Molecular Complexes. Part XIV.[1] Proton Magnetic Resonance Studies of the Interactions of Chloroform with Benzene and Some Alkylbenzenes at Various Temperatures

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The interactions between chloroform and various alkylbenzenes have been studied by ^{1}H n.m.r. at several temperatures. The equilibrium quotients, K_x, and thence ΔG^0, ΔH^0, and ΔS^0, and aromatic-induced chemical shifts Δ_c have been deduced. The changes in ΔG^0, K_x, and Δ_c from reaction to reaction are attributed to three effects, which are identified as an intermolecular electrostatic effect and two steric features of the aromatic compounds, qualitatively referred to as ' trapping ' and ' blocking ' effects of the alkyl substituents. The three effects, characterized by x, y, and z respectively, are quantified in equations for ΔG^0, K_x, and Δ_c and their theoretical significance explained.

RECENT ^{1}H n.m.r. studies of the interactions between polar molecules and non-polar aromatic compounds have revealed two interesting features of the complexes that are formed transiently in solution. First, it appears that the interactions are highly specific between well defined sites in the two compounds, but are such that the complexes are not formed with a unique geometry but with a variety of isomeric configurations.[2,3] Secondly, there is evidence that suggests that the magnitude of the thermodynamic and spectroscopic parameters characteristic of complex formation are governed both by electrostatic and steric factors.[4] In the case of the interactions of acrylonitrile (A) with benzene (B) and several alkylated benzenes (BH) it has been suggested [4] that there are two steric factors, which were described qualitatively as ' blocking ' and ' trapping ' effects of the alkyl groups in the aromatic compounds which affect the formation of complexes with acrylonitrile. It was shown that the equilibrium quotients, $K_x{}^{BH}$, for the reactions and the chemical shifts, $\Delta_c{}^{BH}$, induced in acrylonitrile by the aromatic compounds in the fully complexed state can be predicted accurately using equations (1) and (2). In these expressions δ_{ij} is +1 if the alkyl substituents have

$$K_x{}^{BH} = V_{BH}x + (V_{BH} - V_B)(\delta_{ij}y - z) \qquad (1)$$

$$\Delta_c{}^{BH} = V_{BH}x' + (V_{BH} - V_B)(\delta_{ij}y' - z') \qquad (2)$$

an overall radius greater than the half-thickness of benzene and is zero otherwise, $x \neq x'$, $y \neq y'$, and $z \neq z'$ are respectively electrostatic, ' trapping ', and ' blocking ' factors and V refers to the molar volume of the relevant aromatic compound. To test further equations (1) and (2), examine several hypotheses presented previously,[4] and permit the equations to be given a theoretical rather than the earlier qualitative basis, we have studied, at several temperatures, the complexes formed between chloroform and a variety of aromatic compounds.

EXPERIMENTAL

The aromatic compounds used were benzene, *p*-xylene, mesitylene, *p*-diethyl-, 1,3,5-triethyl-, *p*-di-isopropyl-, and 1,3,5-tri-isopropyl-benzene. These were of the best commercial quality available and used without further purification. Chloroform was purified to remove the ethanol stabilizer.

Each chloroform–aromatic reaction was studied under the conditions and by the method described fully elsewhere.[5] For each system a series of *ca.* 10 samples was prepared in which the mole fraction of chloroform was constant and <0.005, and that of the aromatic x_{BH} varied in the range 0.9—1.0 by the addition of cyclohexane.

The chemical shifts δ_{obs} of chloroform relative to cyclohexane were measured using a Varian HA 100D spectrometer operating in field sweep mode locked on a convenient aromatic absorption. The shift of chloroform in cyclohexane alone, δ_{free}, was measured using external tetramethylsilane to provide the lock signal.

The data for each reaction were processed on an I.C.L. 1905 computer using a curve-fitting procedure to obtain $K_x{}^{BH}$ and $\Delta_c{}^{BH}$ from the gradient and intercept at $x_{BH}^{corr} = 1.0$ corresponding to the modified [5] Benesi–Hildebrand [6] equation (3) in which $\Delta_{obs} = \delta_{obs} - \delta_{free}$ and x_{BH}^{corr} is defined [5] in

$$\frac{1}{\Delta_{obs}} = \frac{1}{K_x{}^{BH}\Delta_c{}^{BH}x_{BH}^{corr}} + \frac{1}{\Delta_c{}^{BH}} \qquad (3)$$

terms of moles, n, and molar volumes in equation (4). The

$$x_{BH}^{corr} = \frac{n_{BH}}{n_{BH} + \dfrac{n_S V_S}{V_{BH}}} \qquad (4)$$

super- and sub-scripts BH refer to the aromatic compounds studied in the order listed above. All molar volumes used in the calculations were deduced from density data given in ref. 7.

RESULTS

The values of $K_x{}^{BH}$ and $\Delta_c{}^{BH}$ deduced for each of the reactions at several temperatures are given in Table 1. It should be noted that when processing the data the calculations were performed throughout using at least three places of decimals at each stage and the results rounded up to give the values quoted, consistent with experimental error (discussed in ref. 4). Using a least squares treatment of ln K_x against T^{-1} the values of ΔH^0 and hence ΔG^0 and ΔS^0 given in Table 2 were deduced.

The data given in Tables 1 and 2 depend on the assumption that the complexes formed all have 1 : 1 stoicheiometry. If this is not the case serious errors could arise from the use of

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equation (3). However, in the present work such errors are unlikely because the compositions of the samples used are such that the binding of two chloroform molecules on opposite sides of a single aromatic molecule is highly improbable. The assumption of 1 : 1 stoicheiometry is substantiated by the good linearity of the ln K_x^{BH} against T^{-1} plots. This suggests that ΔH is independent of temperature, a fact which is taken to be a good test for the presence of a single 1 : 1 or several isomeric 1 : 1 complexes,[8] if the experimental data are processed on this basis.

Reference to Table 1 shows that for a particular reaction K_x decreases with increasing temperature, as expected, and that Δ_c appears to be independent of temperature as was found [4] for the acrylonitrile–aromatic reactions.

DISCUSSION

In arriving at the form of equation (1) it was suggested [4] that the following four main factors could influence the magnitude of K_x: (a) the polarizability of the (non-polar) aromatic molecule, (b) the dipole moment and the polarizability of the polar molecule, (c) steric features of the aromatic molecule, and (d) steric features of the polar molecule. If, as extensive information suggests, the complex formed is stereospecific it would be expected that ΔG^0 for the reaction should be governed by the dipole-induced dipole interaction in the complex and by analogy with the general principles of steric effects in organic chemistry by steric effects, and the electrostatic forces on which these depend, in those bimolecular collisions which result in complex formation. This of course assumes that any changes in the rotational, vibrational, *etc.*, energies of the individual molecules are relatively small. The concern is then with the interaction energy between the molecules in the complex and with special electrostatic or steric effects associated with the aromatic substituents during complex formation.

TABLE 1

Values of K_x and Δ_c deduced for the interactions between chloroform and various alkylated benzenes at several temperatures

Aromatic compound	T/K	K_x	Δ_c/p.p.m.
Benzene	281.8	3.1	1.3
	292.3	2.7	1.3
	302.0	2.4	1.3
	309.1	2.0	1.3
	312.3	1.6	1.3
p-Xylene	286.9	2.5	1.6
	292.9	2.4	1.5
	302.6	2.0	1.5
	311.4	1.9	1.5
	321.9	1.6	1.5
Mesitylene	277.1	3.5	1.7
	288.4	2.8	1.7
	304.8	2.3	1.6
	311.7	2.1	1.6
	322.1	1.8	1.6
p-Diethylbenzene	276.2	2.3	1.7
	288.4	2.1	1.7
	294.5	1.7	1.7
	303.2	1.7	1.6
	311.7	1.4	1.6
	322.1	1.2	1.6
1,3,5-Triethylbenzene	277.1	2.0	2.0
	288.4	1.5	2.0
	302.2	1.4	1.9
	311.7	1.2	1.9
	322.1	1.0	1.9
p-Di-isopropylbenzene	303.8	1.3	1.6
	312.6	1.2	1.5
	322.0	0.9	1.6
1,3,5-Tri-isopropylbenzene	276.2	1.5	2.3
	288.2	1.2	2.2
	304.2	1.1	2.0
	311.7	0.7	2.4
	314.0	0.9	2.1
	322.1	0.7	2.3

TABLE 2

Thermodynamic parameters for the interaction of chloroform with various aromatic compounds at 298.2 K

Aromatic compound	$-\Delta H^0$/ kJ mol^{-1}	$-\Delta G^0$/ kJ mol^{-1} Expt.	Calc.	$-\Delta S^0$/J mol^{-1} K^{-1}
Benzene	13.4	2.2	2.2	37.6
p-Xylene	10.3	1.9	2.1	28.2
Mesitylene	10.7	2.3	2.1	28.5
p-Diethylbenzene	11.1	1.3	1.2	32.7
1,3,5-Triethylbenzene	10.6	0.8	0.9	32.9
p-Di-isopropylbenzene	13.9	1.0	0.8	43.2
1,3,5-Tri-isopropylbenzene	12.3	0.1	0.2	41.0

If the polar solute in the complex adopts a time-averaged orientation such that its dipolar axis is colinear with the aromatic six-fold axis the interaction energy W_{DID} is given [9] by equation (5) where μ_A is the

$$W_{DID} = -4\mu_A{}^2\alpha^{\perp}{}_{BH}/R^6 \qquad (5)$$

dipole moment of the polar molecule, R is the distance between its equivalent or point dipole and the centre of the aromatic ring, the six-fold polarizability of which is $\alpha^{\perp}{}_{BH}$.

The problem of quantifying steric effects, which are basically electrostatic in origin, is notoriously difficult. However, considering the type of compounds studied here it is evident that only dipole-induced dipole and dispersion forces will be significant in influencing the formation of the complex and its stability.

When dealing with intermolecular dispersion forces it is convenient to follow the Barriol–de Montgolfier [10] treatments of these which have found extensive success in the calculation of both thermodynamic parameters and n.m.r. chemical shifts.[11] For this, one molecule is considered to have an instantaneous dipole moment $\vec{\mu}_1$ in a solvent of polarizability α_2. The second molecule (2) is subject to a field $\vec{E}$, produced by the moment of the first molecule. For this situation the interaction energy is given by (6) which because [10] of equation (7) reduces to (8) where ΔE_1 is commonly taken to be the ionization potential of the molecule concerned.

$$W_D = -\alpha_2\bar{\mu}_1{}^2/r^6 \qquad (6)$$

$$\bar{\mu}_1{}^2 = \tfrac{3}{2}\alpha_1\Delta E_1 \qquad (7)$$

$$W_D = -\tfrac{3}{2}\frac{\alpha_2}{r^6}\,\alpha_1\Delta E_1 \qquad (8)$$

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[11] J. Homer, 'Solvent Effects on Nuclear Magnetic Resonance Chemical Shifts,' in Applied Spectroscopy Reviews, ed. E. G. Brame, Marcel Dekker, 1975, vol. 9, p. 1.

By a similar classical approach the average dipole-induced dipole interaction energy is given [9] by equation (9).

$$\overline{W}_{\mathrm{DID}} = -2\alpha_2\mu_1^2/r^6 \qquad (9)$$

It is now possible to correlate equations (5), (8), and (9) with the free energy change for the formation of any complex. In the first instance the interaction between chloroform and benzene may be considered. However, in so doing it must be remembered that ΔG is determined by measurements that depend on the preferential affinity of chloroform for benzene rather than cyclohexane, the ' inert ' solvent. Consequently, because the polarizabilities of benzene and cyclohexane are very similar [12] and the latter has no significant donor characteristics, equation (10) may be written for the benzene–chloroform interaction. It is reasonable to suppose that the values of ΔG^0 for the alkylbenzenes will differ from that given by equation (10) because of the effects of their alkyl groups as governed by equations (8) and (9).

$$\Delta G^0{}_{\mathrm{B}} = 4\alpha^{\perp}{}_{\mathrm{B}}\mu_{\mathrm{A}}^2/R^6 \qquad (10)$$

Consequently, it follows for these that equation (11) holds.

$$\Delta G^0{}_{\mathrm{BH}} = \frac{4\alpha^{\perp}{}_{\mathrm{BH}}\mu_{\mathrm{A}}^2}{R^6} + (\alpha_{\mathrm{BH}} - \alpha_{\mathrm{B}})\left(\frac{3\alpha_{\mathrm{A}}\Delta E_{\mathrm{A}}}{2r^6} + \frac{2\mu_{\mathrm{A}}^2}{r^6}\right) \qquad (11)$$

In this expression R will be approximately constant for the aromatic series whereas r must of course vary. However, in the latter connection it is convenient to adopt a suggestion made by Longuet-Higgins,[13] and given some experimental support by Raynes,[14] that dispersion forces may be additive on a group basis. If, in the alkyl compounds, the number of such groups is defined by the number (X) of alkyl carbon atoms, the radius of each group is given by $[0.293(V_{\mathrm{BH}} - V_{\mathrm{B}})/X]^{1/3}$ and is constant within $\pm 0.7\%$. It is evident therefore that the last term of equation (11) should be the sum of X terms, for each of which the relevant polarizability is $(\alpha_{\mathrm{BH}} - \alpha_{\mathrm{B}})/X$. Finally, because polarizabilities and molar volumes are linearly proportional [4] equation (11) may be rewitten as (12).

$$\Delta G^0{}_{\mathrm{BH}} = V_{\mathrm{BH}}x + (V_{\mathrm{BH}} - V_{\mathrm{B}})(a + b) \qquad (12)$$

Obviously $x \propto 4\mu_{\mathrm{A}}^2/R^6$, $a \propto 3\alpha_{\mathrm{A}}\Delta E_{\mathrm{A}}/2r_1^6$, and $b \propto 2\mu_{\mathrm{A}}^2/r_1^6$ where r_1 is the distance between the electrical centre of chloroform and each alkyl subgroup. While there is no ambiguity about the interpretation of x it must be remembered that despite both a and b representing attractive forces *each* may act in such a way that, depending on the relative orientations of chloroform and the aromatic molecule during collision, they may either hinder or enhance the formation of a complex with its energetically favoured stereospecific form, and for similar reasons the stability of the complex once formed. Consequently, equation (12) has to be modified to the form of (1) for the general case where y and z notionally account for the enhancing (' trapping ') or hindering (' blocking ') steric effects of the alkyl groups to complex formation.

At this stage it must be pointed out that equation (1) should refer to ΔG^0 and not K_{x} in the general case. However because K_{x} is *ca.* unity, $\ln K_{\mathrm{x}} \approx 1 + K_{\mathrm{x}}$, and K_{x} and ΔG^0 should be roughly proportional so that in this special circumstance the equation may be used to investigate the changes in either parameter.

In the work on acrylonitrile the analysis of the values for $K_{\mathrm{x}}{}^{\mathrm{BH}}$ in terms of equation (1) was based on data obtained at one temperature only. To improve the credibility of the approach we have used the values of ΔG^0 and the rationalized value of $K_{\mathrm{x}}{}^{\mathrm{BH}}$ at 298.2 K for the chloroform reactions. Using the values found for these parameters (to three decimal places) in equation (1) with the molar volumes expressed in cm^3 it is found that for the ΔG^0 set $x = +0.024\,024$, $y = -0.012\,391$, and $z = +0.024\,562$ and for the K_{x} set $x = +0.025\,864$, $y = -0.009\,727$, and $z = +0.024\,36$. As predicted above the two values deduced for each of x—z are similar. That these parameters rationalize the respective data is evident from the agreement obtained between the experimental and calculated values which are given in Tables 2 and 3. Nevertheless, it has to be recognized that this internal consistency could be fortuitous and that a more definitive vindication of the use of equation (1) should be established.

TABLE 3

Calculated and experimental values for K_{x} (298.2 K) and Δ_{c} (average)

	K_{x}		Δ_{c}/p.p.m.	
Aromatic compound	Calc.	Obs.	Calc.	Obs.
Benzene	2.3	2.4	1.3	1.3
p-Xylene	2.4	2.2	1.5	1.5
Mesitylene	2.4	2.5	1.6	1.6
p-Diethylbenzene	1.7	1.7	1.7	1.7
1,3,5-Triethylbenzene	1.5	1.4	1.9	2.0
p-Di-isopropylbenzene	1.4	1.5	1.9	1.6
1,3,5-Tri-isopropylbenzene	1.0	1.0	2.2	2.2

From the foregoing derivation of equation (1) it is to be expected that the values for x—z should be different for series of reactions involving the same aromatic molecules with different polar molecules. It is constructive therefore to compare the parameters obtained (from the values for K_{x}) here for chloroform with those, $x = +0.016\,548$, $y = +0.007\,611$, $z = +0.030\,255$, obtained [4] for acrylonitrile in reaction with the same set of aromatic compounds. In the chloroform case the values of y and z indicate that the steric effects hinder complex formation. On the other hand in the acrylonitrile reactions the ' blocking ' factor z hinders complex formation, presumably by reducing the possibility of the two molecules adopting the energetically favoured orientation during collisional approach. Conversely, in this case the ' trapping ' factor y enhances complex formation presumably by aiding the colliding molecules to adopt the energetically favoured orientation for complex formation and, moreover, by increasing the interaction energy once the complex has been formed. Because y and z both have contributions from a and b in equation (12) it is impractical to make a

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theoretically based comparison between the values obtained for y and z from the two sets of reactions.

However, for both chloroform and acrylonitrile the electrostatic factor x has the same sign. This is obviously expected to be positive. Moreover, for this parameter it is possible to predict quantitatively the ratio of the values for the two polar solutes. If the polar solute approaches the aromatic ring such that the time-averaged orientation is with the dipolar axis (along the C–H bond in chloroform and along the C≡N bond in acrylonitrile) and aromatic six-fold axis co-linear, the interaction energy is given by equation (5).[9] It is evident that for a comparison between the two sets of reactions equation (13) approximately represents the ratios of the x values. Assuming the point dipole of

$$\frac{x_{\mathrm{CHCl_3}}}{x_{\mathrm{C_3H_3N}}} = \frac{\mu_{\mathrm{CHCl_3}}{}^2 R_{\mathrm{C_3H_3N}}{}^6}{\mu_{\mathrm{C_3H_3N}}{}^2 R_{\mathrm{CHCl_3}}{}^6} \qquad (13)$$

chloroform lies at the point on the symmetry axis intersecting the plane of the chlorine atoms and that of acrylonitrile at the nitrogen atom, the values for R can be calculated if the pairs of molecules are assumed to be in contact. Using the geometric molecular parameters for acrylonitrile[15] and chloroform[16] together with the half-thickness of benzene[17] and the van der Waals radius of hydrogen[17] it can be estimated that $R_{\mathrm{C_3H_3N}} = 7.4$ and $R_{\mathrm{CHCl_3}} = 4.63$ Å. Substituting these values with $\mu_{\mathrm{CHCl_3}} = 1.2$[18] and $\mu_{\mathrm{C_3H_3N}} = 3.89$ D[19] in equation (6) yields $x_{\mathrm{CHCl_3}}/x_{\mathrm{C_3H_3N}} = 1.58$ which is in excellent agreement with the experimental ratio of 1.56 and provides credibility both for the use of equation (1) and its classical theoretical basis.

Whilst it is difficult to justify theoretically the empirical equation (2), it is evident from work such as that of Berkeley and Hanna[20] that changes in Δ_c between reactions may reflect changes in the solute–aromatic interaction energy. Consequently equation (2) has been used to analyse the average of the values of $\Delta_c{}^{BH}$ given in Table 1, and it is found that $x' = +0.014\,325$, $y' = -0.001\,192$, and $z' = +0.007\,622$. The excellent agreement between the values calculated for Δ_c using these values, and those obtained experimentally is evident from Table 3. It is interesting that the values $x' = +0.014\,564$, $y' = -0.004\,362$, and $z' = +0.007\,239$ obtained for the acrylonitrile–aromatic reactions individually have the same sign and similar magnitude as those obtained for chloroform. The implication here is that in both sets of reactions the steric effects act so as to reduce the screening induced in the solute within the complex.

Conclusions.—From studies of the reactions between chloroform and various alkylbenzenes at several temperatures confirmation has been obtained for a suggestion made elsewhere[4] that ΔG^0, K_x (when close to unity), and Δ_c are governed by three factors which were described as being due to electrostatic and the steric ' blocking ' and ' trapping ' factors of the alkyl groups. The empirical equation used to analyse the data has been derived and the steric factors shown to be due to intermolecular dipole-induced dipole and dispersion interactions. Values characteristic of the three factors have been deduced that accurately rationalize the experimental data and which when compared with the corresponding values for acrylonitrile–aromatic interactions have been shown to be in agreement with general empirical expectations and in the case of one factor (the only one amenable to analysis) with theoretical prediction.

We are grateful to the S.R.C. for providing funds for the purchase of the n.m.r. spectrometer used in this work and a Research Studentship to P. M. W.

[3/2194 *Received*, 25th *October*, 1973]

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