table 6 Values of K and K_2 for complexation of DCP with ethers, R^1OR^2, in cyclohexane at 298 K

R^1	R^2	K/l mol^{-1}	σ	K_2/l mol^{-1}	σ
Me	*t*-Bu	90.8	0.6	12.4	0.4
Et	Et	62.1	1.2	8.7	0.9
n-Pr	*n*-Pr	40.6	0.9	6.6	1.1
i-Pr	*i*-Pr	88.6	3.1	10.9	1.5
n-Bu	*n*-Bu	40.4	1.1	10.3	1.5
i-Bu	*i*-Bu	18.9	1.8	7.1	4.9
n-Octyl	*n*-Octyl	48.6	1.0	9.2	1.0
n-Decyl	*n*-Decyl	50.3	1.4	10.7	1.4
trimethylene oxide		206.9	2.7	17.0	0.5
terahydrofuran		148.4	4.9	12.7	1.5
tetrahydropyran		109.8	2.6	11.9	1.2
1,4-dioxane[a]		54.4	1.4	11.3	1.4

[a] Not statistically corrected.

tetrachloromethane solvent. In order to compare results we have obtained α_2^H and β_2^H for these compounds as follows. Some values of α_2^H for the phenols were available,[31] and the others were calculated through[32,33] eqn. (23),

$$\log K = 7.354\alpha_2^H \beta_2^H - 1.094 \quad (23)$$

In eqn. (23), log K is the hydrogen bond complexation constant in tetrachloromethane, and the 1:1 hydrogen bond acidity and basicity parameters α_2^H and β_2^H refer to the particular reactants.[33] For the ketones studied by Massat *et al.*,[30] a number of β_2^H values were again available,[32] and others were calculated through eqn. (23). Our results are in agreement with those of Massat *et al.*,[30] and show that steric effects amongst alkyl substituted aliphatic ketones are small, unless very bulky groups are present.

In the complexation of DCP with ethers, both polar and steric effects can be seen: *t*-BuOMe (91) and *i*-Pr_2O (89) show increased K values over those for the di-*n*-alkyl ethers, but *i*-Bu_2O (19) has a much reduced K value. As for the ketones, the range of K_2 values suggests that type II complexes are formed. Complexation constants for alkyl ethers against the reference acid 4-chlorophenol in cyclohexane at 293 K have been determined by Bellon *et al.*[34] For 8 common ethers, there is reasonable agreement between the two sets of results, see Fig. 2. If all the data on ethers are considered, it seems as though there is a polar effect of *sec*- and *tert*-alkyl groups that increases log K, counterbalanced by a steric effect that decreases log K, *e.g.* in di-*tert*-butyl ether.

The ratio K/K_2 for the 17 ketones studied is 8.9, and for the 12 ethers is 7.5. Previous workers[28,35,36] have obtained a variety of values for this ratio, but in general the larger the value of K the greater is the ratio of K/K_2. Frange *et al.*[37] showed that alcohol dimers (type II) are about an order of magnitude more acidic than the corresponding monomers in hydrogen bond complexation with pyridine-*N*-oxide in cyclohexane. Now it can be shown that for the complexation,

$$ROH\cdots ROH + B \rightleftharpoons ROH\cdots ROH\cdots B \quad (III)$$

the equilibrium constant is given by KK_2/K_d, where K_2 refers to reaction (II), written more conveniently as,

$$ROH + ROH\cdots base \rightleftharpoons ROH\cdots ROH\cdots base \quad (IV)$$

The average value of KK_2/K_d is 664 for the ketones and 377 for the ethers, as compared to average values for the complexation of the monomeric ROH acid with bases of 116 for the ketones and 80 for the ethers. Hence the dimer of DCP in reaction (III) is a stronger hydrogen bond acid than the monomer of DCP in reaction (I) by a factor of 5.7 or 4.7 towards ketones and ethers, respectively. These factors are in general accord with the analysis of Frange *et al.*[37]

The K values obtained by the FTIR method may be combined with the ΔH° values from the calorimetric method to yield thermodynamic parameters for the 1:1 complexation of DCP with ketones, Table 7, and ethers, Table 8. Taking into account the error in K, and an average experimental error of about 0.1 kcal mol^{-1} for ΔH°, we estimate that the error in ΔS° is *ca.* 0.4 cal K^{-1} mol^{-1}.

In the case of the ketones, none of the three thermodynamic parameters varies very much; ΔS° varies by no more than 1.1 cal K^{-1} mol^{-1}, even including the two cyclic ketones, and a

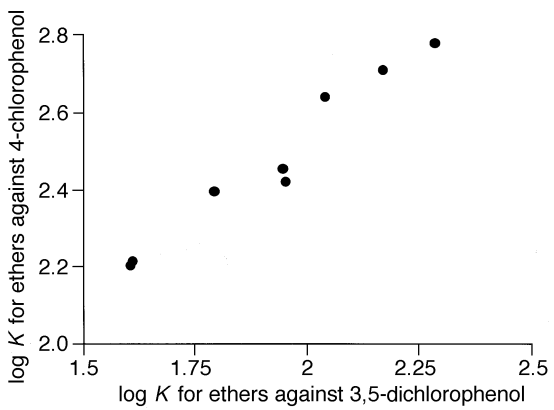

Fig. 2 A plot of log K for ethers against 4-chlorophenol *vs.* log K for ethers against 3,5-dichlorophenol

Table 7 Thermodynamics of complexation of DCP with ketones, R^1COR^2, in cyclohexane at 298 K[a]

R^1	R^2	$-\Delta G^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$
Me	Me	2.83	7.02	14.0
Me	Et	2.79	7.01	14.1
Me	*n*-Pr	2.83	6.86	13.5
Me	*i*-Pr	2.79	6.98	14.0
Me	*n*-Bu	2.82	6.94	13.8
Me	*i*-Bu	2.78	6.82	13.5
Me	*t*-Bu	2.78	6.95	14.0
Me	*n*-Hept	2.82	6.82	13.4
Et	Et	2.73	6.97	14.2
Et	*n*-Bu	2.79	6.86	13.7
n-Pr	*n*-Pr	2.76	6.86	13.7
i-Pr	*i*-Pr	2.73	6.91	14.0
n-Bu	*n*-Bu	2.80	6.82	13.5
t-Bu	*t*-Bu	2.47	6.76	14.4
n-Hex	*n*-Hex	2.86	6.83	13.3
cyclopentanone		3.02	7.08	13.6
cyclohexanone		3.07	7.21	13.9

[a] ΔG° and ΔH° in kcal mol^{-1}; ΔS° in cal K^{-1} mol^{-1}.

Table 8 Thermodynamics of complexation and values of $\Delta\nu_{OH}$ for complexation of DCP with ethers, R^1OR^2, in cyclohexane at 298 K[a]

R^1	R^2	$-\Delta G^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$	$\Delta\nu_{OH}$/cm^{-1}
Me	*t*-Bu	2.67	7.65	16.7	374
Et	Et	2.45	7.06	15.5	342
n-Pr	*n*-Pr	2.19	6.77	15.3	351
i-Pr	*i*-Pr	2.66	7.54	16.4	362
n-Bu	*n*-Bu	2.19	6.79	15.4	357
i-Bu	*i*-Bu	1.74	6.65	16.5	353
n-Octyl	*n*-Octyl	2.30	6.94	15.6	359
n-Decyl	*n*-Decyl	2.32	7.01	15.7	359
trimethylene oxide		3.16	7.55	14.7	330
terahydrofuran		2.96	7.28	14.5	340
tetrahydropyran		2.78	7.17	14.7	347
1,4-dioxane[b]		2.37	5.97	12.1	295

[a] ΔG° and ΔH° in kcal mol^{-1}; ΔS° in cal K^{-1} mol^{-1}. [b] Not statistically corrected.

plot of ΔH° against ΔG° (not shown) is a scatter diagram except for the two cyclic ketones. It should be pointed out that since there are two stereoisomeric complexes formed from a phenol and a ketone, the observed ΔH° will be a weighted sum of the two individual ΔH° values. This will also be the case for ΔG°, although the weights will be different to those for ΔH°. Under these conditions, a plot of ΔH° against ΔG° may have little meaning, anyway.

For the ethers, there is considerably more variation in ΔH°, ΔG° and ΔS° with structure. In order to compare 1,4-dioxane with the mono-ethers, we can make a statistical correction for the two ether sites, giving corrected values of $-\Delta G^\circ = 1.96$ kcal mol^{-1} and $-\Delta S^\circ = 13.5$ cal K^{-1} mol^{-1}. A plot of $-\Delta H^\circ$ against $-\Delta G^\circ$ with the corrected value for 1,4-dioxane, is shown in Fig. 3. There seem to be three separate lines for the *n*-alkyl ethers, the branched chain ethers, and the cyclic ethers. We note that the displacement of the two outermost lines from the central line in Fig. 3 amounts to only 0.3 and 0.5 kcal mol^{-1}, and it is doubtful if the $-\Delta H^\circ$ against $-\Delta G^\circ$ plot could be resolved into three lines if the ΔH° values had been obtained by the van't Hoff method. It should also be noted that the problem of stereoisomeric forms does not occur for the DCP–ether complexes we have studied (see the discussions below).

The Badger–Bauer relationship

Spectra of the complexed OH bands for the ketone adducts of DCP were obtained in cyclohexane using an excess of the ketone base to avoid 2 : 1 complexation. In all cases, the bonded OH band was made up of a high frequency and a low frequency component, with the high frequency contribution increasing as the ketone becomes more sterically hindered. Fritzsche,[38] examined the shape of the hydrogen-bonded OH band for complexes of phenol in tetrachloromethane. For carbonyl complexes, he interpreted the asymmetry of the OH band as due to the superposition of two symmetrical bands originating from two stereoisomeric complexes. The lower frequency component was attributed to an angular complex where the hydrogen bond forms in the direction of the lone pair, and the high frequency component to either a bidendate complex or a π-complex. This two-component model was supported by Korppi-Tommola and Shurvell.[39] Laurence *et al.*[40] have made a very thorough study of the complex OH band resulting from the interaction of methanol and of 2,6-diisopropyl-4-nitrophenol (DINP) with carbonyl compounds. They concluded that there exists two planar stereoisomers; a low frequency angular complex as proposed by Fritzsche,[38] and a high frequency linear complex where the hydrogen bond forms along the axis of the C=O bond. Laurence *et al.*[40] further suggested that the contribution of the two forms was linked to both steric repulsion and electronic effects. In particular, steric effects increase the contribution of the linear geometrical form, *i.e.* the high frequency component. Our results are in line with those of Laurence *et al.*[40] The marked asymmetry of the OH band in the complexes of DCP with ketones, as well as the very small variation in ΔH°, no more than 0.45 kcal mol^{-1} over all the ketones studied, suggests that the DCP–ketone system in cyclohexane is not at all suitable for any analysis of the Badger–Bauer relationship.

Fritzsche[38] recognized that in contrast to carbonyl bases, the complexed OH band of phenol associated with 1,4-dioxane or tetrahydrofuran was essentially symmetrical. We find this also for the complexed OH band of DCP with the various ethers we have studied; in Table 8 are values of $\Delta\nu_{OH}$ for the complexed band, as differences from ν_{OH} for free DCP at 3609 cm^{-1}. A plot of $\Delta\nu_{OH}$ against ΔH° is shown in Fig. 4. Apart from the point for 1,4-dioxane, there is complete scatter. Even for the acyclic ethers there is a very poor relationship between $\Delta\nu_{OH}$ and ΔH°,

$$\Delta\nu_{OH} = 238.5 + 16.8\ \Delta H^\circ \qquad (24)$$

$n = 7$, $\sigma = 7.5$, $r^2 = 0.4349$, $F = 4.6$, where n is the number of results, σ is the population standard deviation, r is the correlation coefficient and F is the F-test value. Our conclusion is quite definite: when values of ΔH° for complexation of DCP with ethers in cyclohexane are determined by a calorimetric method, there is only a very poor relationship between $\Delta\nu_{OH}$ and ΔH°. Even for a restricted set of acyclic ethers, the Badger–Bauer relationship (as defined above) does not hold. It should be noted that the complexation of DCP with ethers has been chosen to provide very good conditions as regards the Badger–Bauer relationship. First, the variables are the same as those used in many studies, *viz.* $\Delta\nu_{OH}$ and ΔH°. Secondly, the values of ΔH° have been obtained by a rigorous calorimetric method. Thirdly, the OH bands in the DCP–ether complexes are symmetric and do not suffer from the complications seen with the DCP–ketone complexes. Fourthly, the bases are all within a family, so that there is no possibility of any relationship between $\Delta\nu_{OH}$ and ΔH° being family dependent. If, under these conditions, there is almost no connection between $\Delta\nu_{OH}$ and ΔH°, we can conclude that the Badger–Bauer relationship is not general and that such a relationship cannot be assumed even within a family of bases.

It has been suggested that steric effects in the aliphatic ether series may render the Badger–Bauer relationship questionable. Certainly, steric effects on hydrogen bond complexation may be one reason why the Badger–Bauer relationship does not generally hold. But this cannot be the entire reason for the collapse of the relationship in the present case. Even if methyl *tert*-butyl ether and diisopropyl ether are omitted, and only the five acyclic ethers with primary alkyl groups are considered, there is still no relationship between $\Delta\nu_{OH}$ and ΔH°. A fundamental reason for lack of such a relationship is that

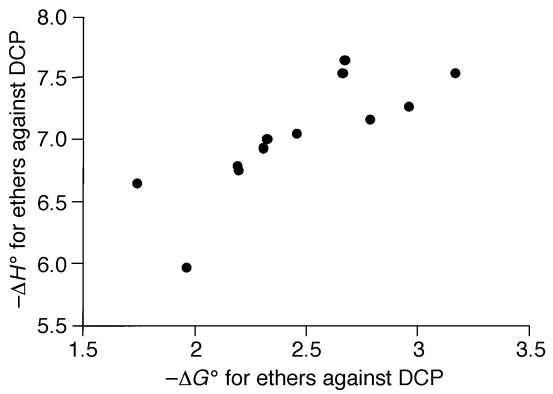

Fig. 3 A plot of $-\Delta H^\circ$ for ethers against DCP *vs.* $-\Delta G^\circ$ for ethers against DCP

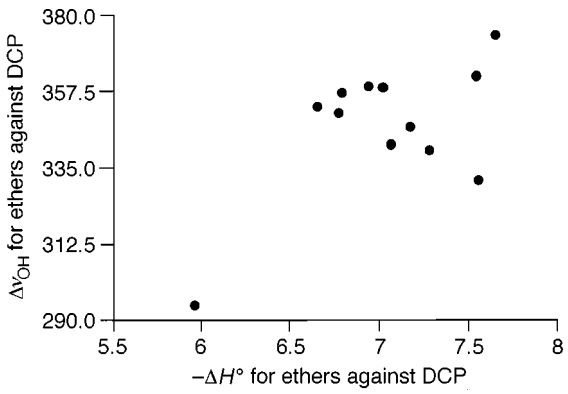

Fig. 4 The Badger–Bauer relationship: a plot of $\Delta\nu_{OH}$ for ethers against DCP *vs.* $-\Delta H^\circ$ for ethers against DCP

$\Delta\nu_{OH}$ is not a thermodynamic quantity at all, but because of the Franck–Condon principle, refers to a situation in which the solvent around an excited state is not in equilibrium with the excited state. A relationship between $\Delta\nu_{OH}$ and ΔH° thus involves a comparison of structural effects on (i) the difference in spectroscopic energy between an excited complex that is not in equilibrium with the solvent and a ground state complex that is in equilibrium with the solvent, and (ii) the difference in enthalpy between a complex that is in equilibrium with the solvent, and the reactants that are in equilibrium with the solvent. There is therefore no fundamental reason why such a relationship should hold.

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