Thermochemistry of Molecular Complexes. 2. Enthalpies of Formation and Formation Constants for Molecular Complexes of I₂ with Methylbenzenes

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A new technique recently developed in our laboratory has been used to determine the formation constants and enthalpies of formation for the 1:1 molecular complexes that form between I_2 and benzene or methyl-substituted benzene derivatives in carbon tetrachloride solution. The results are in good agreement with those found in previous studies. A linear relationship exists between the enthalpy of formation for the molecular complex and the number of methyl groups attached to the benzene ring, with ΔH becoming more negative by approximately 1.1 kJ/mol per methyl group. A linear relationship also exists between $\ln(K)$ and the number of methyl groups on the benzene ring. These results are consistent with a simple model where the contributions to the π -electron density of the benzene ring from the attached methyl groups are, to a first approximation, additive.

Molecular complexes formed by noncovalent interactions appear in a wide variety of chemical and biochemical systems. There is great interest in the thermochemical and spectroscopic properties of such complexes, and they have therefore been extensively studied by using many experimental techniques.¹⁻³

In a recent publication, Morales and co-workers⁴ presented a new method, based on an earlier procedure first proposed by Tamres,⁵ for determining the enthalpy of formation of a weakly bound 1:1 molecular complex

$$D + A \rightleftharpoons DA$$
 (1)

In the above reaction D is a donor molecule, A an acceptor molecule, and DA the corresponding molecular complex. They defined an apparent enthalpy of formation, ΔH_{app} , as

$$\Delta H_{\rm app} = -R\partial \ln A_{\rm CT} / \partial (1/T) \tag{2}$$

where $A_{\rm CT}$ is the absorbance due to the complex, and showed that for conditions where the equilibrium concentration of free donor molecules is large compared to the concentration of bound donor molecules, a plot of ΔH_{app} versus initial donor concentration has an intercept equal to ΔH , the enthalpy of formation, and a limiting slope equal to $-K\Delta H$, where K is the equilibrium constant for the reaction. This procedure was used to determine the enthalpy of formation for a series of molecular complexes of I₂ with chlorinated benzene derivatives in carbon tetrachloride solution. The results in all but a few cases represented the first experimental determinations of the formation enthalpies for these complexes.

The present paper is a study of the enthalpies of formation and equilibrium constants for molecular complexes of iodine with the complete set of methylbenzene donor molecules. The purpose of the study is to determine the thermodynamic parameters for the iodine-methylbenzene complexes and to find out if there is a simple relationship between the degree of substitution on the donor molecule and the enthalpy of formation and equilibrium constant for the corresponding iodine-donor molecular complex.

Such a relationship between formation enthalpy and degree of substitution has previously been noted for iodine-methylbenzene complexes.^{1,6-8} The present work extends these previous studies by examining the complete set of complexes of iodine with methylbenzene molecules. A comparison of the present results with those previously obtained for iodine-methylbenzene complexes also serves as a test of the procedure used in this paper.

Results and Discussion

Figure 1 presents a plot of ΔH_{app} versus donor concentration for a representative set of compounds investigated in the present study. For each compound the apparent enthalpy of formation has been determined for several concentrations of donor molecules. The intercept in a plot of ΔH_{app} versus donor concentration is equal to the enthalpy of formation for the molecular complex. The formation constant for the complex can also be found from a plot of the data by using the relationship $K = -m/b^4$, where m is the slope and b the intercept in the data plot.

The values for the formation for iodine-methylbenzene molecular complexes obtained in the present study are given in Table I. Results for the enthalpy and entropy of formation for the complexes are presented in Table II. All data have been reported at T = 25 °C. Error limits have been calculated and reported at the 95% confidence limits by using standard statistical techniques.¹⁶ Also given in Table I and Table II are results obtained from previous studies of iodine-methylbenzene molecular complexes in carbon tetrachloride. For those cases where a comparison can be made, there is excellent agreement between the present results and those previously reported.

A plot of the experimental values for the enthalpy of formation against the number of methyl groups substituted on the benzene ring of the donor molecule is given in

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Table I. Formation Constants for Donor-I₂ Molecular Complexes (T = 25 °C)

		K (L/mol)		
donor	N^a	this work ^b	lit.	
benzene	10	0.18 ± 0.02	0.15, ^{c,d} 0.167, ^e 0.175, ^f 0.18 ^g	
methylbenzene	6	0.20 ± 0.05	$0.15,^{h} 0.16,^{d} 0.25^{f}$	
1,2-dimethylbenzene	7	0.32 ± 0.06	$0.27,^{d} 0.29^{f}$	
1.3-dimethylbenzene	9	0.29 ± 0.09	$0.31,^{d} 0.33^{f}$	
1,4-dimethylbenzene	8	0.27 ± 0.04	$0.30, 10.31, 0.32^{\circ}$	
1.2.3-trimethylbenzene	6	0.43 ± 0.05		
1.2.4-trimethylbenzene	8	0.41 ± 0.02		
1,3.5-trimethylbenzene	7	0.43 ± 0.07	0.55, ^f 0.58, ^c 0.70, ^e 0.82 ^d	
1,2,3,4-tetramethylbenzene	10	0.86 ± 0.3	0.78	
1.2.3.5-tetramethylbenzene	7	0.78 ± 0.16		
1.2.4.5-tetramethylbenzene	8	0.59 ± 0.09	$0.63^{c,d}$ 0.64^{f}	
pentamethylbenzene	11	1.28 ± 0.3	$0.82, 10.88^{d}$	
hexamethylbenzene	8	1.45 ± 0.2	$1.00,^{i}$ $1.29,^{f}$ $1.35,^{d}$ $1.52,^{c}$ 2.09^{j}	

^a Number of measurements. ^bError limits for this work reported at the 95% confidence limits. ^cReference 7. ^dReference 6. ^eReference 10. ^fReference 11. ^gReference 12. ^hReference 13. ⁱReference 14. ^jReference 15.

Table II. Enthalpy and Entropy of Formation for Donor-I₂ Molecular Complexes (T = 25 °C)

$-\Delta H (kJ/mol)$		
this work ^a	lit.	– $\Delta S~(J/{ m mol}{\cdot}{ m K})$ this work "
7.83 ± 0.10	6.4, ^b 6.44 ^c	40.5 ± 1.0
8.99 ± 0.17		43.6 ± 2.4
9.83 ± 0.17		42.4 ± 1.8
10.3 ± 0.2		44.9 ± 3.2
9.67 ± 0.12	10.0 ^c	43.4 ± 1.4
11.00 ± 0.09		43.9 ± 1.1
10.94 ± 0.06		44.1 ± 0.5
12.48 ± 0.16	12.9 ^c	48.9 ± 1.6
11.2 ± 0.5		38.8 ± 3.9
12.9 ± 0.2		45.4 ± 2.0
12.3 ± 0.2	12.6 ^c	45.7 ± 1.5
13.4 ± 0.6		42.9 ± 3.4
14.3 ± 0.5	15.03, ^d 15.7, ^e 16.5, ^c 18.1 ^f	44.9 ± 2.1
	$\begin{array}{c} - \\ \hline \\ \hline \\ \hline \\ \hline \\ \\ \\ \hline \\ \hline \\ \\ \hline \\ \\ \hline \\ \\ \hline \\ \hline \\ \hline \\ \\ \hline \\ \\ \hline \\ \hline \\ \\ \hline \\ \hline \\ \\ \hline \\ \\ \hline \\ \hline \\ \\ \hline \\ \hline \\ \hline \\ \\ \hline \\ \hline \\ \\ \hline \\ \hline \\ \hline \\ \\ \hline \\ \hline \\ \hline \\ \hline \\ \\ \hline \hline \\ \hline \\ \hline \\ \hline \\ \hline \hline \\ \hline \\ \hline \\ \hline \\ \hline \hline \\ \hline \\ \hline \\ \hline \\ \hline \hline \\ \hline \\ \hline \hline \\ \hline \\ \hline \\ \hline \hline \\ \hline \\ \hline \hline \\ \hline \\ \hline \\ \hline \hline \\ \hline \\ \hline \hline \\ \hline \\ \hline \\ \hline \\ \hline \hline \hline \\ \hline \hline \\ \hline \hline \hline \\ \hline \hline \hline \\ \hline \hline \hline \\ \hline \hline \hline$	$\begin{tabular}{ c c c c c } \hline & & & & & & \\ \hline \hline this work^a & & & & & & \\ \hline \hline this work^a & & & & & & \\ \hline \hline this work^a & & & & & & \\ \hline \hline this work^a & & & & & & \\ \hline \hline this work^a & & & & & \\ \hline \hline 1.7 & & & & & & \\ \hline 1.83 \pm 0.17 & & & & & \\ \hline 10.3 \pm 0.2 & & & & & \\ \hline 10.94 \pm 0.06 & & & & & \\ \hline 12.48 \pm 0.16 & & & & & \\ \hline 12.48 \pm 0.16 & & & & & \\ \hline 12.48 \pm 0.16 & & & & & \\ \hline 12.48 \pm 0.2 & & & & & \\ \hline 12.3 \pm 0.2 & & & & & \\ \hline 12.3 \pm 0.2 & & & & & \\ \hline 12.48 \pm 0.6 & & & & \\ \hline 14.3 \pm 0.5 & & & & & \\ \hline 15.03,^d 15.7,^e 16.5,^c 18.1^f & & \\ \hline \end{tabular}$

^aError limits for this work reported at the 95% confidence limits. ^bReference 12. ^cReference 7. ^dReference 14. ^eReference 6. ^fReference 15.



Figure 1. Plot of $-\Delta H_{app}$ vs initial donor concentration $[D]_0$ for (1) methylbenzene; (2) 1,3-dimethylbenzene; (3) 1,2,4,5-tetramethylbenzene. The slope and intercept of the plot are related to the enthalpy of formation and formation constant of the corresponding molecular complex, as described in the text.

Figure 2. It is clear that to a first approximation there is a linear relationship between the enthalpy of formation and the number of methyl groups. A weighted least-squares fit of the data¹⁶ gives the result

$$-\Delta H = 7.90 \text{ kJ/mol} + (1.09 \text{ kJ/mol})N \qquad (3)$$

where N is the number of methyl groups on the benzene ring. Deviations from eq 3 are small, except for the iodine complex with 1,3,5 trimethylbenzene, which has an enthalpy of formation 1.3 kJ/mol more negative than predicted.



Figure 2. Plot of $-\Delta H$ vs number of methyl groups in the substituted benzene derivative. The vertical lines represent the error in the enthalpy at the 95% confidence limits.

Figure 3 presents a plot of $\ln K$ versus the number of methyl groups in the donor molecule. Although there is considerably more error in the experimental data for the formation constants than for the enthalpy data, it again appears that to a first approximation a linear relationship exists in the data. A weighted least-squares fit to the data gives the result

$$\ln K = -1.95 + 0.40N \tag{4}$$

that is, the formation constant for the iodine-methylbenzene molecular complex increases by aproximately 50% per additional methyl group substituted onto the benzene ring.



Figure 3. Plot of $\ln K$ vs number of methyl groups in the substituted benzene derivative. The vertical lines represent the error in $\ln K$ at the 95% confidence limits.

The above results can be explained by a simple model for the interaction of iodine with the π -electron density of a substituted benzene molecule. For a weakly perturbing substituent group such as a methyl group, we assume that the electron-donating or electron-withdrawing effects are, to first order, additive and dependent only on the number and type of substituent. If the enthalpy of formation for the molecular complex is proportional to the available π -electron density of the donor molecule, then the above model predicts a linear relationship between the formation enthalpy and degree of substitution for a benzene derivative containing a single type of substituent group. Further, if the entropy change for formation of the complex is independent of the particular substituted molecule acting as the electron donor in the reaction, then it follows from the relationship

$$\Delta G = -RT \ln K = \Delta H - T\Delta S \tag{5}$$

that a plot of ln K versus degree of substitution should also be linear. In fact, if eq 5 is used to determine the entropy change for the formation of molecular complexes between iodine and methylbenzene donors, ΔS does in fact appear to be either independent or only weakly dependent on the number of methyl groups, as can be seen in the data reported in Table II. Assuming that ΔS is independent of the degree of substitution, the results from the present study give a value for the entropy change upon formation of the iodine-methylbenzene molecular complex of -43.8 \pm 1.4 J/mol·K, with the error limits again reported at the 95% confidence limits.

To the extent that the above model is correct, it should be possible to use the present results to estimate the formation constant for molecular complexes of iodine with benzene derivatives containing other weakly perturbing substituent groups. For example, a previous study of molecular complexes of iodine with chlorine-substituted benzene molecules found a linear relationship between the enthalpy of formation of the complex and the number of chlorine atoms attached to the benzene ring.⁴ However, the formation constants for the iodine-chlorobenzene molecular complexes were in all but a few cases too small to be directly determined. The present results suggest that values for the formation constant for these complexes can be estimated by using eq 5, the experimental value for the enthalpy of formation, and the value for the entropy change reported above. This procedure should also be useful for estimating formation constants for other molecular complexes with extremely weak donor-acceptor interactions. Since it has to this point proved impossible to directly determine the formation constant for complexes of iodine with benzene derivatives containing fluorine, chlorine, or other electron-withdrawing groups, the above procedure represents the only means at present by which values for the formation constants for these molecular complexes can be determined.

Finally, it should also be noted that even for a nonpolar solvent such as carbon tetrachloride, solvent effects still play a part in determining the stability and thermodynamic parameters for weakly bound molecular complexes. A study of the thermodynamics of the above complexes in the vapor phase, where such solvent effects will be absent, is in progress.

Experimental Section

Benzene and methyl-substituted benzene compounds used in the present study were purchased from Aldrich at a minimum of 98% purity and used without further purification, except as follows: 1,2,3 trimethylbenzene (90%), 1,2,3,4 tetramethylbenzene (95%), and 1,2,3,5 tetramethylbenzene (85%). These three compounds were purified either by repeated vacuum distillation or by recrystallization from pentane at -60 °C. Iodine (Mallinkrodt, 99.8%) and carbon tetrachloride (Fisher, spectral grade) were used without further purification. Solutions of iodine and donor molecules were prepared in carbon tetrachloride by using quantitative techniques.

Spectral measurements were taken on either a Perkin-Elmer Lambda 3 or Shimadzu 265 UV-vis spectrophotometer with a temperature-regulated cell holder. For each solution, absorbances were measured at five wavelengths in the range 320-360 nm. Wavelengths were selected to avoid absorbance by the donor molecule and to obtain the largest possible absorbance by the molecular complex. Data were taken at approximately 5 deg intervals in the range 20-40 °C, with absolute values of temperature determined to an accuracy of ± 0.1 °C, by using a thermocouple sensor. Experimental absorbances were corrected for absorbance of free iodine and for changes in absorbance due to changes in solution density with temperature. Values for $\Delta H_{\rm app}$ were then obtained from the slope of a plot of ln $A_{\rm CT}$ versus 1/T.

Further details of the experimental procedure can be found in ref 4.

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Registry No. I₂, 7553-56-2; benzene, 71-43-2; methylbenzene, 108-88-3; 1,2-dimethylbenzene, 95-47-6; 1,3-dimethylbenzene, 108-38-3; 1,4-dimethylbenzene, 106-42-3; 1,2,3-trimethylbenzene, 526-73-8; 1,2,4-trimethylbenzene, 95-63-6; 1,3,5-trimethylbenzene, 108-67-8; 1,2,3,4-tetramethylbenzene, 488-23-3; 1,2,3,5-tetramethylbenzene, 527-53-7; 1,2,4,5-tetramethylbenzene, 95-93-2; pentamethylbenzene, 700-12-9; hexamethylbenzene, 87-85-4.