A Test of Electrostatic and Reaction-field Theories: Equilibria in Isodesmic Reactions of some Chlorobenzenes

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The enthalpy of solvation of chlorobenzene and 1,2-, 1,3-, and 1,4-dichlorobenzene has been measured in two solvents of different polarity. The results have allowed us to construct several isodesmic reactions and to evaluate their reaction enthalpies in solution. These values agree at least semiquantitatively with the reaction-field theory but the results are very sensitive to the choice of parameter and modification of the basic equations. It follows that the success of the reaction-field theory has been essentially fortuitous and almost every experimental finding can be reproduced by choosing a suitable modification from a number of those recommended in the literature. The alternative electrostatic calculation (the 'Kirkwood–Westheimer' model) yields still worse results and cannot be extended outside ionic equilibria.

The most popular theoretical approach to solvent effects on chemical equilibria represents the solute as an isolated molecule and the solvent as a homogeneous continuum. Two practical procedures have been developed.

(*a*) The reaction Gibbs energy, ΔG_N, in a given solvent N is calculated from the interaction between electric centres in the solute molecule (charge–charge, charge–dipole or dipole–dipole), while to the interjacent space is attributed a uniform effective permittivity (ε_{eff}). To this procedure, often connected with the names of Kirkwood and Westheimer,[1,2] we apply the description electrostatic theory.[3] It has been applied both to ionization equilibria [1–7] and conformational equilibria.[8–13] For an interaction between several point charges q, separated by distance r, the equation has the form:

$$E = (N_A/4\pi\varepsilon_0\varepsilon_{eff}) \sum_{i \neq j} q_i q_j / r_{ij} \qquad (1)$$

(*b*) The relative solvation Gibbs energy ($\delta\Delta G^\circ$, see the Figure) is calculated from the interaction of the solvent with the solute molecules, the latter being characterized by their overall dipoles and quadrupoles. This approach, called the reaction-field theory,[14–16] has been applied mainly to conformational equilibria.[14–19] A typical equation (2) consists of three terms: the

$$\Delta E_{solv} = -(N_A/4\pi\varepsilon_0)[K_u X_v/(1 - L_u X_v) + 3H_u X_v/(5 - X_v)] - B_u F_v[1\text{-exp}(-B_u F_v/16RT)] \qquad (2)$$

dipolar term comprises a function (K_u) of the solute dipole and the function (L_u) of the refractive index; the quadrupolar term depends on the function (H_u) of the solute quadrupole; and the third, direct polar term contains the function (B_u) of both the dipole and quadrupole. The solvent is characterized by its bulk permittivity expressed by two functions, (X_v) and (F_v). (The subscripts u and v were added by us wherever necessary to distinguish clearly the solute and solvent.) This equation was complemented by further, non-electrostatic terms[20,21] (extended reaction-field theory[12]). This means that it was combined with solvophobic theory[22] and/or scaled-particle theory.[23]

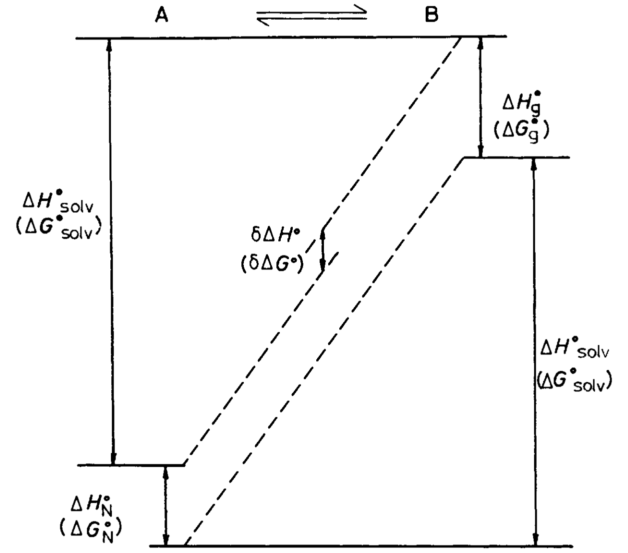


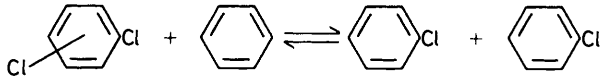
Figure. Schematic representation of the thermodynamic quantities involved and their interrelations.

Our intention was to confront the two theoretical approaches with a set of new experimental data. The data used up to now have been rather inhomogeneous and seldom suitable for both theories. For ionization equilibria, ΔG°_N is mostly known in aqueous solvents, and for conformational equilibria ΔG°_N or ΔH°_N are known in non-polar solvents, although in both cases the data are rather unreliable. For instance, an IR determination of ΔH°_N assumes invariable molar absorption coefficients; and for ΔG°_N they are even supposed to be equal (see the criticism in ref. 12). In order to obtain $\delta\Delta G^\circ$, ΔG°_g is still needed, which is rarely available for conformational equilibria. Therefore, Gibbs energies were replaced by enthalpies, measured directly calorimetrically.[12,18] Since equation (2) relates to Gibbs energies,[12,24,25] (at variance with ref. 13) a correction term[12,14] had to be added. Our investigations of the two conformers of methyl 2-fluorobenzoate failed to yield exact

Table 1. Thermodynamics of solvation of chlorobenzenes (kJ mol^{-1}, 298 K).

	Benzene	Chlorobenzene	Dichlorobenzenes 1,2	1,3	1,4
ΔH_{sol} (CCl_4)	0.5[a]	0.7	1.4	0.7	18.6
ΔH_{sol} (CH_3NO_2)	4.6	5.1	6.1	6.2	24.3
ΔH_v[a]	33.9	41.0	48.4	47.9	64.9[b]
ΔH°_{solv} (CCl_4)	−33.4[c]	−40.3[d]	−47.0[e]	−47.2	−46.3[e]
ΔH°_{solv} (CH_3NO_2)	−29.3	−35.9	−42.3	−41.7	−40.6

[a] Ref. 26. [b] Enthalpy of sublimation. [c] Ref. 29 gives −33.2. [d] Ref. 30 gives −39.7. [e] Ref. 29 gives −46.1 and −46.7 for the isomers 1,2 and 1,4, respectively.



Scheme 1.

values and were therefore extended to 3- and 4-fluorobenzoates.[12] This means that we dealt with equilibria of isomers not present under normal conditions. In a similar approach, $\delta\Delta H^\circ$ for the $E \rightleftharpoons Z$ isomerization of 1,2-dichloroethenes was determined,[25] irrespective of whether the equilibrium could be attained. Pursuing this idea further we focused attention on isodesmic reactions of the type shown in the Scheme called disproportionations. (The term isodesmic in the broader sense requires only that the number of bonds of each kind remains unchanged, *e.g.* two C–Cl bonds.) The ΔH°_g values for the reactions in the Scheme were obtained from tables of thermodynamic data[26] and are reasonably reproduced[27] by equation (1) with $\varepsilon_{eff} = 1$.

In this paper we report on the experimental heats of solvation of the three dichlorobenzenes, chlorobenzene, and benzene in one non-polar and one polar solvent. These results allowed us to determine ΔH°_N in solution for the three reactions in the Scheme and for three isomerization reactions. These values were then compared with the predictions based on equations (1) and (2). The reaction-field theory was applied only in its parent form, equation (2); a detailed test of additional terms and of the values of all parameters involved would require further data. We are aware of the fact that the reactions in the Scheme could appear somewhat artificial since these reactions do not actually proceed in the solvents given. However, electrostatic theories do not make preliminary assumptions about the rate at which the equilibrium is established; a knowledge of ΔG° or ΔH° is sufficient.

Experimental

Materials.—Chlorobenzene, n_D^{25} 1.5219; 1,2-dichlorobenzene, n_D^{25} 1.5512; 1,3-dichlorobenzene, n_D^{25} 1.5434; and 1,4-dichlorobenzene, m.p. 55–56 °C were of at least 99.95% purity according to the melting curve. The purity of liquid compounds was checked by GLC (99.5% at least).

Calorimetric Measurements.—The enthalpies of solution (ΔH_{sol}) were measured partly by the method[12] based on breaking an aluminium foil (1,4-dichlorobenzene) and partly by the titrimetric method[28] (in the remaining cases). The enthalpies of solvation (ΔH_{solv}), corresponding to the transfer of 1 mol of solute from the gas phase to the infinitely dilute solution were obtained by subtracting the enthalpies of vaporization[26] (ΔH_v). The results are listed in Table 1.

The apparent partial molar volumes were determined from the densities of four or five solutions within the concentration range 0.5–2 wt%, measured in a vibrational densitometer DMA 02C (A. Pear, Graz). The results are listed in Table 2.

Results

Electrostatic Calculations.—Equation (1) was used in the same way as previously.[12] The point charges were obtained by the decomposition of the bond moment of C_{Ar}–Cl, equal to the experimental dipole moment of chlorobenzene (Table 2). There is only a small difference between the results[27] obtained with standard bond moments.[31] The bond lengths used were (in pm) C_{Ar}–C_{Ar} 139 and C_{Ar}–Cl 170, and the benzene ring is assumed to be hexagonal. The differences between our data and the most recently reviewed bond lengths[32] and non-hexagonal geometry[33] are immaterial. Alternatively, the point charges were obtained by MINDO/3. The effective permittivity, ε_{eff} was treated as a disposable parameter. The results for various isodesmic reactions are given in Table 3 and compared with 'experimental' values which in turn were constructed from our ΔH_{solv} values and from known[35] ΔH°_f and S° values in the gas phase.

The solute dipole moment μ_u from the function $K_u = \mu_u^2/a^3$, equation (2), is either the experimental value or that calculated by MINDO/3 (Table 2). The cavity radius, a, was estimated by several procedures, either from the solute molar volume[14,15] (or partial molar volume[25]) according to equation (3), or alternatively as a sum of the radii of solute and solvent,[21] $a = a_u + a_v$, both calculated separately in the same way. The function L_u is defined[14] by the equation (4), while X_v was taken either in the common form,[14,15] equation (5) or with a merely empirical correction,[17] equation (6). In the latter case too the constant 1 in the first term of equation (2) is to be replaced by 2.

$$a^3 = 3V/4\pi N_A \qquad (3)$$

$$L_u = 2(n^2 - 1)/(n^2 + 2) \qquad (4)$$

$$X_v = (\varepsilon - 1)/(2\varepsilon + 1) \qquad (5)$$

$$X_v = (\varepsilon - 2)/(2\varepsilon + 2) \qquad (6)$$

In the quadrupole term the function H_u is expressed most conveniently[36] through the components $\theta_{\alpha\beta}$ of the quadrupole tensor, equation (7). For molecules of higher symmetry the non-

$$H_u = a^{-5}(\theta_{xx}^2 + \theta_{yy}^2 + \theta_{zz}^2 + 2\theta_{xy}^2 + 2\theta_{xz}^2 + 2\theta_{yz}^2) \qquad (7)$$

diagonal elements equal zero and the diagonal elements are related as $\theta_{xx} = -2\theta_{yy} = -2\theta_{zz}$. The function H_u is then obtained only from the element θ_{xx} in the direction of the symmetry axis, according to equation (*7a*).

$$H_u = 3\theta_{xx}^2/2a^5 \qquad (7a)$$

The values of θ_{xx} were calculated either by MINDO/3 or from the point charges arising by decomposition of the C_{Ar}–Cl bond moments. This means that the H–C_{Ar} bond moment was taken

Table 2. Molecular and physico-chemical properties of chlorobenzenes (298 K).[a]

			Dichlorobenzenes		
	Benzene	Chlorobenzene	1,2	1,3	1,4
$V/(\mathrm{cm^3\ mol^{-1}})$	89.41	102.22	113.05	114.60	114.40[b]
$\bar{V}\ (\mathrm{CCl_4})/\mathrm{cm^3\ mol^{-1}}$	88.9[c]	101.2[c]	113.3[c]	113.5[c]	113.7[c]
$\bar{V}\ (\mathrm{CH_3NO_2})/\mathrm{cm^3\ mol^{-1}}$	86.8	96.0	106.0	107.4	105.9
a_{u}[d]/pm	328.5	343.5	355.2	356.8	356.6
$a_{\mathrm{u}}\ (\mathrm{CCl_4})$[e]/pm	327.9	342.3	355.5	355.7	355.9
$a_{\mathrm{u}}\ (\mathrm{CH_3NO_2})$[e]/pm	325.2	336.4	347.7	349.2	347.6
n_{D}^{25}	1.4979	1.5219	1.5494	1.5434	1.5460[b]
$\mu_{\mathrm{g}}/10^{-30}\ \mathrm{C\ m}$	0	5.94	8.37	5.60	0
μ_{calc}[f]$/10^{-30}\ \mathrm{C\ m}$	0	6.511	9.734	6.198	0
θ_{xx}[f,h]$/10^{-40}\ \mathrm{C\ m^2}$	0.8	0.7	−12.0	−40.0	−52.1
θ_{xx}[f,i]$/10^{-40}\ \mathrm{C\ m^2}$	0.8	−28.0	−29.9	−32.6	−52.1
θ_{xx}[g,h]$/10^{-40}\ \mathrm{C\ m^2}$	0	0	−13.3	−39.9	−53.2
θ_{xx}[g,i]$/10^{-40}\ \mathrm{C\ m^2}$	0	−26.6	−33.3	−46.6	−53.2

[a] Experimental values unless otherwise noted. [b] Extrapolated to 298 K. [c] Ref. 34 gives 90.5, 101.4, 111.6, 111.4, and 113.7, respectively. [d] Calculated from the molar volumes above. [e] Calculated from the partial molar volumes above in the respective solvent. [f] Calculated by MINDO/3. [g] Calculated from C–Cl dipoles only. [h] The origin in the centre of gravity of the charges. [i] The origin in the centre of the benzene ring.

Table 3. Thermodynamics of the disproportionation and isomerization reactions of dichlorobenzenes (kJ mol^{-1}, 298 K).

	Disproportionation (Scheme)			Isomerization		
	1,2	1,3	1,4	$1,2 \rightleftharpoons 1,3$	$1,2 \rightleftharpoons 1,4$	$1,3 \rightleftharpoons 1,4$
$\Delta H_{\mathrm{g}}^{\circ}$[a]	−9.20	−5.69	−2.26	−3.51	−6.94	−3.43
$\Delta G_{\mathrm{g}}^{\circ}$[a]	−14.02	−9.92	−8.49	−4.10	−5.53	−1.43
$\Delta G_{\mathrm{g}}^{\circ} + T\Delta S_{\sigma}$	−9.58	−5.48	−2.33	−4.10	−7.25	−3.15
ΔE_{elst}[b,c]	−18.1	−6.2	−4.8	−11.9	−13.3	−1.4
ΔE CNDO/2[c]	−9.5	−2.4	−2.9	−7.1	−6.6	0.5
ΔE MINDO/3	−13.5	−1.0	−4.4	−12.5	−9.1	3.4
ΔE_{elst} (CNDO/2)[c,d]	−19.9	3.7	−7.7	−23.6	−12.2	11.4
ΔE_{elst} (MINDO/3)[d]	−78.7	32.4	−41.9	−111.1	−36.8	74.3
$\Delta H_{\mathrm{N}}\ (\mathrm{CCl_4})$	−9.4	−5.7	−3.2	−3.7	−6.2	−2.5
$\Delta H_{\mathrm{N}}\ (\mathrm{CH_3NO_2})$	−9.4	−6.5	−4.2	−2.9	−5.2	−2.3
ΔE_{elst}[e]	−9.0	−3.1	−2.4	−5.9	−6.6	−0.7

[a] Calculated from $\Delta H_{\mathrm{f}}^{\circ}$ and ΔS° values of individual compounds as given in ref. 35. [b] Equation (1) with $\varepsilon_{\mathrm{eff}} = 1$, the charges from bond moments. [c] Ref. 27. [d] Equation (1) with $\varepsilon_{\mathrm{eff}} = 1$, the charges from quantum chemical calculation. [e] Equation (1) with $\varepsilon_{\mathrm{eff}} = 2$, the charges from bond moments.

conventionally as zero.[31] The definition of θ_{xx} has the form in equation (8); the origin of co-ordinates is either in the centre of

$$\theta_{xx} = \sum_{i} q_i(x_i^2 - y_i^2/2 - z_i^2/2) \qquad (8)$$

gravity of all charges,[18] in the centre of mass,[36,37] or in the centre of the benzene ring.[37] The values of θ_{xx} are given in Table 2.

In the direct polar term the functions B_{u} and F_{v} were used according to their original definitions:[15]

$$B_{\mathrm{u}} = 4.35(T/300)^{1/2} r_{\mathrm{uv}}^{-3/2}[(N_{\mathrm{A}}/4\pi\varepsilon_0) \times (\mu^2 + 3\theta_{xx}^2/2r_{\mathrm{uv}}^2)]^{1/2} \qquad (9)$$

$$F_{\mathrm{v}} = [(\varepsilon - 2)(\varepsilon + 1)/\varepsilon]^{1/2} \qquad (10)$$

Equation (9) in the form given assumes that a is in pm and μ is in C m. The radius r_{uv} was taken either[15] as $r_{\mathrm{uv}} = a_{\mathrm{u}} + 180$ or as[21] $r_{\mathrm{uv}} = (a_{\mathrm{u}} + a_{\mathrm{v}})/2^{1/2}$.

Conversion of ΔE_{calc} values (corresponding[12,25] to ΔG) into ΔH was accomplished by an additional term:

$$\Delta H - \Delta G = -T(\mathrm{d}\Delta E_{\mathrm{calc}}/\mathrm{d}T) \qquad (11)$$

In equation (2) the dependence on temperature comes into existence through several experimental values (ε_{v}, n_{u}, d_{u}, and d_{v}, in which the densities affect a_{u} and a_{v}, respectively) but for calculating the derivative in equation (11) only the temperature dependence of ε was taken into consideration. The calculated three terms of equation (2) and one term in equation (11) are listed in Tables 4 and 5.

Quantum Chemical Calculations.—The MINDO/3 method with total optimization of geometry was used in standard parametrization.[38] The results are given in Table 3.

Discussion

Three kinds of experimental quantities can be compared with the theoretical predictions: $\Delta H_{\mathrm{N}}^{\circ}$, ΔH_{solv}, and $\delta\Delta H$ (Figure 1).

(*a*) The reaction enthalpies, $\Delta H_{\mathrm{N}}^{\circ}$, are surprisingly similar in the two, very different, solvents and also, surprisingly, to the gas phase values $\Delta H_{\mathrm{g}}^{\circ}$ (Table 3, lines 1, 9, and 10). The latter were semiquantitatively predicted by equation (1) with $\varepsilon_{\mathrm{eff}} = 1$ for a larger number of compounds, and also for other substituents than chlorine.[27] Some deviations for *ortho* derivatives were explained by steric effects.[27] Approximately the same degree of qualitative agreement is now reached for $\Delta H_{\mathrm{N}}^{\circ}$ with $\varepsilon_{\mathrm{eff}} = 2$

Table 4. Experimental and calculated relative solvation enthalpies, $\delta\Delta H$, for isodesmic reactions (kJ mol^{-1}, 298 K).

					ΔE_{solv}[c]	$\delta\Delta H$	ΔE_{elst}[d]
Reaction	ΔE_{dip}[a]	ΔE_{qdr}[a]	ΔE_{dp}[a]	$-Td\Delta E/dT$[b]	Calc. (2)	Exp.	Calc. (1)
In CCl_4							
Scheme 1,2	−0.02	−0.03	0.00	−0.03	−0.08	−0.2	0.82
Scheme 1,3	−0.18	0.04	0.00	−0.03	−0.17	0	0.28
Scheme 1,4	−0.32	0.09	0.00	−0.08	−0.31	−0.9	0.22
(1,2) $\rightleftharpoons$ (1,3)	0.16	−0.07	0.00	0.00	0.09	−0.2	0.54
(1,2) $\rightleftharpoons$ (1,4)	0.30	−0.12	0.00	0.05	0.23	0.7	0.60
(1,3) $\rightleftharpoons$ (1,4)	0.14	−0.05	0.00	0.05	0.14	0.9	0.06
In CH_3NO_2							
Scheme 1,2	−0.05	−0.11	−0.04	−0.09	−0.29	−0.2	2.58
Scheme 1,3	−0.62	0.15	0.00	−0.06	−0.53	−0.8	0.89
Scheme 1,4	−1.08	0.32	0.02	−0.09	−0.83	−1.9	0.68
(1,2) $\rightleftharpoons$ (1,3)	0.57	−0.26	−0.04	−0.03	0.24	0.6	1.70
(1,2) $\rightleftharpoons$ (1,4)	1.03	−0.43	−0.06	0.00	0.54	1.7	1.90
(1,3) $\rightleftharpoons$ (1,4)	0.46	−0.17	−0.02	0.03	0.30	1.1	0.20
In CH_3NO_2–CCl_4							
Scheme 1,2	−0.03	−0.08	−0.04	−0.06	−0.21	0	1.76
Scheme 1,3	−0.44	0.11	0.00	−0.03	−0.36	−0.8	0.61
Scheme 1,4	−0.76	0.23	0.02	−0.01	−0.52	−1.0	0.46
(1,2) $\rightleftharpoons$ (1,3)	0.41	−0.19	−0.04	−0.03	0.15	0.8	1.16
(1,2) $\rightleftharpoons$ (1,4)	0.73	−0.31	−0.06	−0.05	0.31	1.0	1.30
(1,3) $\rightleftharpoons$ (1,4)	0.32	−0.12	−0.02	−0.02	0.16	0.2	0.14

[a] The three terms of equation (2), calculated with parametrization as in Table 5, line 2. [b] The term transforming ΔG into ΔH, equation (11). [c] Sum of the four preceding terms. [d] Calculated with $\varepsilon_{\text{eff}} = 2$, 2.2, and 2.8 for vacuum, tetrachloromethane, and nitromethane, respectively.

Table 5. Effect of parametrization in the reaction-field theory: tested on the disproportionation of 1,4-dichlorobenzene (Scheme) in nitromethane (kJ mol^{-1}, 298 K).

Parametrization	ΔE_{dip}[a]	ΔE_{qdr}[a]	ΔE_{dp}[a]	$-Td\Delta E/dT$[b]	Total
1 Physically best[c]	−1.08	0.71	0.13	0.24	0.00
2 Empirically best[d]	−1.08	0.32	0.02	−0.09	−0.83
3 a_u only[e]	−6.40	12.70	0.04	0.83	7.17
4 Equation (6*b*)[e]	−2.53	12.14	0.04	1.97	11.62
5 Equation (6*b*) and a_u[e]	−0.43	0.68	0.13	0.33	0.71
6 With $\bar{V}$[e]	−1.12	0.77	0.15	0.18	−0.02
7 MINDO/3[e]	−1.30	0.68	0.11	0.12	−0.39
8 Centre of mass[e]	−1.08	0.61	0.10	0.15	−0.22
Experimental					−1.9

[a] The three terms of equation (2). [b] Equation (11). [c] Parametrization: $a = a_u + a_v$; V determined in the liquid phase; μ experimental; approximate θ values obtained from bond moments; centre of the quadrupole in the centre of all charges; and X_v from equation (6). [d] Parametrization as in line 1, only the centre of the quadrupole in the centre of the benzene ring. [e] Parametrization as in line 1 with the appropriate change as indicated.

(Table 3, last line). However, the mutual relations are not reproduced, not even qualitatively. The calculated values in solution are exactly one half of those calculated for the gas phase but the experimental values are of the same order. Use of the same effective permittivity ($\varepsilon_{\text{eff}} = 2$) for the two solvents (bulk permittivities 2.2 and 37.7, respectively) is inadequate since in the case of ionization equilibria ε_{eff} changes considerably with solvent.[1–4] Another problem is caused by the accuracy of experimental ΔH°_N values derived from the values of $\Delta H^\circ_{\text{solv}}$ and ΔH°_g which represent a small difference between two large numbers. A conservative estimate of their accuracy[35] of ΔH°_g is ± 3 kJ mol^{-1}; one must realize, however, that such an error could affect the results dramatically. We have therefore concluded that the approach is more suitable for ionization equilibria, dominated by the electrostatic effect of the charge.

(*b*) The enthalpies of solvation, $\Delta H^\circ_{\text{solv}}$, of individual compounds could be compared with values calculated from equation (2). However, no agreement can be expected since it is known that these values are largely controlled by dispersion forces and solvent–solvent interactions (cavity terms), both neglected in equation (2). In fact the calculated values (not listed in this paper) would be of the order of several kJ mol^{-1}, while experimental values are an order of magnitude larger (Table 1).

(*c*) For these reasons the main attention should be focused on relative solvation enthalpies, $\delta\Delta H$ (Figure 1). As double differences they depend only on measured solvation enthalpies, are relatively reliable, and can be predicted in principle by both equations (1) and (2). In general the two equations cannot hold simultaneously since they are based on different and independent facts. Let us consider the disproportionation of 1,4-dichlorobenzene (Scheme) as an example. According to equation (1) the solvent effect is given exclusively by the interaction of the two dipoles in 1,4-dichlorobenzene, and depends on its structure, particularly on r and θ. These factors are not involved in equation (2) which in turn ascribes the solvent effect to the chlorobenzene dipole. It is true that some apparently independent factors are interrelated in particular structures (*e.g.* large r in dichlorobenzene implies large a_u in chlorobenzene) but this does not hold for all structures. It is not therefore surprising that equation (1) does not give even a qualitatively correct picture (Table 4, last column). To determine $\delta\Delta H$, equation (1) needs to be applied twice with different ε_{eff} values for the solution and for the gas phase, respectively, and subtracted. For the gas phase not only $\varepsilon_{\text{eff}} = 1$ but also values 2 or 1.5 were considered.[17,18] For tetrachloromethane the choice of $\varepsilon_{\text{eff}} = 2.2$ appears to be very reasonable since there is no difference between internal and external permittivity. For nitromethane a quantitative idea is lacking, but we may consider ε_{eff} to be a disposable parameter with a value between 2.2 and 37. The results in Table 4 are not very sensitive to the particular value within this interval. The solvent effect on isomerization reactions of dichlorobenzenes is well reproduced and increases in the sequence *para* < *meta* < *ortho*. However, for the disproportionations such calculations give the wrong sign in all cases. The experimental values may be well summarized by the statement that polar molecules are stabilized in polar solvents, when we consider two molecules of chlorobenzene on the right side of the Scheme as being more polar than one molecule of dichlorobenzene. This is what equation (1) cannot, in principle, reproduce.

The application of equation (2) is more complex since there are too many possible modifications and parametrizations.[14–21,24,36] We selected the reaction in the Scheme, which for 1,4-dichlorobenzene in nitromethane gave the clearest experimental results, and tested on it all possible parametrizations: a_u calculated according to equation (3), either from V or from $\bar{V}$; a taken as a_u or as $(a_u + a_v)$; X_v according to equation (5) or (6); μ experimental or MINDO/3; and θ_{xx} calculated either from bond moments or by MINDO/3, in either case with the origin of co-ordinates either in the centre of all charges, in the centre of gravity of the molecule, or in the centre of the benzene ring. There are in total 96 possibilities of which we have calculated 36 since some combinations are incompatible. The best combinations were subsequently tested on all reactions and a selection of the results is presented in Table 5. The choice of the best parametrization is impossible from a mere comparison with experiment. What we can compare is only a sum of four terms, of which the direct polar term and the correction for enthalpy are so small that their effect on the final agreement cannot be estimated. Therefore, these terms were taken out of equations (9) and (11), respectively, and their improvement was not attempted. For the choice of the most suitable parametrization not only was the final agreement with experiment decisive but also the relative values of the dipolar and quadrupolar terms as well. Finally, also the possible physical meaning and general applicability were considered.

It turned out that the most important parameter was the cavity radius a and its only acceptable value was the sum $a_u + a_v$, as recommended by Tvaroška and Kožár.[21] Simple a_u, as originally used,[14,15] leads to dipolar terms which are too large and still larger quadrupolar terms of the opposite sign (Table 5, line 3). Allinger's modification,[17] expressed in equation (6), which should similarly reduce the dipolar term, does not remedy the quadrupolar term, so that the final result is less satisfactory (Table 5, line 4). Simultaneous application of the two corrections, $a_u + a_v$ and equation (6), has never been attempted but does not appear to be any better (line 5). In previous work these discrepancies were not revealed; the reason may have been that the molecules investigated had only small quadrupole moments. This applies also to the choice of other parameters.

When the cavity radius is defined as $a_u + a_v$, it is immaterial whether V or $\bar{V}$ is used for calculation (lines 1 and 6 in Table 5). We believe that V is the simpler possibility; measurements of $\bar{V}$ are not very precise and certainly not worth the effort. In some cases even an estimate of V from increments[39] could be useful, while the use of a parallelepiped circumscribed to the molecule[20] is obsolete. For dipole moments, experimental values should be certainly preferred whenever available, but MINDO/3 gives relatively close results (Table 5, line 7). Quadrupoles, which have rarely been experimentally[40] determined, cause more problems. We estimated them from bond moments and assumed a zero dipole for the H–C_{Ar} bond.[31] This approximation would predict a zero quadrupole moment for benzene—a fact at variance with the experiment.[40] Nevertheless our estimates and MINDO/3 give very similar results (Table 5, lines 1 and 7). More important is the position of the quadrupole in the molecule.[18,36,37,41] Although its position in the centre of gravity[36,37,41] (line 8) or, still better, in the centre of the benzene ring (line 2) gives better results, we consider the position in the centre of charges to be the only physically meaningful possibility. The underlying theory affirms that every distribution of charges can be expressed by a convergent series of centralized terms: pole, dipole, quadrupole, octupole, *etc.* Only in the case of a centralized position might the series possess several terms for simple molecules, *e.g.* for simple dipoles or simple quadrupoles just one term. With the centre of co-ordinates placed in the centre of gravity, the series would be infinite even for the simplest charge distributions and its restriction to just two terms would be unfounded. For this reason we give in Table 5 the parametrization with the centre of charge as a physically meaningful solution (line 1), and that with the centre of benzene ring as empirically best (line 2). Within the latter parametrization we also calculate theoretical terms for the remaining reactions (Table 4), although we are aware that such a calculation is physically meaningless and cannot even be applied to compounds of another type. Even so, the agreement with experiment is poor, with a correlation coefficient $r = 0.952$, and calculated values are systematically smaller (slope $b = 0.38$). Multiple regression was attempted with the dipolar and quadrupolar terms only: multiple correlation coefficient $R = 0.948$. The best turned out to be the correlation with the dipolar term alone: $r = 0.946$ and $b = 0.56$.

The quadrupole term is in fact not so negligible as is often believed: with its sensitivity to cavity radius (to the fifth power) and with the definition sufficiently vague it may become the weakest part of the theory. From this point of view the proposals to extend the calculations further to octupoles[25,36] or to consider a non-central charge distribution[19] do not appear to be very promising. Concerning the direct-polar term, we cannot confirm its significance due to uncertainties in the remaining terms. It may be of importance when solvents of different polarity are compared[19] but the results of other studies apparently do not depend on whether this term is used[15,18,21,41] or not.[17,20,25,36] The entropic term is the most mysterious since it has been introduced with another, quite obscure meaning,[14] sometimes omitted[15,18,24] and introduced again.[17,25] As an entropy correction it has a physical meaning since the electrostatic theory should in principle represent ΔG as soon as the experimental permittivity has been introduced,[12,24,25] but the temperature dependence of the permittivity alone (or even of several properties of the liquid phase) can hardly give an estimate of the entropy of solvation.

Conclusions

It is true that the reaction-field theory has undoubtedly had some success in the case of conformational equilibria:[19] it is believed that some additional effects may compensate in such cases. We have, however, gained unsatisfactory results even for equilibria between isomers and our criticism is based not only on the disagreement with our experiments but still more on the confusion within the theory itself. Apparently the strongest and simplest part of the theory is the dependence of solvation energy on solvent permittivity: once the parameters are well chosen for a given reaction the dependence on solvent may be reproduced reasonably well. On the other hand, a parametrization which is applicable more generally can hardly be suggested: in a particular case the choice may become quite arbitrary. In our opinion the electrostatic theories have already reached the limits of their possibilities. They are, however, still useful in their simplest forms, especially for a qualitative estimation.

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