compared with the values 185, 300, 395 and 256 found to fit the heat capacity curves, respectively, of $TlNO_3$,[15] $AgNO_3$[16] $NaNO_3$[17] and KNO_3[17] from 15 to about 60°K. The single frequency of 236^{-1} cannot have a sharp physical significance because the geometry of the nitrate ion requires at least two different frequencies; nevertheless, it serves a useful purpose in estimating the contribution of the nitrate ion to the total heat capacity.

The onset of torsional oscillation of the ammonium ion requires the addition of the third term, with $\Theta = 400$, corresponding to a frequency of 278 cm.$^{-1}$ This value compares favorably in magnitude with the θ values 560, 482 and 400 for the torsional oscillation of the ammonium ion in ammonium chloride, bromide and iodide, respectively. However, the analysis of the heat capacities was much simpler in the ammonium halides than in ammonium nitrate. The contribution of the nitrate ion to the heat capacity could not be represented satisfactorily above 60°K. in the other nitrates, and the agreement to 100°K. for ammonium nitrate is no doubt fortuitous. The Einstein term with $\Theta = 400$ probably includes some contribution from the nitrate ion as well as the ammonium ion.

This analysis, although approximate in nature, does confirm the fact that both the ammonium and nitrate ions are undergoing torsional oscillations rather than rotations at low temperatures. An analysis at higher temperatures becomes more difficult because the vibrations are anharmonic, the difference between C_p and C_v becomes appreciable, and the internal vibrations are excited. However, the decrease in heat capacity from phase IV to phase III suggests that the ammonium ion is rotating in phase III.

The decrease in heat capacity from phase V to phase IV of 1.63 cal. deg.$^{-1}$ mole^{-1} is of the order of magnitude to be expected from a change in the frequency spectrum for vibrations in the two modifications. The decrease in heat capacity from phase IV to III, 5.3 cal. deg.$^{-1}$ mole^{-1}, is too large to be accounted for in this manner. A reasonable explanation of this large decrease in heat capacity is to attribute three degrees of freedom of rotation in the ammonium ion in phase III, in contrast to fully excited torsional oscillation in phase IV. On this basis, a decrease of $3/2R$ cal. mole^{-1} would be expected. A study of the heat capacity of phase II at lower temperatures, to be presented later, in the form of a solid solution with potassium nitrate, lends support to this hypothesis.

We are indebted to Mr. George Feick, of Arthur D. Little, Inc., for discussions of the thermodynamic properties of ammonium nitrate. This research was assisted by a contribution from the Linde Air Products Division of Union Carbide and Carbon Corporation.

CAMBRIDGE, MASS.

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[15] W. M. Latimer and J. E. Ahlberg, THIS JOURNAL, **54**, 1900 (1932).

[16] W. V. Smith, O. L. I. Brown and K. S. Pitzer, *ibid.*, **59**, 1213 (1937).

[17] J. C. Southard and R. A. Nelson, *ibid.*, **55**, 4865 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

The Heats, Free Energies and Entropies of Formation of Alkylbenzene–Iodine Complexes

BY R. M. KEEFER AND L. J. ANDREWS

RECEIVED NOVEMBER 26, 1954

Values of ΔH, ΔF and ΔS for the interaction of a number of polyalkylbenzenes with iodine in carbon tetrachloride solution have been determined by spectrophotometric methods. In general as ΔH becomes increasingly negative corresponding decreases in ΔF and ΔS values are observed, and these variations are linear. Except for the hexaethylbenzene and *sym*-tri-*t*-butylbenzene complexes the thermodynamic constants become increasingly negative with increasing alkyl substitution of the aromatic donor nucleus. The alkyl groups of hexaethylbenzene must prevent the close approach of the iodine acceptor to the π-electrons of the donor. The complex bond is, therefore, weak, and its formation is accompanied by relatively small entropy changes. Similar, but less marked, steric phenomena influence the stability of the *sym*-tri-*t*-butylbenzene complex.

Values of the order of magnitude of -1 to -2 kcal./mole have been obtained for the heats of formation of iodine complexes of alkylbenzenes and related electron donors.[1-3] The interaction of aromatic compounds with other acceptors such as sulfur dioxide, maleic anhydride, chloranil and polynitro-organic substances in non-polar media are also reported to be mildly exothermic.[4] In no case have marked changes in the heats of complex formation with variations in donor substituents been noted. However these previous investigations have been restricted to a limited series of donors the relative basicities of which, as measured by the equilibrium constants for complex formation, do not vary markedly with a given acceptor.

This report presents data, obtained by ultraviolet spectrophotometric study, concerning the influence of temperature changes on the extent of complex formation in carbon tetrachloride solutions of iodine and a series of alkylated benzenes of rather widely differing donor strengths. It can be shown that the heat and entropy changes which occur in the formation of this series of complexes are related to each other and to the free energy changes in approximately linear fashion.

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[1] T. M. Cromwell and R. L. Scott, THIS JOURNAL, **72**, 3825 (1950).

[2] K. Hartley and H. A. Skinner, *Trans. Faraday Soc.*, **46**, 621 (1950).

[3] C. van de Stolpe, Thesis, "Solvatie van Jodium in Organische Oplosmiddelen," University of Amsterdam, 1953.

[4] See L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954) for a summary.

Experimental

Materials.—With exceptions as noted below all materials were of Eastman Kodak Co. Organic Chemicals white label grade. The benzene and *p*-xylene were fractionated before use. The mesitylene and *sym*-triethylbenzene were purified by sulfonation procedures.[5,6] The crude triethylbenzene sample was obtained from Matheson Chemical Company. The *sym*-tri-*t*-butylbenzene[7] sample, which was received through the courtesy of Dr. A. P. Lien, was recrystallized from ethanol, m.p. 73.4–73.9°. Carbon tetrachloride was distilled and stored over Drierite for some time before it was used. The *t*-butyl alcohol was distilled from sodium. Other materials were used without further purification. The authors are indebted to Mr. Naomi Ogimachi for his contribution of the purified samples of mesitylene, *sym*-triethylbenzene and *sym*-tri-*t*-butylbenzene.

The Equilibrium Measurements.—These measurements were made by determining the variations in the intensity of absorption of ultraviolet light by the aromatic–iodine solutions as a function of changes in the concentrations of the complex components. Many of the details of the method have been described in earlier publications.[8] Only those modifications which are important in the present temperature effect studies are emphasized in this discussion.

Solutions of known concentrations of iodine and of the donors were prepared at 25°. Samples of these were mixed by weighing them into ten-ml. volumetric flasks. The flasks were diluted to the mark with weighed samples of carbon tetrachloride which had previously been brought to 25°. These solutions varied in mole fraction of donor from 0.15 to 0.01 except for benzene (0.4 to 0.01) and hexamethylbenzene and hexaethylbenzene (0.04 to 0.004). The iodine concentration of the solutions was such (10^{-3}–10^{-4} *M*) that the optical densities in the region of the complex absorption maximum were of the order of magnitude of 0.5 at 25°.

Samples of these solutions were transferred to 1-cm. glass stoppered silica absorption cells and were examined on the Beckman spectrophotometer using pure carbon tetrachloride in the blank cell. The optical densities of each of the iodine solutions of a given donor were measured at a series of wave lengths near the complex absorption maximum within the close vicinity (±0.2°) of each of three temperatures, 25.0, 1.6 and 45.8°. After the series of measurements at the three temperatures was completed, the solutions were returned to 25°, and the optical densities were again measured. In all cases the initial and final readings at 25° were in close agreement. It is evident that reactions leading to the loss of iodine did not occur during the time required to make the spectrum studies. The total iodine concentrations of the solutions at 1.6 and 45.8° were calculated from the known iodine concentrations of the solutions at 25° on the assumption that the change in volume of the solutions with temperature could be measured in terms of density changes[9] of pure carbon tetrachloride.

Temperatures were controlled during these readings by circulation of water from constant temperature baths through the cell block. The cells were allowed to equilibrate to each block temperature until constancy of optical density readings was assured. Usually 20 minutes was sufficient time for equilibration. A special cover for the cell housing was devised from a piece of Masonite, which was slotted to accommodate a thermometer and inlet and outlet tubes for circulation of dry nitrogen through the housing. Nitrogen circulation was essential during measurements at the lowest temperature for prevention of cell fogging. The temperature was held constant to within 0.1° during the course of measurement of each solution at any one temperature.

The optical densities of solutions of known concentrations of each aromatic substance in carbon tetrachloride at wave lengths used in measurements on the complexes were also determined at the three temperatures. Similar measurements were made for solutions of iodine in carbon tetrachloride. As has been observed elsewhere,[10] it was found that the extinction coefficients of the aromatic substances varied somewhat with changes in temperature.

Results

The Equilibrium Constants as a Function of Temperature.—At any given temperature and wave length the extinction coefficient, ϵ_{o}, of the 1:1 aromatic–halogen complex which is in equilibrium with its components in carbon tetrachloride solution may be related to the mole fraction of the aromatic compound (N_{Ar}) by the expression[11]

$$\frac{1}{\epsilon_{\text{a}} - \epsilon_{\text{I}_2}} = \frac{1}{K(\epsilon_{\text{o}} - \epsilon_{\text{I}_2})N_{\text{Ar}}} + \frac{1}{\epsilon_{\text{c}} - \epsilon_{\text{I}_2}} \qquad (1)$$

In equation 1 ϵ_{I_2} represents the extinction coefficient of pure iodine in the pure solvent and $\epsilon_{\text{a}} = d_{\text{c}}/l(\text{I}_2)_{\text{t}}$. The term d_{c} represents the measured optical density of the solution of the complex and its components less the contribution of the free aromatic component to the measured value, and l is the length of the light path (1 cm. in this work). The term $(\text{I}_2)_{\text{t}}$ represents the total concentration of both free and complexed iodine. The term K represents the equilibrium constant for formation of the complex (see equation 2).

$$\text{Ar} + \text{I}_2 \rightleftarrows \text{Ar}\cdot\text{I}_2 \quad K = \frac{(\text{ArI}_2)}{(\text{I}_2)N_{\text{Ar}}} \qquad (2)$$

Since $(\text{Ar}\cdot\text{I}_2)$ and (I_2) are determined by their effects on the optical density of the solution, it has proved convenient to express them in molar concentration units. It has been assumed, in evaluating K, that the activities of the aromatic substances in dilute solution are given by their mole fractions (*i.e.*, that Henry's law is obeyed).

The spectrophotometric data taken at each of three temperatures for the aromatic-iodine solutions in carbon tetrachloride, as described in the Experimental section, were interpreted graphically by equation 1. Points obtained by plotting $1/(\epsilon_{\text{a}} - \epsilon_{\text{I}_2})$ values, taken at fixed wave lengths, against the corresponding $1/N_{\text{Ar}}$ values were fitted to straight lines. The intercepts $1/(\epsilon_{\text{c}} - \epsilon_{\text{I}_2})$ were calculated by standard least squares procedures. For each of the complexes investigated it was observed that $1/(\epsilon_{\text{c}} - \epsilon_{\text{I}_2})$ values were independent of temperature changes within the limits of experimental error. The data of Table I, which lists the variations in slopes and intercepts of the linear plots for hexamethylbenzene–iodine solutions as influenced by wave length and temperature changes, are illustrative. The last column of Table I demonstrates the range in magnitude of the equilibrium constants for hexamethylbenzene–iodine interaction which were determined from data recorded at various wave lengths at 25.2°.

Since $\epsilon_{\text{c}} - \epsilon_{\text{I}_2}$ values for a complex at any fixed wave length are temperature independent, values of ΔH for complex formation may be evaluated from the graphs (according to equation 1) of data taken at any wave length at temperatures T_1 and T_2 by use of equation 3.

$$2.303 \log \frac{(\text{slope})_{T_1}}{(\text{slope})_{T_2}} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (3)$$

For each complex values of ΔH were evaluated by

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(5) L. I. Smith and O. W. Cass, THIS JOURNAL, **54**, 1606 (1952).

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

(7) D. A. McCaulay, A. P. Lien and P. J. Launer, *ibid.*, **76**, 2354 (1954).

(8) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952).

(9) "International Critical Tables," Vol. III, First Edition, McGraw–Hill Book Co., Inc., New York, N. Y., 1928, p. 28.

(10) V. A. Yarborough, J. F. Haskin and W. J. Lambdin, *Anal. Chem.*, **26**, 1576 (1954).

(11) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

TABLE I

INTERPRETATION OF HEXAMETHYLBENZENE–IODINE DATA BY EQUATION 1

λ, mμ	$10^3/(\epsilon_0 - \epsilon_{I_2})$ at temperature			$10^3/K(\epsilon_0 - \epsilon_{I_2})$ at temperature			$K_{(25.2°)}$
	1.4°	25.2°	46.0°	1.4°	25.2°	46.0°	
350	2.02	2.03	1.96	0.0767	0.1284	0.1925	15.6
355	1.90	1.69	1.87	.0678	.1174	.1709	15.5
360	1.70	1.63	1.66	.0621	.1067	.1595	15.6
365	1.60	1.58	1.55	.0582	.0994	.1509	15.9
376	1.50	1.51	1.55	.0553	.0951	.1440	16.0
385	1.64	1.55	1.66	.0565	.1012	.1510	16.0
390	1.72	1.59	1.71	.0602	.1075	.1606	15.5
400	2.15	2.08	2.06	.0714	.1263	.1910	16.6

this procedure from data taken at each wave length at 1.6 and 25° and also from data taken at 25 and 45.8°. The average over the entire wave length range of values of ΔH calculated from data at the two lower temperatures (ΔH 1.6°, 25°) and at the two higher temperatures (ΔH 25°, 45.8°) are given in Table II. The wave length regions over which solutions of the complexes were investigated are also listed, and the average $K_{25°}$ values for the complexes are recorded.

TABLE II

VALUES OF ΔH AND K FOR THE COMPLEXES[a]

Donor	$-\Delta H$ (1.6°, 25°), kcal./mole	$-\Delta H$ (25°, 45.8°), kcal./mole	Range of λ, mμ	$K_{25°}$[b] l./mole fraction
Benzene	1.38	1.25	278–310	1.55 ± 0.15
p-Xylene	2.10	2.27	306–330	3.25 ± .06
Mesitylene	2.82	2.90	310–360	5.98 ± .04
sym-Triethylbenzene	..	2.64	336–360	5.25 ± .08
sym-Tri-*t*-butylbenzene	2.28	2.08	315–360	2.88 ± .05
Durene	..	2.78	315–360	6.49 ± .15
Hexamethylbenzene	3.76	3.70	350–400	15.7 ± .2
Hexaethylbenzene	1.80	1.78	360–410	3.78 ± .18
t-Butyl alcohol	3.1	3.7	460–540	11.1 ± .1

[a] The estimated error in ΔH values is ±0.10 kcal./mole for all donors except *t*-butyl alcohol. In this case the estimated error is ±0.3 kcal./mole. [b] These values for K are in good agreement with those reported previously, *cf.* M. Tamres, D. R. Virzi and S. Searles, THIS JOURNAL, **75**, 4358 (1953); H. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949); L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952); R. M. Keefer and L. J. Andrews, *ibid.*, **75**, 3561 (1953). Spectrophotometric data on *sym*-triethylbenzene- and *sym*-tri-*t*-butylbenzene–iodine complexes have not been reported previously. Values of the wave length and ϵ_0 values at the absorption maximum for these complexes in carbon tetrachloride at 25° are, respectively, for triethylbenzene 335 mμ and 8520 and for *sym*-tri-*t*-butylbenzene 338 mμ and 5860.

The average values for ΔH for each of the complexes over the entire temperature range investigated are listed in Table III. The values for ΔF and ΔS which are given in this table have been evaluated from the reported values of ΔH and from the equilibrium constants, $K_{25°}$. These values for ΔF and ΔS are referred to a standard state of hypothetical pure liquid donor, a reference state which appears to be unrealistic for the solid aromatic donors. However it should be noted that changes in ΔF and ΔS with changes in ring substituents on aromatic donors are independent of the choice of a standard state for the donors. The ΔH values of Table III should differ by approximately 300 cal. from those derived from equilibrium constants which are based on molar concentrations of the donors.[11] The thermodynamic data for the *t*-butyl alcohol–iodine complex, which are also reported in Tables II and III, were determined by applying the present techniques for temperature variation to methods previously used[12] in the determination of equilibrium constants.

TABLE III

HEAT, FREE ENERGY AND ENTROPY CHANGES ACCOMPANYING IODINE COMPLEX FORMATION IN CARBON TETRACHLORIDE[a]

Donor	$-\Delta H_{25°}$, kcal./mole	$-\Delta F_{25°}$, kcal./mole	$-T\Delta S_{25°}$, kcal./mole	$-\Delta S_{25°}$, cal./mole deg.
Benzene	1.32	0.26	1.06	3.6
p-Xylene	2.18	.70	1.48	5.0
Mesitylene	2.86	1.06	1.80	6.0
sym-Triethylbenzene	2.64	0.98	1.66	5.6
sym-Tri-*t*-butylbenzene	2.18	.63	1.55	5.2
Durene	2.78	1.11	1.67	5.6
Hexamethylbenzene	3.73	1.63	2.10	7.1
Hexaethylbenzene	1.79	0.79	1.00	3.4
t-Butyl alcohol	3.4	1.43	2.0	6.7
Dioxane[b]	3.30	1.31	1.99	6.7

[a] The estimated errors in ΔH and $T\Delta S$ values are ±0.10 kcal. except for *t*-butyl alcohol where the estimated error is ±0.30 kcal. The estimated error in ΔF is ±0.02 kcal./mole. [b] Data of J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

Variations in Heat and Entropy Changes with Changes in Donors.—The quantities ΔH, ΔF and ΔS which are tabulated for the several alkylbenzene–iodine interactions encompass changes in solvent–solute association which accompany complex formation. Any differences in the relative contributions of such solvent effects to the data reported for the different donor systems would likely result primarily from differences in the heat, free energy and entropy changes attending the desolvation of the several donors as they become associated with iodine. It is customarily assumed that contributions of such solvation effects to heats of complex formation are small when the solvent is non-polar.[13] In the present discussion of the effects of changes in donor structure on the thermodynamic changes accompanying complex formation it is assumed that contributions from such solvation effects are small or are, at least, independent of changes in donor structure.

Previously it has been customary to compare the electronic influences of different ring substituents in aromatic donors on the tendency for complex formation with a particular type of acceptor molecule in terms of the variations in the logarithms of the equilibrium constants (*i.e.*, the free energy changes) for complex formation.[4] As has been pointed out[14] this may be a safe criterion only if the entropy changes do not vary with changes in

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(12) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **75**, 3651 (1953).

(13) J. Weiss, *J. Chem. Soc.*, 245 (1942).

(14) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 78.

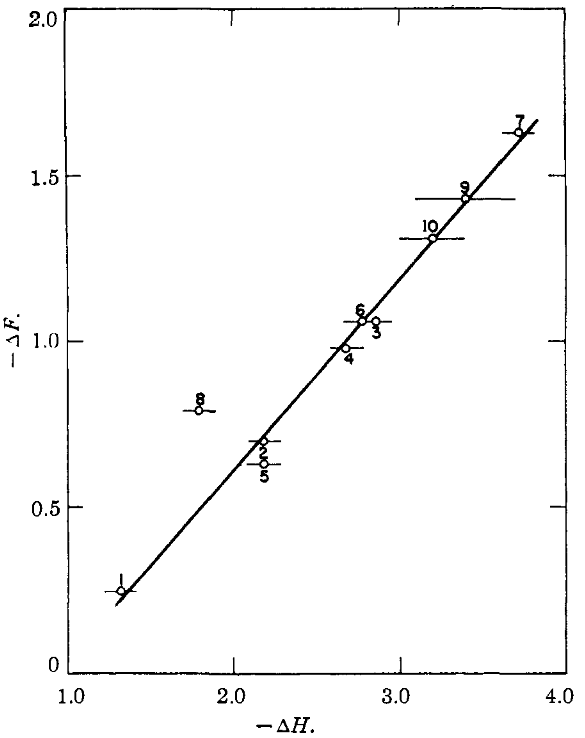

Fig. 1.—Variations in $\Delta F_{25°}$ with $\Delta H_{25°}$: the numbers 1–10 refer, respectively, to iodine complexes of benzene, *p*-xylene, mesitylene, *sym*-triethylbenzene, *sym*-tri-*t*-butylbenzene, durene, hexamethylbenzene, hexaethylbenzene, *t*-butyl alcohol and dioxane.

the donor substituents. While the entropy changes which occur during complex formation do not vary widely for a series of monosubstituted benzene donors,[15] it is apparent from the data of Table III that the ΔS values for iodine complex formation of alkylbenzenes show a definite downward trend with an increase in the number of alkyl substituents on the aromatic nucleus. In all cases both ΔH and $T\Delta S$ terms have appreciable influence on the magnitude of ΔF for complex formation.

Yet qualitatively, with the notable exceptions of the data for hexaethylbenzene and *sym*-tri-*t*-butylbenzene complexes, the changes in ΔF with increasing alkylation of the benzene ring are consistent with anticipated electronic influences of alkyl substituents on the π-electron density of the donor nucleus.[16] Such trends in ΔF values are by no means restricted to the use of iodine as the acceptor[4] and are particularly apparent in the results of recent work on polyalkylbenzene–iodine monochloride complexes.[17] The free energies of formation of the iodine monochloride complexes decrease in almost linear fashion with increasing alkylation of the donor; and these decreases are, with certain exceptions, independent of the nature of the alkyl group. In this regard it should be noted that in the present study the values of ΔF of formation of mesitylene and triethylbenzene complexes are about the same.

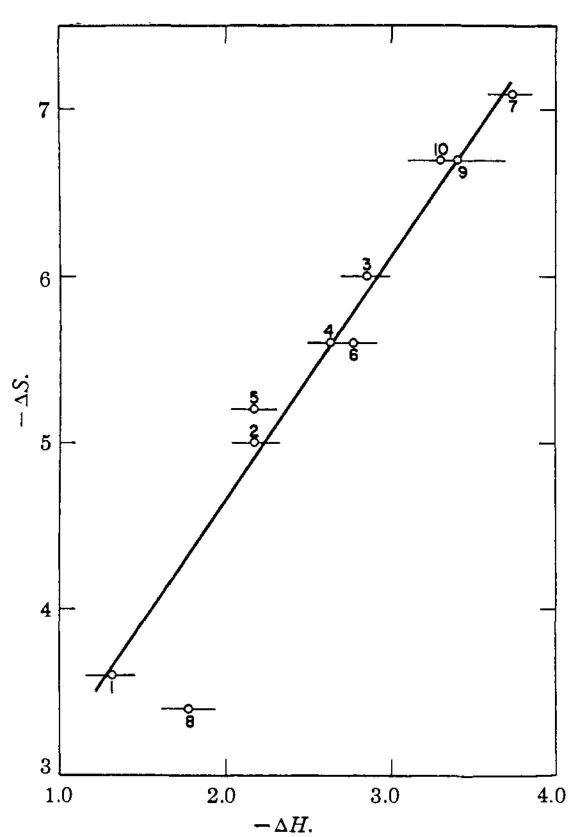

Fig. 2.—Variations in $\Delta S_{25°}$ with $\Delta H_{25°}$. The numbering system is the same as that used in Fig. 1.

Actually the observed variations in ΔH with ΔF for iodine–alkylbenzene complexes are linear (see Fig. 1). This can only be true either if ΔS is invariant with changes in donor structure or, as is actually the case, ΔS also varies in linear fashion with ΔH (see Fig. 2). In other words, barring unusual steric effects in donor molecules, one can in the present instance measure the effects of alkyl substitution on the tendency for complex formation equally well in terms of variations in ΔF, ΔH or ΔS.

It is particularly interesting that as ΔH values become more negative, corresponding decreases in ΔS are observed. The simultaneous decrease in these terms may serve as an indication of the physical restraints imposed upon the complex components as the strength of the bond between then increases. It is remarkable that the data for the dioxane and *t*-butyl alcohol complexes also conform to the linear plots of Figs. 1 and 2, and it seems possible that the observed correlation in thermodynamic constants for iodine complexes may not be restricted to benzenoid donor systems.

The abnormally low value for $K_{25°}$ for hexaethylbenzene as compared to hexamethylbenzene is undoubtedly correctly accounted for on the assumption that the six ethyl groups constitute a formidable barrier between the π-electrons of the

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[15] C. van de Stolpe[3] reports values for $\Delta S_{25°}$ of formation of a number of such iodine complexes which are all of the order of magnitude of 4 to 5 e.u. These data are based on an expression of the equilibrium constants in reciprocal mole fraction units.

[16] Similar effects of methyl substituents on the susceptibility of the aromatic nucleus to attack by an electrophilic reagent are generally ascribed to favorable electronic influences of the alkyl groups. See, for example, results on the kinetics of ozonization of a series of polymethylbenzenes (J. P. Wibaut, E. L. J. Sixma, L. W. F. Kampschmidt and H. Boer, *Rec. trav. chim.*, **69**, 1355 (1950)).

[17] N. Ogimachi, L. J. Andrews and R. M. Keefer, unpublished work.

aromatic nucleus and the acceptor molecule.[8,18] Although the points for the hexaethylbenzene complex do not lie close to the straight lines of Figs. 1 and 2, it is obvious that the general relationship concerning the variations in ΔF, ΔH and ΔS probably can be extended to include the hexaethylbenzene case. The relatively small negative value of ΔF for this complex is matched by those for ΔH and ΔS. In other words it would appear, in the light of the small magnitude of the value for ΔS, that in this complex the iodine component has not penetrated the steric barrier. Rather it must interact feebly with the π-electrons of the ring at a distance away from them which is sufficiently great to provide for smaller heat and entropy differences between the complex and its components than is observed for a similarly constituted non-hindered donor.

One point concerning the hexaethylbenzene complex which remains unexplained is the fact that its ultraviolet absorption maximum appears at about the same wave length as that for hexamethylbenzene.[8,18] In general the position of the maximum shifts toward the visible as the complex becomes more stable. On this basis the $\lambda_{\text{max.}}$ value for the hexaethylbenzene complex should appear much further toward the ultraviolet region than it actually ($\lambda_{\text{max.}}$ 375 mμ) does. It is obvious from the present work that this anomaly cannot be explained through consideration of heat or entropy effects.[19]

The thermodynamic data for the *sym*-tri-*t*-butylbenzene complex fit the linear plots of Figs. 1 and 2 quite well. However the ΔF value in this case is much less than those for the mesitylene and *sym*-triethylbenzene complexes. Since toluene, ethylbenzene and *t*-butylbenzene all show the same tendency for halogen interaction,[8] it seems that the rather low stability of the *sym*-tri-*t*-butylbenzene complex must be accounted for in terms of unfavorable steric effects of the three bulky alkyl groups in the donor molecule. This effect is even more apparent in the case of the iodine monochloride–*sym*-tri-*t*-butylbenzene complex.[17]

While it is impossible to assert with certainty that small-sized alkyl substituents offer no steric inhibition to complex formation, a consideration of molecular models for the polymethylbenzenes suggests that no marked steric barrier toward interaction exists even when the acceptor molecule is as large as iodine. This conclusion is based on the assumption that in the complex the acceptor lies above the ring plane of the donor.[4] It is interesting that there are indications of a linear variation in the ΔF values for complexes of polymethylbenzenes and halogen acceptors with those for a variety of other types of acceptors.[4] These facts suggest that the ΔF values (except in the most unfavorable steric situations in which the closeness of approach of donors and acceptors is not controlled primarily by electronic factors) are reasonable standards for the comparison of electronic influences of alkyl substituents on the π-electron density of the aromatic nucleus.

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

Davis, California

[18] M. Tamres, D. R. Virzi and S. Searles, This Journal, **75**, 4358 (1953).

[19] Recently J. S. Ham, *ibid.*, **76**, 3875 (1954), has studied the spectra of the hexaethylbenzene–iodine complexes at room temperature and liquid nitrogen temperatures and has found that temperature reduction causes a marked shift of $\lambda_{\text{max.}}$ to the ultraviolet. He has suggested that different types of complexes exist at the two temperatures. It is not yet clear how the steric effects of the ethyl groups might be manifested in the formation of the two types of complex.

Contribution from the College of Chemistry and Physics, The Pennsylvania State University]

Thermodynamic Properties of Neon Adsorbed on Titanium Dioxide[1]

By R. J. Tykodi,[2] J. G. Aston and G. D. L. Schreiner[3]

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The heat capacity of neon adsorbed on TiO_2 has been determined, in the region below the monolayer, for three surface concentrations, in the temperature range 16 to 30°K. Isotherms have been determined at 30.00 and 45.93°K. Isosteric heats of adsorption have been determined calorimetrically, and differential and integral entropies of adsorbed neon have been calculated at 30°K. The zero-point entropy calculated for the three coverages was found to be essentially zero, within experimental error.

Calorimetric studies of simple gases adsorbed on non-porous media yield basic facts about adsorption systems which any serious theory of adsorption must take into account. The number of such studies is still relatively small.[4-7] The present paper deals with neon adsorbed on titanium dioxide (rutile).

Experimental

Materials.—The neon was from a cylinder of reagent neon purchased from the Air Reduction Sales Company,

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[2] American Cyanamid Fellow 1951–1952. Submitted in partial fulfillment for the degree of Doctor of Philosophy at the Pennsylvania State University.

[3] The University of the Witwatersrand, Johannesburg, S. Africa.

[4] J. Morrison and G. Szasz, *J. Chem. Phys.*, **16**, 280 (1948).

[5] J. G. Aston, G. Szasz and G. Kington, This Journal, **73**, 1937 (1951).

[6] J. Morrison, J. Los and L. Drain, *Trans. Faraday Soc.*, **47**, 1023 (1951).

[7] L. Drain and J. Morrison, *ibid.*, **48**, 1 (1952).