The Free Energies and Heats of Formation of the Polyalkylbenzene–Iodine Monochloride Complexes

By N. Ogimachi, L. J. Andrews and R. M. Keefer

Further evidence for steric interference by donor alkyl substituents to the formation of halogen–aromatic complexes has been obtained through measurement of equilibrium constants for the interaction of a large number of polyalkylbenzenes with iodine monochloride. As few as three *t*-butyl substituents or five ethyl substituents on a benzene donor constitute a steric barrier to this type of interaction. The heats of interaction of iodine monochloride and substituted benzenes in carbon tetrachloride have been found to vary in linear fashion with the free energy and entropy changes which accompany the reaction. These variations may be described on the same graphs as have been prepared previously to summarize corresponding linear variations in thermodynamic constants for the interaction of substituted benzenes with iodine. The problem of comparing complex equilibrium constants expressed in molar concentration units with those given in mole fraction units has been considered.

The observed changes in the stabilities of benzenoid-donor type complexes with increases in the number of donor alkyl substituents are generally explained in terms of the electronic influences of the alkyl groups.[1] In view of the recent observation that the equilibrium constants for iodine or iodine monochloride complexes of hexaethylbenzene in carbon tetrachloride solution are much less than those for hexamethylbenzene,[2,3] it now appears that this electronic interpretation is in some cases, at least, insufficient. Presumably the alkyl groups of hexaethylbenzene serve as a bulky screen to shield the π-electrons of the aromatic nucleus against the close approach of a halogen molecule.

To establish more fully the relative importance of the unfavorable steric (as opposed to electronic) effects of alkyl groups in controlling the degree of polyalkylbenzene–halogen interaction, the equilibrium constants for formation of a large number of 1:1 polyalkylbenzene–iodine monochloride complexes have now been measured. The aromatic substances for which such data are now available for theoretical interpretation include all of the polymethylbenzenes, most of the polyethylbenzenes and *p*-di- and 1,3,5-tri-*t*-butylbenzene. Iodine monochloride has been chosen as the halogen for these studies, since the equilibrium constants for its interactions are relatively large (and can be accurately evaluated) and vary appreciably with changes in the number of donor substituents. This report also includes data on the heats of formation of certain of the complexes. These have been measured to determine whether there is any generality to the conclusion, based on the results of an investigation of polyalkylbenzene–iodine interactions,[4] that variations in ΔH of complex formation with changes in donor structure are accompanied by parallel variations in ΔF and ΔS.

Experimental

Materials.—Eastman Kodak Co. Organic Chemicals white label carbon tetrachloride was purified according to the directions of Fieser,[5] dried over Drierite and distilled. Several of the aromatic hydrocarbons were donated by the Standard Oil Company of Indiana through the courtesy of Dr. A. P. Lien. Of these the 1,3,5-tri-*t*-butylbenzene was recrystallized from ethanol (m.p. 73.4–73.9°), and the *p*-di-*t*-butylbenzene was recrystallized from ether (m.p. 76–77.5°). The crude samples of 1,2,4-trimethylbenzene (pseudocumene), 1,2,3-trimethylbenzene (hemimellitene) and 1,2,3,5-tetramethylbenzene (isodurene) were shaken with dilute solutions of iodine monochloride in carbon tetrachloride to remove impurities which reacted with halogen. The excess halogen was removed by washing the solutions with aqueous potassium iodide and sodium thiosulfate. After drying and removal of carbon tetrachloride the hydrocarbons were fractionated through an efficient column to provide pure samples of 1,2,4-trimethylbenzene, (b.p. 169°, n^{20}D 1.5042), 1,2,3-trimethylbenzene (b.p. 176–177°, n^{20}D 1.5143) and 1,2,3,5-tetramethylbenzene (b.p. 197–197.5°, n^{20}D 1.5126).

Eastman Kodak Co. Organic Chemicals white label hexamethylbenzene and hexaethylbenzene were recrystallized from ethanol–benzene mixtures to provide samples of m.p. 165.8–166.6° and 128.7–129.5°, respectively. Eastman Kodak Co. *p*-xylene was subjected to efficient fractionation (b.p. 136°, n^{20}D 1.4952). Eastman Kodak Co. mesitylene was purified by sulfonation procedures[6] to yield a sample of b.p. 164°, n^{20}D 1.4990.

Pure samples of 1,3,5- and 1,2,4-triethylbenzenes were isolated from a commercial mixture (Matheson, Coleman and Bell, Inc.) by methods described previously.[7] The former distilled at 102–102.5° (17 mm.) and the latter at 96.8–97.1° (12.8 mm.). Their refractive indices were n^{20}D 1.5015 and n^{20}D 1.4951, respectively. A sample of pure *m*-diethylbenzene (b.p. 70–70.3° (16 mm.) and n^{20}D 1.4951) was obtained from Coleman, Matheson and Bell diethylbenzene by a procedure described previously.[8]

Samples of 1,2,3,5- and 1,2,4,5-tetraethylbenzenes were obtained by alkylation of commercial triethylbenzene with ethyl iodide. The procedures for alkylation and for separation of the isomers were essentially those used by Smith and Guss.[9] The properties of the 1,2,3,5- and 1,2,4,5-isomers were, respectively, b.p. 115–116° (11.4 mm.), n^{20}D 1.5059 and b.p. 118–118.7° (11.5 mm.), n^{20}D 1.5054. A sample of 1,2,3,4-tetramethylbenzene (b.p. 97–99.1 (25 mm.) and n^{20}D 1.5190) was prepared from Eastman Kodak Co. white label durene by the Jacobsen reaction.[10]

Commercial samples of *p*-chlorotoluene (Matheson, Coleman and Bell) and *m*-chlorotoluene (Eastman Kodak Co.) were purified by fractionation (b.p. 161.1-161.3° and 158.0°, respectively). The sample of *p*-methoxytoluene (b.p. 177–178.5°, n^{20}D 1.5138) was prepared from *p*-cresol by the procedure described by Shirley[11] for the preparation of 3,5-dimethylanisole.

Samples of 1,3,5-triisopropylbenzene (received from Dr. A. P. Lien) and one of 1,2,3,4-tetraethylbenzene (prepared according to Smith and Guss[9]) reacted rapidly with iodine

(1) See L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954), for a summary of earlier work.

(2) L. J. Andrews and R. M. Keefer, This Journal, **74**, 4500 (1952).

(3) M. Tamres, D. R. Virzi and S. Searles, *ibid.*, **75**, 4358 (1953).

(4) R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955).

(5) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Edition, D. C. Heath and Co., New York, N. Y., 1941, p. 365.

(6) L. I. Smith and O. W. Cass, This Journal, **54**, 1603 (1932).

(7) W. B. Dillingham and E. E. Reid, *ibid.*, **60**, 2606 (1938).

(8) J. E. Copenhaver and E. E. Reid, *ibid.*, **49**, 3157 (1927).

(9) L. I. Smith and C. O. Guss, *ibid.*, **62**, 2625, 2630, 2631 (1940).

(10) L. I. Smith, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 282.

(11) D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 126.

monochloride to liberate iodine and, therefore, could not be included in the complex equilibrium studies.

Pentaethylbenzene was prepared from 267 g. (2.0 moles) of anhydrous aluminum chloride, 81.1 g. (0.5 mole) of commercial triethylbenzene and 46 g. (1 mole) of ethanol by the procedure described for the preparation of 1,3,5-triethylbenzene from benzene.[12] The crude product was poured into 1 l. of chopped ice containing 50 ml. of concentrated hydrochloric acid. This mixture was extracted with 200 ml. of ether. From the dried extract two fractions were recovered by distillation. The first (82.7 g.) distilled over a range of 107–131° (5–6 mm.) and the second (11.5 g.) from 131–150° (5–6 mm.). The second fraction, probably hexaethylbenzene, solidified on cooling. The first fraction was cooled to about −20°, and the precipitated solids were filtered. The filtrate was subjected to efficient fractionation. A slightly yellow sample (28.5 g., 26.2% yield) of pentaethylbenzene of b.p. 184–185° (63 mm.), $n^{20}D$ 1.5157, was recovered. This was further purified by the method of Smith and Guss[9] to provide a product of b.p. 182–182.9° (60 mm.), $n^{20}D$ 1.5151.

Anal. Calcd. for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C. 87.98; H, 12.09.

The Equilibrium Studies.—The K_C values for aromatic-iodine monochloride interaction at 25°, which are reported later in Table I, were obtained by the spectrophotometric method which has been described previously.[2] These procedures were also used to study the pentaethylbenzene-iodine complex. With few exceptions the aromatic and halogen concentrations of the several solutions prepared for the measurements on each complex ranged from approximately 0.1–1 M and from 10^{-3}–10^{-4} M, respectively. The reported K_C values are the averages of several values obtained from measurements at a number of different wave lengths in the vicinity of the absorption maxima of the complexes.

The heats of complex formation, which are reported in Table II, were obtained spectrophotometrically by a slight modification of the procedure used in determining the heats of iodine complex formation.[4] For each complex investigated optical densities at the complex absorption maximum were determined at 25° for a series of four solutions of the aromatic and halogen in carbon tetrachloride. The aromatic concentrations were so chosen that the amounts of halogen bound in the complex over the range of the four solutions were approximately 50, 30, 20 and 10% of the total iodine monochloride. The total iodine monochloride concentrations were chosen so that the measured optical densities were about 0.5. Carbon tetrachloride solutions of corresponding concentrations of the aromatics were used as blanks in each of these measurements. These measurements were repeated at 45.8 and at 1.6° using solutions of approximately the same concentrations as those of the solutions measured at 25°.

The aromatic and iodine monochloride solutions which were mixed to provide the samples for spectrophotometric study were brought to temperature (at which measurements were to be conducted) prior to their mixing. This procedure minimized the time required for equilibration of the samples to the temperature of the absorption cell. Since some of the aromatics showed a tendency to undergo slow reaction to consume iodine monochloride (with the simultaneous production of iodine), relatively rapid operations were desirable. This tendency for reaction was most noticeable in the measurements at 1.6° and was sufficiently small at 45.8° so that rapid measurement probably was not an essential feature of the method.

The concentrations of all solutions were established through the mixing of known volumes of solutions or of pure components, the densities of which were known. It was assumed that the volumes were additive in all cases.

Results

The Effects of Donor Alkylation on Equilibrium Constants.—The equilibrium constants K_C at 25° and the molar extinction coefficients at the absorption maxima for the various 1:1 iodine monochloride complexes which were investigated are

(12) J. F. Norris and J. N. Ingraham, THIS JOURNAL, 60, 1421 (1938).

reported in Table I. These were obtained in the usual fashion[4] by graphical interpretation of the data according to equation 1

$$\frac{1}{\epsilon_a - \epsilon_{x_2}} = \frac{1}{K(Ar)} \frac{1}{\epsilon_c - \epsilon_{x_2}} + \frac{1}{\epsilon_c - \epsilon_{x_2}} \quad (1)$$

In this equation ϵ_{x_2} and ϵ_c are, respectively, the extinction coefficients of free and complexed halogen and $\epsilon_a = d/(ICl)_t l$, where d is the measured optical density of the solution containing the complex, $(ICl)_t$ is the total concentration of halogen (free and complexed) and l is the width of the absorption cell (1 cm.).

TABLE I

EQUILIBRIUM CONSTANTS FOR ICl COMPLEXES AT 25° IN CARBON TETRACHLORIDE

Aromatic	λ_{max}, $m\mu$	ϵ_{max}, $\times 10^{-3}$	K_C
p-Di-t-butylbenzene	292	7.3	1.41
m-Diethylbenzene	299	7.9	1.46
p-Xylene	292	6.4	1.85
1,3,5-Tri-t-butylbenzene	313	6.8	0.88
1,2,4-Triethylbenzene	302	6.5	2.36
1,2,4-Trimethylbenzene	299	6.8	2.82
1,2,3-Trimethylbenzene	306	6.0	3.01
1,3,5-Triethylbenzene	310	6.3	3.28
Mesitylene	305	9.7	3.70
1,2,4,5-Tetraethylbenzene	311	7.4	3.09
1,2,3,5-Tetraethylbenzene	316	7.9	3.26
1,2,3,4-Tetramethylbenzene	312	7.0	3.99
1,2,3,5-Tetramethylbenzene	312	7.9	5.60
Hexaethylbenzene	340	5.7	1.55
Hexamethylbenzene	334	6.2	13.2
p-Chlorotoluene[a]	..	..	0.32
m-Chlorotoluene[a]	..	..	0.24
p-Methoxytoluene[a]	..	..	5.19

[a] The position of maximum complex absorption could not be ascertained. Reported K_C values are based on measurements between 300–310 $m\mu$, 305–315 $m\mu$ and 337–345 $m\mu$, respectively, for p-chlorotoluene, m-chlorotoluene and p-methoxytoluene.

Table I includes results for p- and m-chlorotoluene and for p-methoxytoluene. Originally the screening of a large variety of substituted benzenes was planned but most of these, for one reason or another, proved to be unsuitable for study. The observed effects of the chloro substituents on the donor strength of toluene are compatible with the results of earlier work on aromatic–halogen complexes.[13] The large observed equilibrium constant for p-methoxytoluene may encompass specific interactions of iodine monochloride with the oxygen of the ring substituent.[13]

Although the constants K_C reported in Table I are calculated using mole/liter units to express the concentrations of the donors, equilibrium constants for complex formation are frequently recorded as K_N values which are calculated from donor concentrations expressed in mole fraction units. It can be shown that K_C and K_N values evaluated graphically from experimental data by equation 1 are related to each other by equation 2

$$K_C = K_N V_0 + (V_0 - V_s) \quad (2)$$

in which V_0 and V_s are, respectively, the molar volumes of solvent (carbon tetrachloride) and solute

(13) R. M. Keefer and L. J. Andrews, *ibid.*, 72, 4677 (1950).

(donor).[14] The values of $\epsilon_c - \epsilon_{x_2}$ at the complex absorption maxima are also dependent on the choice of donor concentration units as indicated by equation 3

$$(\epsilon_c - \epsilon_{x_2})_N / (\epsilon_c - \epsilon_{x_2})_C = 1 + \frac{V_0 - V_s}{K_N V_0} \quad (3)$$

Except in circumstances in which the equilibrium constants are relatively small and the differences in molar volumes of solvent and solute are appreciable the $(V_0 - V_s)$ term of equation 2 is small and may be neglected. The K_N and K_C values for the hexaethylbenzene–iodine complex which are reported from different laboratories[2,3] seem incompatible if the molar volume term of equation 2 is overlooked. For the iodine complexes (but not for the iodine monochloride complexes) the extinction coefficient ratio of equation 3 may deviate markedly from unity. The values of $(\epsilon_c - \epsilon_{x_2})_N / (\epsilon_c - \epsilon_{x_2})_C$ for iodine complexes of benzene, hexaethylbenzene and 1,3,5-tri-t-butylbenzene in carbon tetrachloride solution are 1.05, 0.51 and 0.32, respectively. The extinction coefficients at the absorption maxima (calculated on a mole fraction basis) for the iodine and iodine monochloride complexes of the more highly alkylated benzenes are approximately the same.

At this time the authors cannot justify the preferential use of either K_N or K_C values. It should be noted that the qualitative aspects of the conclusions drawn in the following discussion are not altered by the choice of donor concentration units.

In surveying the data of Table I and of an earlier publication[2] for evidences of steric repression of complex formation, it has seemed reasonable to adopt the viewpoint that the free energies of halogen–polyalkylbenzene interactions serve as comparative measures of the electronic influences of alkyl substituents on donor strengths in the absence of unfavorable steric situations. This view has recently been supported experimentally by studies of iodine–aromatic complex formation.[4] Accordingly the log K_C values for the polyalkylbenzene–iodine monochloride complexes at 25° have been plotted against the number of alkyl donor substituents (see Fig. 1). Most of the data, when so plotted, conform reasonably well to a straight line. Marked deviations from linearity, which may be associated with the structures or relative positions of alkyl groups on the donor ring, are generally not observed. The log K_C values for toluene, ethyl-, isopropyl- and t-butylbenzenes are almost identical, and there is

little difference in log K_C values for o-, m- and p-xylenes, m-diethylbenzene and p-di-t-butylbenzene. Since evidence for steric repression of complex formation by the bulkier alkyl groups in these mono- and dialkylbenzenes is lacking, it is reasonable to assume that these groups have very similar influences on the π-electron density of the donor ring.

With the exception of the point for 1,3,5-tri-t-butylbenzene the log K_C values for the trialkylbenzenes do not vary widely. The variations noted for the several trimethyl- and triethylbenzenes may stem largely from variations in the combined electrical effects of the alkyl groups with changes in positions of ring substitution. The abnormally low log K_C value for tri-t-butylbenzene (point 9—Fig. 1), like that of hexaethylbenzene (point 21—Fig. 1) may be ascribed to steric repression of complex formation by the accumulated bulk of the alkyl substituents. The points for the tetramethyl- and tetraethylbenzenes cluster about the straight line of Fig. 1. The log K_C values for 1,2,4,5- and 1,2,3,5-tetraethylbenzene complexes are low enough so that it cannot be stated with certainty that the alkyl group effects are, in these cases, purely electronic in nature.

The critical point on Fig. 1 for the pentaethylbenzene complex could not be obtained because the available sample of the hydrocarbon reacted rapidly in dilute solutions of iodine monochloride to liberate iodine. The K_C value for the iodine complex of this hydrocarbon in carbon tetrachloride was measured, however, without difficulty. A value of $K_C = 0.435$ (λ_{max} 355 mμ, ϵ_{max} 9510) was found for this complex as compared to previously recorded K_C values[2,4] (in parentheses) at 25° in carbon tetrachloride for iodine complexes of 1,3,5-triethylbenzene (0.42), mesitylene (0.54), durene (0.50), pentamethylbenzene (0.88) and hexamethylbenzene (1.44). It appears that the ethyl group steric effect which so markedly influences the complexing capacity of hexaethylbenzene is also manifested to a smaller degree in the formation constant for the pentaethylbenzene complex. This point may be demonstrated clearly by plotting (as in Fig. 1) available[2,4] log K values for the iodine–alkylbenzene complexes versus the number of donor alkyl substituents.

In summary it may be concluded that steric effects of donor alkyl substituents on the tendency for benzene–halogen type interaction are non-existent with methyl substituents. These steric effects are not pronounced for less than five ethyl substituents but may become apparent with more than two branched chain alkyl groups.

Heats of Complex Formation.—The heats of formation for several of the iodine monochloride complexes were calculated from spectrophotometric data taken at three different temperatures as described in the Experimental section and in a previous publication.[4] The ratios of equilibrium constants at two different temperatures which were required to calculate ΔH values were obtained from the ratios of slopes of plots of the data according to equation 1 at the temperatures in question. Donor concentrations were expressed in mole frac-

(14) Equation 2 is derived using the expression $C_s = N_s/[V_0 + V_s(V_s - V_0)]$ which relates the solute concentration to its mole fraction. Additivities of volumes of solvent and solute are assumed in this treatment. Many of the V_s values for the aromatic donors used in this investigation are given by J. H. Hildebrand and R. L. Scott, "The Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, N. Y., 1950, p. 435. Additional values as required for the heats of complex formation studies were calculated from published or measured densities of the donors. The molar volumes of solids were calculated from measurements of the total volumes of solutions prepared by mixing weighed quantities of the donors and carbon tetrachloride (V_0 for carbon tetrachloride is 0.097 l. at 25°). Additional V_s values (in liters) which were measured and which are not reported elsewhere are: isopropylbenzene (0.14), 1,3,5-triethylbenzene (0.19), 1,3,5-tri-t-butylbenzene (0.29), 1,2,4,5-tetramethylbenzene (0.15), hexamethylbenzene (0.18), hexaethylbenzene (0.27), p-chlorotoluene (0.12). For polyalkylbenzenes, in general, V_s increases by about 0.017 l. per added carbon in ring substituents.
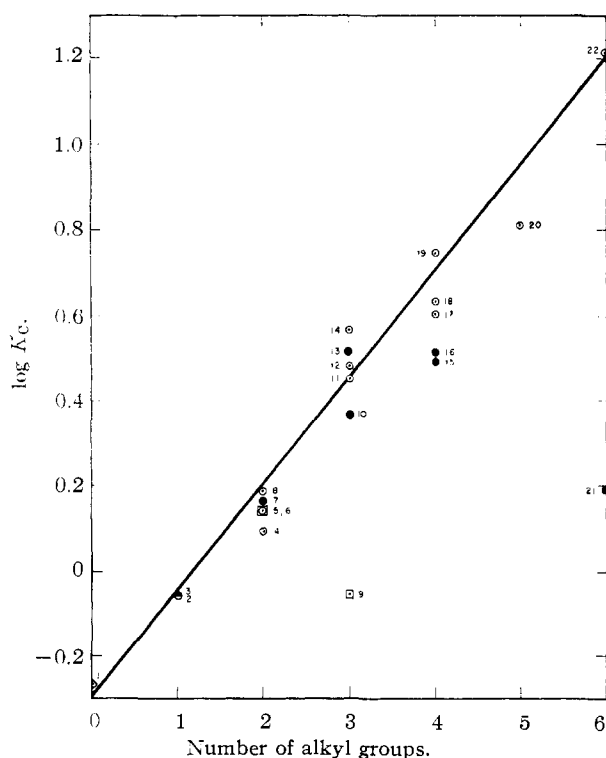
Fig. 1.—Variations in log K_C (25°) with the number of alkyl substituents on the donor ring for polyalkylbenzene–ICl complexes. The numbers 1–22 refer to the following donors: 1, benzene; 2, toluene; 3, ethyl-, isopropyl- and t-butylbenzene; 4, o-xylene; 5, m-xylene; 6, p-di-t-butylbenzene; 7, m-diethylbenzene; 8, p-xylene; 9, 1,3,5-tri-t-butylbenzene; 10, 1,2,4-triethylbenzene; 11, 1,2,4-trimethylbenzene; 12, 1,2,3-trimethylbenzene; 13, 1,3,5-triethylbenzene; 14, mesitylene; 15, 1,2,4,5-tetraethylbenzene; 16, 1,2,3,5-tetraethylbenzene; 17, 1,2,3,4-tetramethylbenzene; 18, 1,2,4,5-tetramethylbenzene; 19, 1,2,3,5-tetramethylbenzene; 20, pentamethylbenzene; 21, hexaethylbenzene; 22, hexamethylbenzene. The data for points 1, 2, 3, 4, 5, 18 and 20 were taken from L. J. Andrews and R. M. Keefer, THIS JOURNAL, 74, 4500 (1952). The following designations have been used to differentiate points for benzene, and methyl, ethyl and t-butyl substituted benzenes, respectively ▷, ⊙, ● and ◻. Point 3 which corresponds to data for three donors is represented by ◓.

tion units in making these plots. The heats of formation measured over the temperature ranges 1.6–25° and 25–45.8° are summarized in Table II, which also includes the free energy and entropy changes which accompany complex formation at 25°. The reported free energies are based on K_N values for complex formation which were calculated from the available constants, K_C, by use of equation 2. The reported entropy changes are based on average values of $(\Delta H)_N$ given in Table II.

As in the case of iodine complexes,[4] decreases in ΔH of formation of iodine monochloride–substituted benzene complexes with changes in donor substituents are accompanied by parallel decreases in ΔF and ΔS of the interactions. Indeed the thermodynamic data for the iodine monochloride complexes conform well to the linear plots of ΔH versus ΔF and ΔH versus ΔS for iodine–substituted ben-

TABLE II
HEATS, FREE ENERGIES AND ENTROPIES OF FORMATION OF ICl COMPLEXES IN CARBON TETRACHLORIDE SOLUTION

Aromatic	$-(\Delta H)_N$ 1.6, 25°, kcal.	$-(\Delta H)_N$ 25, 45.8°, kcal.	$-(\Delta F)_N$ 25°, kcal.	$-(\Delta S)_N$ 25°, cal./deg.
p-Chlorotoluene	1.67	1.75	0.75	3.22
Benzene[a]	2.54	3.14	1.01	6.15
p-Xylene	3.60	3.82	1.76	6.55
1,2,4-Triethylbenzene	4.22	4.46	1.91	8.15
Mesitylene	4.75	4.68	2.16	8.60
Pentamethylbenzene[a]	5.20	4.97	2.49	8.70
Hexamethylbenzene	5.25	5.39	2.91	8.09
Hexaethylbenzene	3.59	3.35	1.71	5.91

[a] K_N values used to calculate $(\Delta F)_N$ were calculated from K_C values reported previously (L. J. Andrews and R. M. Keefer, THIS JOURNAL, 74, 4500 (1952)).

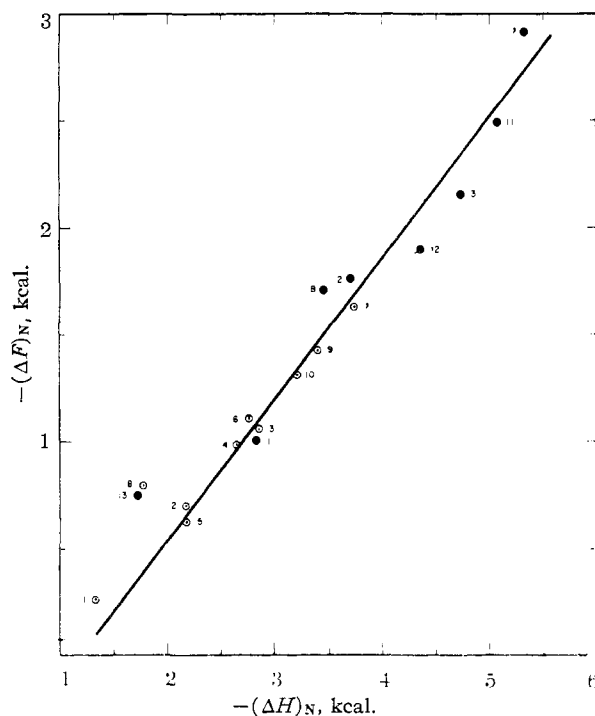zene interaction in carbon tetrachloride (see Figs. 2 and 3).

Fig. 2.—Variations in $\Delta F_{25°}$ with $\Delta H_{25°}$ for iodine and iodine monochloride complexes. The open circles refer to iodine complexes and the blackened circles to iodine monochloride complexes. The numbers 1–13 refer to the following donors: 1, benzene; 2, p-xylene; 3, mesitylene; 4, 1,3,5-triethylbenzene; 5, 1,3,5-tri-t-butylbenzene; 6, durene; 7, hexamethylbenzene; 8, hexaethylbenzene; 9, t-butyl alcohol; 10, dioxane; 11, pentamethylbenzene; 12, 1,2,4-triethylbenzene; 13, p-chlorotoluene.

It has previously been concluded[4] that the simultaneous decreases in ΔH and ΔS serve as an indication that more physical restraint is imposed on the complex components as the bond between them becomes stronger. It is conceivable that ΔS might reach a maximum negative value beyond which it would not increase with further changes in ΔH. Indeed the ΔS values for the more strongly bonded iodine monochloride complexes (points 3, 7 and 11

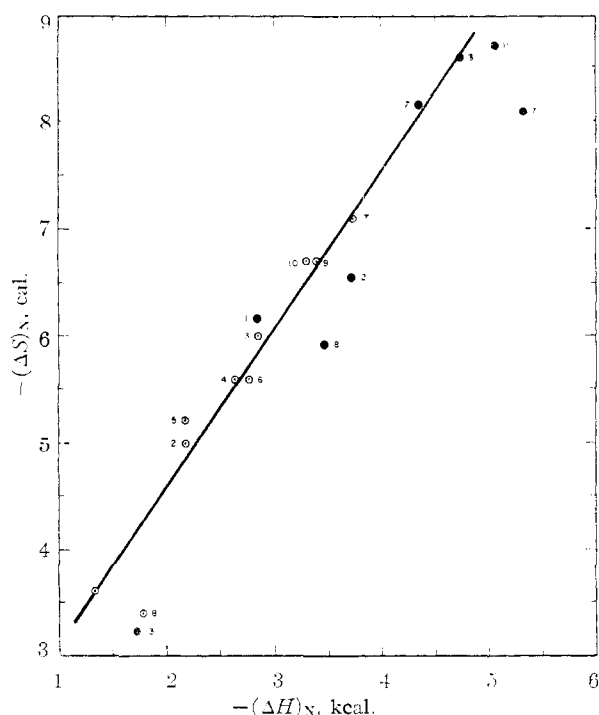Fig. 3.—Variations in $\Delta S_{25}°$ with $\Delta H_{25}°$ for the iodine and iodine monochloride complexes. The significance of symbols and numbers is the same as in Fig. 2.

of Fig. 3) are similar. Since, however, relatively small errors in ΔF and ΔH have an appreciable ef-

fect on the magnitude of ΔS, no unqualified interpretation of these similarities seems justified.

It is apparent from the studies[4] on iodine complexes that the treatment of Figs. 2 and 3 is applicable to at least a few donors other than the alkylbenzenes. It is not surprising (in view of the results on iodine complexes) that the thermodynamic data for aromatic–iodine monochloride complexes conform to linear plots, but it is remarkable that a single graph suffices reasonably well to correlate data for the two halogens. It is possible that such a correlation would not be observed were the acceptor structures more different in chemical properties and in physical dimensions.

For all of the complexes which owe their low stabilities to alkyl group steric effects (those of 1,3,5-t-butyl-, pentaethyl- and hexaethylbenzene[3]), the wave lengths of maximum complex absorption are close to those of complexes of the corresponding polymethylbenzenes. In other words the position of maximum absorption is approximately characteristic of the number of alkyl substituents in the benzene nucleus[15] and is not obviously related to the thermodynamic constants.

Acknowledgment.—The authors are indebted to Research Corporation for a grant in support of this research.

(15) It has previously been suggested that the complex absorption frequency is a function of the ionization potential of the donor molecule; cf. H. McConnell, J. S. Ham and J. R. Platt, J. Chem. Phys., 21, 66 (1953); S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, THIS JOURNAL, 75, 2901 (1953).

DAVIS, CALIFORNIA

The Catalytic Effect of Water upon the Addition of Hydrogen Chloride Gas to Solid Sodium Sulfate[1]

BY SIDNEY W. BENSON AND RYDEN L. RICHARDSON

HCl gas reacts rapidly and completely with a mixture of the solid $Na_2SO_4 + Na_2SO_4 \cdot 10H_2O$ to give $NaCl + NaHSO_4 + H_2O(g)$ at partial pressures of HCl which are less than 0.1 mm. A second mole of HCl can be added to the system at higher pressures to give what must be a solid solution of $H_2SO_4 + NaCl$. This last stage is reversible at 25° but the first stage is not. This is concordant with free energy data for the system. Anhydrous Na_2SO_4, however, will not add HCl gas at low pressures and only to a slight extent and very slowly at pressures up to 40 atmospheres. Thus water vapor acts as a true catalyst in this system.

I. Introduction

In the course of some work on the use of thermostated $Na_2SO_4 \cdot 10H_2O$ as a source of constant vapor pressure H_2O it was discovered that the salt undergoes spontaneous reaction with HCl gas. We then set about measuring the sorption isotherm of the salt with HCl. In a further effort to clarify the nature of this isotherm it was decided to study the simpler anhydrous system: $Na_2SO_4(s) + HCl(g)$. To our surprise there was no detectable reaction of the gas with the anhydrous material even after several days contact time. It thus appeared that (a) either water vapor was a true catalyst for the reac-

tion or (b) the reaction of HCl with Na_2SO_4 required the presence of hydrated salt as an intermediate. To elucidate further the behavior of the anhydrous system we studied the reaction at sufficiently high partial pressures of HCl to permit comparison of HCl and H_2O as adsorbates. Under these conditions there is a very slow reaction between HCl and dry Na_2SO_4 which we have not followed to completion.

II. Experimental

For the low pressure, sorption isotherms, measurements were made using a modified McBain sorption balance.[2] This consisted of a Pyrex, sample boat supported by a quartz helix having a sensitivity of 47.09 mg./cm., mounted in a Pyrex cylinder. Extensions of the helix were measured with a Gaertner Cathetometer, the probable error in read-

(2) J. W. McBain and A. M. Bakr, THIS JOURNAL, 48, 690 (1926).