^{1}H and ^{13}C Nuclear Magnetic Resonance Shift Measurements and Association Constants of Some Chloroform, Trinitromethane, Pentachloroethane, and 1,1,1-Trichloro-2,2-bis-(*p*-chlorophenyl)ethane (DDT) Complexes in Cyclohexane Solution

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Association constants for the interactions of benzene and of hexamethylbenzene with chloroform, with pentachloroethane, and with DDT, of chloroform with acetone, and of trinitromethane with hexamethylbenzene, all in cyclohexane solution, have been determined from high resolution n.m.r. measurements. The results, together with the observed changes in chemical shift, are discussed.

THE stabilities of the complexes of DDT with the typical π-donors benzene and hexamethylbenzene (HMB) have been determined. Because we considered that the complexing in these systems might, at least in part, occur *via* hydrogen bonding of the doubly benzylic proton of DDT with the π-electrons of the aromatic donor, comparative studies have also been made on other systems where this type of bonding is well substantiated.

Association constants (K) have been determined from the changes in the line positions of high-resolution nuclear magnetic resonances in one component as the concentration of the second component, usually in large excess, is altered. In most cases the nucleus chosen has been the proton which is likely to be involved in the hydrogen bond, although in one system a ^{13}C magnetic resonance has been used to obtain an independent estimate of the association constant.

EXPERIMENTAL

For systems measured under the condition [hydrogen-donor molecule] $\ll$ [electron donor], the method of Foster and Fyfe [1,2] was used. The n.m.r. line position of the measured nucleus in the presence of a concentration [D] of the electron donor, relative to the line position of the same nucleus in the absence of donor (Δ) was determined for a series of solutions. It may be shown that if only 1 : 1 complexing occurs then equation (1) applies, where Δ_0 is

$$\Delta/[\mathrm{D}]_0 = -K\Delta + K\Delta_0 \qquad (1)$$

the chemical shift of the measured nucleus in the pure complex relative to the shift of the same nucleus in the free hydrogen-donor molecule, all in solution. A plot of $\Delta/[\mathrm{D}]_0$ *vs.* Δ gives K directly as the negative gradient. The linearity of this plot over a wide range of saturation fraction, s (defined as the ratio of the concentration of the less concentrated component in the complexed state to the total concentration, free and complexed, of this component) may be taken as an indication of the absence of termolecular complexes.[3,4] In the present work the widest possible s ranges were used, subject to the condition that the solutions remained reasonably dilute. In some cases the range was further restricted by the solubility of the more concentrated component. Within these limitations, the plots appropriate to equation (1) were linear in all cases.

In systems where equimolar concentrations of the two components were used, the method of Foster and Twiselton,[5] in which the relationship (2) is employed, has been applied.

$$\Delta/[\mathrm{D}]_0 = K(\Delta_0 - 2\Delta + \Delta^2/\Delta_0) \qquad (2)$$

In all the evaluations the data were processed by using appropriate standard programs on an Elliott 4130 computer. N.m.r. measurements were made on a Bruker HX-90 spectrometer operating at 90·00 MHz in the case of ^{1}H and at 22·63 MHz in the case of ^{13}C nuclei. Solutions made up by weight in 5 mm (^{1}H) or 10 mm (^{13}C) tubes were used. The ^{1}H signal of the solvent cyclohexane was used for the field-lock and as the internal reference in all determinations of K, both for ^{1}H and for ^{13}C. In some of the ^{13}C measurements, the signal : noise ratio was enhanced by a Northern 500 Compiler of Average Transients. Probe temperatures were checked before and after each experiment by means of an independent thermocouple placed in the sample tube. Shift measurements for each solution were repeated at least five times and the arithmetic average was taken. The estimated error in ^{13}C shifts is $\pm 0{\cdot}5$ Hz and in ^{1}H shifts $\pm 0{\cdot}1$ Hz.

Materials.—Cyclohexane (Fisons ' spectrograde ' reagent), benzene (Hopkin and Williams ' Pure for Molecular Weight determination '), chloroform (34 and 90% ^{13}C enriched, Prochem) were all used without further purification. Trinitromethane, prepared by Chattaway and Harrison's method,[6] as modified by Young, Holt, and Walker,[7] was recrystallised (×2) from light petroleum at −50°, and had m.p. 27·8° (lit.,[7] 27°). 1,1,1-Trichloro-2,2-bis-(*p*-chlorophenyl)ethane, recrystallised (×3) from ethanol, had m.p. 108—109° (lit.,[8] 107—108°). Other materials were prepared and purified by standard methods.

RESULTS

Chloroform–Acetone.—On addition of acetone to dilute solutions of chloroform in cyclohexane, shifts of the chloroform proton line position to low field were observed. For a series of solutions in which [acetone] = $[\mathrm{D}]_0 \gg$ [chloroform], plots of $\Delta/[\mathrm{D}]_0$ *vs.* Δ were linear over a wide satur-

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ation-fraction (s) range [see equation (1)]. This linearity provides reasonable evidence for the 1 : 1 stoicheiometry of the complex, and the absence of significant amounts of complexes of other molecular ratios.[2,3,9] From the gradient and intercept of the above plot, K and Δ_0 were determined (Table 1). K has also been estimated from the change in the line position of ^{13}C resonance of 90% enriched chloroform as the concentration of acetone was altered (Table 1). No change in the coupling constant $J(^{13}C–^{1}H)$ with concentration of acetone was observed.

TABLE 1

Association constant (K_r) for chloroform–acetone in cyclohexane at 288 K

Nucleus	s range	K/l mol^{-1}	Δ_0 [a]
^{13}C	0·2—0·5	0·81 ± 0·18	2·0 ± 0·3
^{13}C	0·2—0·4	0·84 ± 0·06	2·0 ± 0·3
^{1}H	0·04—0·3	0·84 ± 0·12	0·87 ± 0·13
^{1}H	0·2—0·6	0·74 ± 0·015	0·93 ± 0·02

[a] Relative chemical shift in p.p.m.

Chloroform–Benzene and Chloroform–Hexamethylbenzene.—Addition of benzene or hexamethylbenzene to dilute solutions of chloroform in cyclohexane caused upfield shifts of the ^{1}H resonance of chloroform. Association constants were evaluated by application of equation (1) (Table 2). The changes in chemical shift of the ^{1}H resonance of benzene on addition of chloroform under the reverse conditions $[C_6H_6] \gg [CHCl_3]$, were too small (*ca.* 3 Hz downfield in the presence of 8M-acetone) to enable a reasonable estimate to be made of K by this technique under these conditions.

TABLE 2

Association constants (K_r) and Δ_0 values for ^{1}H of chloroform in complexes with benzene and with hexamethylbenzene in cyclohexane

$[CHCl_3]$/ 10^{-3} mol kg^{-1}	[electron donor]/ mol kg^{-1}	K_r [a]/kg mol^{-1}	Δ_0 [b]	s [c]	T/K
Benzene					
3·64	0·25—4·47	0·19 ± 0·04	0·94 ± 0·05	0·33—0·90	307·3
3·00	0·19—3·20	0·2 ± 0·1	0·87 ± 0·05	0·28—0·87	306·8
HMB					
3·64	0·08—0·52	0·53 ± 0·09	1·78 ± 0·03	0·04—0·22	307·4
3·00	0·02—0·51	0·6 ± 0·1	1·61 ± 0·04	0·01—0·24	307·9

[a] In kg solution per mol. [b] Relative chemical shift in p.p.m. [c] Saturation fraction.

The line position of ^{13}C of chloroform in a 34% enriched sample as a 0·06M-solution in cyclohexane was moved *ca.* 5 Hz downfield by the presence of 3M-benzene. Again the change in these shifts was insufficient to enable an independent evaluation of K from them. The isotopic dilution was such that concentrations of chloroform sufficiently high for the ^{13}C resonance to be observed were too large for any change in the line position to be detected when benzene up to 3M was added to chloroform containing ^{13}C in natural abundance, all in cyclohexane as the diluting solvent. In the chloroform–hexamethylbenzene system, the solubility of the hydrocarbon limited its concentration in cyclohexane to *ca.* 0·4M, at which concentration no perturbation of the line position of ^{13}C in a 34% enriched specimen of chloroform could be observed.

Trinitromethane–Hexamethylbenzene.—Plots of $\Delta/[D]_0$ *vs.* Δ involving ^{1}H resonance of trinitromethane in a series of solutions containing large excesses of donor species yielded linear plots over wide saturation fraction ranges. From an application of equation (1) the association constants were obtained. The association constants were also evaluated under the condition [trinitromethane] = [HMB] by using the method described by Foster and Twiselton[5] (see Experimental section). The results are summarised in Table 3. Values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ obtained from the variation of ln$K$ and of ln$K\Delta_0$ with T^{-1} are also given in Table 3.

TABLE 3

Association constants (K_r),[a] Δ_0, enthalpy ($\Delta H^{\ominus}$), and entropy ($\Delta S^{\ominus}$), of complex formation for the interaction of trinitromethane (TNM) with hexamethylbenzene (HMB) in cyclohexane solution

Rel. concn.	T/K	K/kg mol^{-1} [a]	Δ_0 [b]	s [c]	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/J mol^{-1} K^{-1}
	296·5	21·6 ± 1·1	2·64 ± 0·05	0·13—0·81		
[TNM] ≪ [HMB]	306·8	15·6 ± 0·5	2·57 ± 0·63	0·10—0·76	−21·0 ± 5·9 [d]	−45 ± 13 [d]
([HMB] = 0·007—0·2 mol kg^{-1})	317·5	12·1 ± 1·0	2·45 ± 0·07	0·08—0·71	−24·0 ± 6·2 [e]	−55 ± 15 [e]
	328·6	9·3 ± 0·7	2·35 ± 0·05	0·06—0·65		
	296·9	27·3 ± 2	2·52 ± 0·08	0·26—0·69		
[TNM] = [HMB]	310·0	18·1 ± 1	2·42 ± 0·05	0·20—0·63	−24·8 ± 4·1 [d]	−56 ± 10 [d]
([HMB] = 0·017—0·26 mol kg^{-1})	318·6	14·0 ± 1	2·37 ± 0·05	0·16—0·60	−26·9 ± 3·8 [e]	−63 ± 10 [e]
	328·0	10·5 ± 1	2·32 ± 0·05	0·13—0·55		

[a] In kg solution per mol. [b] Relative chemical shift in p.p.m. [c] Saturation fraction. [d] From plot of ln K *vs.* T^{-1}. [e] From plot of ln $K\Delta_0$ *vs.* T^{-1}.

Pentachloroethane–Benzene and Pentachloroethane–Hexamethylbenzene.—For both systems linear plots of $\Delta/[D]_0$ *vs.* Δ_0 were obtained from the observed upfield shifts of the single proton in pentachloroethane. The values of K and Δ_0 obtained from an application of equation (1) are summarised in Table 4.

TABLE 4

Association constants (K_r) [a] and Δ_0 values for pentachloroethane–electron donor complexes in cyclohexane

Donor	T/K	K_r/kg mol^{-1}	Δ_0 [b]	s [c]
Benzene	307·5	0·10 ± 0·04	1·17 ± 0·08	0·03—0·5
HMB	306·9	1·0 ± 0·2	1·73 ± 0·04	0·01—0·4

[a] In kg solution per mol. [b] Relative chemical shifts in p.p.m. [c] Saturation fraction.

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Small changes in the ^{13}C resonance of C(2) of 1,1,1,2,2-pentachloroethane were observed when large excesses of benzene were added to cyclohexane solutions of the former.

DDT–Benzene and DDT–Hexamethylbenzene.—Values of K and Δ_0 for these two systems have been estimated from linear plots of $\Delta/[\mathrm{D_0}]$ *vs.* Δ by using the upfield shifts of the $\mathrm{Ar_2C}H$ signal of DDT in the presence of large excess concentrations of the π-donor. The DDT concentrations were kept in the range 5·4—7·0 × 10^{-2}M. The results are summarised in Table 5.

Only very small changes (*ca.* 1 Hz) occurred in the line positions of the aromatic protons of DDT on addition of large excesses of hexamethylbenzene or benzene. They were insufficient to permit estimates of K from their concentration dependence.

TABLE 5

Association constants (K_r) [a] and Δ_0 values for DDT–electron donor complexes in cyclohexane

Donor	[DDT]/M	T/K	K_r/kg mol^{-1}	Δ_0 [b]	s [c]
Benzene	5·4 × 10^{-3}	306·9	0·13 ± 0·05	0·51 ± 0·05	0·01—0·42
Benzene	7·0 × 10^{-3}	307·6	0·15 ± 0·05	0·45 ± 0·03	0·06—0·43
HMB	5·6 × 10^{-3}	306·7	4·9 ± 1·6	0·12 ± 0·01	0·05—0·57
HMB	5·6 × 10^{-3}	306·9	5·6 ± 1·1	0·09 ± 0·01	0·04—0·62

[a] In kg solution per mol. [b] Relative shift in p.p.m. [c] Saturation fraction.

DISCUSSION

Where it has been possible to analyse the chemical-shift data quantitatively, the results can in all cases be explained in terms of a 1 : 1 molecular association. Although this does not in itself rule out the presence of termolecular or higher order complexes, neither is it necessary to postulate their presence in the way found necessary recently for some π-donor–π-acceptor charge-transfer interactions.[9]

The chloroform–acetone system is a well recognised complex in which the chloroform proton is involved in a hydrogen bond with the oxygen atom of the acetone. Although earlier estimates [10,11] of the stability of the complex in cyclohexane have included determinations based on proton chemical shifts [10] (Table 6) there has been no previous determination involving ^{13}C measurements. Indeed, this appears to be the first successful attempt to use ^{13}C resonance in this way. An earlier attempt [12] to estimate the association constant for an electron-donor–acceptor interaction by this means was unsuccessful.

The close agreement between the values of K in Table 1 vindicates the n.m.r. method and lends support to the proposed 1 : 1 stoicheiometry of the complex. The values are in accord with some earlier published values, namely 0·81 l mol^{-1} from optical data [11] and 0·751 ± 0·012 l mol^{-1} from ^{1}H n.m.r. measurements,[10] although two other ^{1}H n.m.r. experiments have been reported to give rather different values, namely 0·21 l mol^{-1} [13] and (estimated on a molar scale) 0·19 ± 0·06 l mol^{-1}.[14]

The observed shifts of the chloroform ^{1}H signal on addition of acetone have been noted previously and are consistent with the deshielding effects consequent upon hydrogen bonding.[15,16]

Lichter and Roberts [17] were unable to account for the downfield shift of the ^{13}C resonance of chloroform with increasing concentration of acetone in terms of an anisotropic effect, since the measured shift changes (in p.p.m.) are greater for ^{13}C than for ^{1}H, whereas the opposite would be expected, since the proton of chloroform, being nearer to the anisotropic centre, should experience a greater change. If an explanation of the shift is sought in terms of hydrogen-bonding properties, the direction of the shift is at first surprising. However this downfield shift of the ^{13}C chloroform resonance is in harmony with Ramsey's formulation of chemical shifts.[18,19] The paramagnetic screening constant, dependent on the electron distribution in both ground and electronically excited states, becomes very large when an asymmetric distribution of charge with low-lying excited states is near the nucleus of measurement. Thus the ^{13}C chemical shifts are dominated by paramagnetic effects. From Ramsey's shielding formula, Lichter and Roberts [17] relate the repulsion of the C–H bonding electrons in chloroform towards the carbon nucleus to the shortening of a hypothetical radius around the carbon atom, which in Ramsey's model is inversely related to the paramagnetic screening constant. This assumes that any effect of carbon–chlorine bonding electrons can be ignored.

The upfield shifts observed for the ^{1}H resonance of chloroform in cyclohexane solution on addition of benzene or hexamethylbenzene have been interpreted [17,20] as a primarily anisotropic effect of the aromatic ring in a hydrogen-bonded complex in which the C–H bond of the chloroform lies on the six-fold axis of the benzene molecule. By contrast, the effect on the ^{13}C resonance of chloroform is small and down-field.[17]

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The association constant for the chloroform–benzene interaction obtained in the present work (Table 2), converted to reciprocal mole-fraction units, is $K_x = 2{\cdot}5 \pm 1$. This is larger than that obtained by Creswell and Allred,[21] *viz.* $K_x = 1{\cdot}06 \pm 0{\cdot}03$ at 298 K, although the comparison is hardly justified since their solutions were considerably more concentrated with respect to chloroform and less concentrated with respect to benzene. Likewise the value quoted by Slejko, Drago, and Brown,[22] namely $K_x = 1{\cdot}31 \pm 0{\cdot}07$ at 298 K, involves solutions up to 0·98 mole fraction with respect to benzene. Such solutions bear little correspondence to the dilute solutions used in the present study. The association constant for the chloroform–hexamethylbenzene interaction in cyclohexane obtained under the condition $[CHCl_3] \ll [HMB]$ in the present work (Table 2), converted to reciprocal molar units, is $K_c = 0{\cdot}72 \pm 0{\cdot}1$ l mol^{-1}. This is about ten times the value for the same complex in hexane obtained by Dörr and Buttgereit[23] under the conditions $[CHCl_3] \gg [HMB]$, namely $6 \pm 1{\cdot}5 \times 10^{-2}$ l mol^{-1}. Under the latter conditions there may be a significant degree of 2 : 1 complexing. This could partly account for the reported difference.

The values of K obtained for the trinitromethane–hexamethylbenzene association under the conditions $[CH(NO_2)_3] \ll [HMB]$ and $[CH(NO_2)_3] = [HMB]$ show some disagreement (Table 3). Since in the equimolar experiments the most concentrated solutions contained *ca.* 0·2M-trinitromethane, consideration was given to the possibility that in some way the trinitromethane in these solutions was not behaving ideally. However, the effect cannot be explained in terms of simple dimerisation, since this would lead to lower values of association constant at higher concentrations, contrary to observation. It was found that under the condition $[CH(NO_2)_3] \ll [HMB]$ the value of K_r at 296·5 K was depressed from 21·6 to 14·6 kg mol^{-1} when the concentration of trinitromethane was increased ten-fold. The value of the association constant in reciprocal mole-fraction units quoted by Homer and Huck[24] ($K_x = 279{\cdot}40$ at 286·6 K) is larger than that obtained in the present work, which, converted to mole fraction units, is $K_x = 187 \pm 5$. However, consistent with the above observations, Homer and Huck's measurements were made on solutions which were *ca.* 25 times more concentrated with respect to trinitromethane.

Although there are significant differences in the values of K_r obtained under the two experimental conditions $[CH(NO_2)_3] \ll [HMB]$ and $[CH(NO_2)_3] = [HMB]$, the values for the enthalpy ($\Delta H^\ominus$) and entropy ($\Delta S^\ominus$) of complex formation obtained by van't Hoff plots of either $\ln K_r$ *vs.* T^{-1} or $\ln K_r\Delta_0$ *vs.* T^{-1} are in reasonable agreement (Table 3).

Attempts to determine the association constant of a trinitromethane–π-donor under the conditions $[CH(NO_2)_3] \gg$ [donor], using 1,2,4,5-tetramethylbenzene as the π-donor, were unsuccessful because the changes in line position of the aromatic protons on addition of 0·25M-trinitromethane were only 6·6 Hz. We consider such changes too small to provide under these conditions an adequate estimate of K. Under the same conditions, no change was observed in the line position of the methyl protons of 1,2,4,5-tetramethyl- or of hexamethyl-benzene.

The relatively large upfield shifts observed for the ^{1}H line position of trinitromethane in the presence of large excesses of benzene, but the small shifts of the ^{1}H line position of benzene in the presence of large excesses of trinitromethane indicate the dominance of the anisotropic effect of benzene corresponding to the analogous chloroform interaction.

In considering the complexing ability of DDT, pentachloroethane was taken as a simple model in which the hydrogen-bonding potentiality of DDT is still present. Whilst it might be argued that degrees of association of these two species with benzene are too small for comparisons to be made, there is a significant difference in the stabilities of the corresponding hexamethylbenzene complexes (Tables 4 and 5). It is tentatively suggested that this difference is due at least in part to the larger polarisability of the DDT molecule.

After this work was initiated, Wilson[25] reported the results of a study of the association of DDT with several π-donors, including benzene, in carbon tetrachloride. The concentration dependence of ^{1}H line positions of DDT were analysed in terms of two equilibria, (3) and (4),

$$A + D \rightleftharpoons AD \qquad K_1 = [AD]/[A][D] \qquad (3)$$

$$AD + D \rightleftharpoons AD_2 \qquad K_2 = [AD_2]/[AD][D] \qquad (4)$$

where A = DDT and D = benzene. At 298·16 K, the values $K_1 = 0{\cdot}157$ kg mol^{-1} and $K_2 = 0{\cdot}148$ kg mol^{-1} were obtained. In our experiments we obtained no evidence for termolecular complexing. Even if we had observed significant deviations from linearity of the plots of $\Delta/[D]_0$ *vs.* Δ for this system, experience with other systems where the overall interaction is as weak suggests that we would not have had any success in attempting to evaluate K_1 and K_2.

The suggestion made above that more than hydrogen bonding is involved in the interaction of DDT with π-donors is supported by the relationship between the values of Δ_0 for the DDT complexes of benzene and of hexamethylbenzene, Δ_0 (benzene complex) $> \Delta_0$ (HMB complex), relative to the corresponding values for the complexes of chloroform and pentachloroethane where the converse holds. Indeed, Wilson[25] suggests that hydrogen bonding makes no important contribution to complexing of DDT with aromatic hydrocarbons.

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