

Thermochemistry of Molecular Complexes of Iodine Monochloride, Iodine Monobromide, and Bromine with Benzene and Benzene Derivatives

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Beginning with the first studies 50 years ago by Benesi and Hildebrand,¹ there has been great experimental and theoretical interest in weakly bound molecular complexes. Thermodynamic information on such complexes can be used to predict chemical reactivity of organic compounds^{2–5} and as the basis for establishing general systems for the acid-base properties of molecules.^{6–8}

Recently a method has been developed that makes use of the change in complex absorbance with temperature to determine the enthalpy of formation of weakly bound molecular complexes, and, in some cases, the equilibrium constant for complex formation.⁹ Under conditions where one of the compounds involved in complex formation is in large excess an apparent enthalpy of formation (ΔH_{app}) can be defined by the relationship

$$\Delta H_{\text{app}} = -R\partial(\ln A_c)/\partial(1/T) \quad (1)$$

where A_c is the absorbance of the complex. The apparent enthalpy of formation is related ΔH , the enthalpy of formation in the limit of ideal solution behavior, by the expression

$$\Delta H_{\text{app}} = \Delta H\{1 - K[D]_0 + (K[D]_0)^2 - \dots\} \quad (2)$$

$$= \Delta H(1 + K[D]_0)^{-1} \quad (3)$$

where $[D]_0$ is the initial concentration of donor molecule (it is assumed that the donor molecule is in large excess compared to the acceptor molecule), and K is the equilibrium constant for complex formation. The above method has been used to study a variety of complexes of iodine with benzene and benzene derivatives,^{9–13} as well

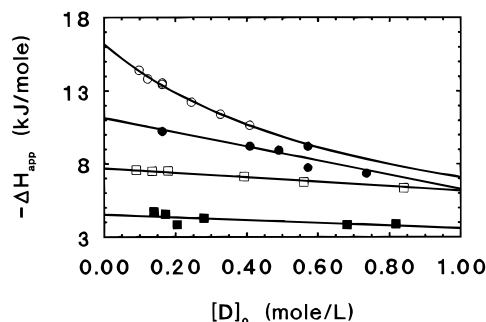


Figure 1. Plot of ΔH_{app} vs donor molecule concentration for complexes of (○) 1,4-dimethylbenzene + ICl, (●) ethylbenzene + IBr, (□) benzene + Br₂, and (■) 1,4-dichlorobenzene + ICl. Lines indicate best fit of the data to eq 3 (for 1,4-dimethylbenzene + ICl) or eq 2, as discussed in the text.

as complexes of 7,7,8,8-tetracyanoquinodimethane with benzene and several chlorinated benzene derivatives.¹⁴

The purpose of the present note is to report thermodynamic data on molecular complexes of iodine monochloride, iodine monobromide, and bromine with benzene and a number of benzene derivatives in carbon tetrachloride solution. Formation enthalpies are given and compared to previous results obtained using molecular iodine as a donor.

Results and Discussion

Five to twelve separate determinations of ΔH_{app} were carried out for each pair of donor and acceptor compounds. Values for ΔH were then found by plotting ΔH_{app} vs $[D]_0$. In most cases, data were analyzed using eq 2, keeping terms up to $K[D]_0$ in the term in parentheses. For complexes where $|\Delta H| > 10$ kJ/mol, curvature in the plots was observed at low donor concentration. In those cases, eq 3 was used in the data analysis. Figure 1 presents a representative sample of the experimental data. For complexes of bromine with toluene and the xylene compounds, fast reaction between the aromatic compound and bromine made it impossible to obtain absorbance data of sufficient accuracy to find a value for ΔH .

Values for ΔH for complex formation of donor molecules with iodine monochloride, iodine monobromide, and bromine are given in Table 1. For the purposes of comparison, formation enthalpies for donor–iodine complexes previously determined in our laboratory^{9–11,13} have also been given in the table. In general, the magnitude of the formation enthalpy for methylbenzene–acceptor complexes increases in the order $I_2 < IBr < ICl$. For chlorobenzene–acceptor complexes the formation enthalpies are small ($|\Delta H| < 8$ kJ/mol) and do not show systematic differences with different acceptors. For both methylbenzene–acceptor and chlorobenzene–acceptor complexes the major factor determining the value of ΔH appears to be the number of substituent groups attached to the benzene ring, with substituent location playing only a minor role in determining ΔH . Such behavior was previously noted for complexes of iodine with benzene derivatives.^{9–11}

For a few of the complexes it was possible to determine values for the equilibrium constant for complex formation.

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Table 1. Enthalpy of Formation of Molecular Complexes^a

donor	acceptor			
	ICl	IBr	Br ₂	I ₂ ^b
benzene	10.6 ± 0.4	11.4 ± 0.8	7.78 ± 0.12	7.83 ± 0.10
toluene	13.7 ± 0.6	12.7 ± 2.0		8.99 ± 0.17
1,2-dimethylbenzene	14.0 ± 0.8	13.8 ± 1.5		9.83 ± 0.17
1,3-dimethylbenzene	18.1 ± 1.1	14.4 ± 0.6		10.3 ± 0.2
1,4-dimethylbenzene	16.2 ± 0.4	11.6 ± 0.4		9.67 ± 0.12
ethylbenzene	14.5 ± 1.4	11.0 ± 0.8		8.59 ± 0.18
chlorobenzene	6.0 ± 0.2	7.2 ± 0.4	5.85 ± 0.05	5.9 ± 0.3
1,2-dichlorobenzene	4.9 ± 0.4	3.2 ± 0.8	3.90 ± 0.07	4.1 ± 0.2
1,3-dichlorobenzene	3.5 ± 0.3	3.6 ± 0.9	4.11 ± 0.11	4.1 ± 0.2
1,4-dichlorobenzene	4.5 ± 0.3	4.1 ± 0.7	4.18 ± 0.14	4.4 ± 0.3
1,2,3-trichlorobenzene	1.8 ± 0.7	2.6 ± 1.0	3.3 ± 0.6	2.3 ± 0.5
1,2,4-trichlorobenzene	2.90 ± 0.05	3.2 ± 0.2	3.07 ± 0.06	2.7 ± 0.4
1,3,5-trichlorobenzene	2.0 ± 0.3	2.2 ± 1.0	2.0 ± 0.3	1.9 ± 0.7
fluorobenzene	7.2 ± 0.6	7.2 ± 0.7	5.64 ± 0.08	5.7 ± 0.4
bromobenzene	8.8 ± 0.8	7.2 ± 0.3	4.1 ± 0.2	6.1 ± 0.2

^a Values in the table are $-\Delta H$ for complex formation and are in kJ/mol. Error reported at 95% confidence limits. ^b Data for I₂ complexes is from references 9–11 and 13.

Table 2. Formation Constants for Molecular Complexes

donor	acceptor	K (M ⁻¹)	
		present	literature
benzene	ICl	0.51 ± 0.11	0.54, ^a 0.53 ^b
	IBr	0.4 ± 0.2	0.44 ^a
	Br ₂	0.25 ± 0.03	0.10 ^c
toluene	ICl	0.61 ± 0.14	0.87, ^a 0.87, ^d 0.83 ^e
	IBr	0.7 ± 0.3	0.51 ^a
1,2-dimethylbenzene	IBr	0.9 ± 0.5	0.78 ^a
1,3-dimethylbenzene	ICl	1.3 ± 0.4	1.39 ^a
1,4-dimethylbenzene	ICl	1.32 ± 0.09	1.51 ^a
chlorobenzene	IBr	0.02 ± 0.02	
	Br ₂	0.06 ± 0.03	0.09 ^c

^a Reference 18. ^b Reference 17. ^c Reference 15. ^d Reference 16. ^e Reference 19.

Results are reported in Table 2. For the cases where comparison can be made, there is satisfactory agreement with previous results.^{15–19}

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Experimental Section

Benzene and benzene derivatives were purchased from Aldrich at a minimum purity of 98% and used without further purification. 1.00 M stock solutions of iodine monochloride and iodine monobromide in carbon tetrachloride, also from Aldrich, were used to prepare more dilute solutions of the electron acceptors, while liquid bromine (Aldrich) was used to prepare a bromine stock solution of known concentration. Mixtures of donor and acceptor compounds were prepared in carbon tetrachloride (Fisher, spectral grade) by quantitative techniques.

For determination of ΔH_{app} , the apparent formation enthalpy of the molecular complex, a Shimadzu 265 UV-visible spectrophotometer with a temperature regulated cell holder was used. Five wavelengths in the range 300–340 nm were chosen for absorbance measurements and were selected to maximize absorbance of the molecular complex and minimize overlapping absorbance from the donor and/or acceptor molecules. Data were taken at 26.0, 30.6, 35.4, 40.2, and 45.2 °C, with temperature determined to an accuracy of ± 0.1 °C using a thermocouple sensor. After correcting the experimental absorbances for absorbance by free donor and/or acceptor molecules and for changes in solvent density with temperature, values for ΔH_{app} were found from a plot of $\ln A_c$ vs $1/T$.

Further details of the experimental procedure are given in ref 9.

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Additions and Corrections

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Lawrence T. Scott* and Atena Necula. Synthesis and Characterization of the Three Dicyclopentapyrenes.

Page 386. We thank Prof. L. W. Jenness for a kind exchange of manuscripts prior to the appearance of his paper on independent syntheses of these compounds; his paper has now appeared: Sarobe, M.; Flink, S.; Jenness, L. W.; Van Poecke, B. L. A.; Zwikker, J. W. *J. Chem. Soc., Chem. Commun.* **1995**, 2415–2416.

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