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Thermochemistry of Molecular Complexes. 4. Molecular Complexes of I_2 with Chloromethylbenzenes

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Abstract. The enthalpy of formation for twelve molecular complexes of I_2 with chloromethylbenzene molecules in CCl_4 have been determined. The wavelength of maximum absorption for each complex is also reported. The formation enthalpy for the complexes appears to depend strongly on the number and type of substituent groups attached to the benzene ring, but only weakly on the location of the substituent group on the ring. This suggests that it should be possible to predict formation enthalpies for a wide variety of complexes of this type based on a limited number of experimental measurements.

Key words. Iodine complex, enthalpy of formation.

1. Introduction

Molecular complexes formed by noncovalent interactions have been the focus of research for over forty years [1–5]. There has not, however, been much study of complexes formed by extremely weak interactions between donor and acceptor molecules ($|\Delta H| < 10$ kJ/mol) because of the difficulty of using standard techniques for the analysis of spectroscopic data (such as the Benesi–Hildebrand [6], Rose–Drago [7], and related equations) for cases where complexes are produced at low concentration. Recently Morales and coworkers [8] developed a spectroscopic technique that can be used to determine the enthalpy change for the 1 : 1 complex that forms between a donor (D) and acceptor (A) molecule by the process

$$D + A \rightleftarrows DA; \quad K_{eq} = [DA]/[D][A] \qquad (1)$$

even for cases where the change in enthalpy associated with complex formation is small. The method has been used to study molecular complexes of I_2 with chlorine [8], methyl [9], bromine [10], fluorine [10], and iodine [10] substituted benzene molecules, to determine the factors which influence the strength of the donor–acceptor interaction. In most cases, it has been found that the enthalpy of formation for the iodine–benzene derivative complex depends only on the number of substituent groups, and not on the location of the substituents on the benzene ring.

Previous work on the iodine–benzene derivative complexes has been limited to substitution by a single type of group. In the present paper, enthalpies of formation are determined for a series of complexes between I_2 and chloromethylbenzene donor molecules. Regularities in the formation enthalpies for the complexes are discussed.

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2. Experimental

Donor molecules were purchased from Aldrich at the following minimum purity: 2-chlorotoluene (99%), 3-chlorotoluene (98%), 4-chlorotoluene (98%), 2,3-dichlorotoluene (98%), 2,4-dichlorotoluene (99%), 2,5-dichlorotoluene (98%), 2,6-dichlorotoluene (99.5%), 3,4-dichlorotoluene (97%), 2-chloro-*m*-xylene (97%), 2-chloro-*p*-xylene (99%), 4-chloro-*o*-xylene (90%), and 2,4,5,6-tetrachloro-*m*-xylene (98%). Compound purity was checked by UV-visible spectroscopy and/or GC and GC/MSD. 3,4-Dichlorotoluene and 4-chloro-*o*-xylene were further purified by recrystallization at low temperature from hexane, and 2,4,5,6-tetrachloro-*m*-xylene was further purified by sublimation. In these cases the additional purification was carried out to remove trace amounts of a UV absorbing impurity. 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 using quantitative techniques.

Absorption measurements were made on a Shimadzu 265 UV-visible spectrophotometer with a temperature regulated cell holder. For each iodine–donor solution, absorbances were measured at five wavelengths in the range 320–340 nm. Wavelengths were selected to minimize absorbance by the donor molecule and to obtain the largest possible absorbance from the molecular complex. Data were taken at five temperatures in the range 20–40°C, with the absolute value for temperature determined to an accuracy of ± 0.1°C using a thermocouple sensor. Experimental absorbances were corrected for absorbance by free iodine and donor molecules, and for changes in the density of the solution with temperature.

The value for ΔH_{app}, defined by the relationship

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

where A_{DA} is the absorbance of the complex, was found from the slope of a plot of $\ln A_{\mathrm{DA}}$ vs $1/T$. The value for ΔH, the enthalpy change for reaction (1), is then given by the intercept in a plot of ΔH_{app} vs concentration of donor molecule [8].

For determination of λ_{max}, the wavelength of maximum absorbance of the molecular complex, a Shimadzu 265 spectrophotometer was again used. Measurements were made in the double beam mode, using a solution of iodine and donor molecule in the sample cuvette, and donor molecule, at the same concentration as in the sample cuvette, in the reference cuvette. Because the donor molecules all possess a strong absorption band in the region 260–320 nm that overlaps the absorption band of the molecular complex, low concentrations of donor molecule (<10 mM) were used in the measurements.

Further details concerning the experimental method are given in [8].

3. Results and Discussion

Experimental values are given in Table I for the enthalpy of formation for complexes of various donor molecules with molecular iodine. Error limits for the enthalpy values are given at the 95% confidence limits. In principle, the method used to determine the enthalpy of formation can also be used to find the value for the equilibrium constant for complex formation [8, 9]. However, for extremely weak

Table I. Enthalpy of formation for donor–iodine molecular complexes

Compound	N^a	$-\Delta H$(kJ/mol)^b	λ_{max}(nm)^c
2-chlorotoluene	8	5.91 ± 0.22	291
3-chlorotoluene	8	6.78 ± 0.29	286
4-chlorotoluene	6	6.13 ± 0.18	278
2,3-dichlorotoluene	6	4.73 ± 0.19	279
2,4-dichlorotoluene	7	4.36 ± 0.13	280
2,5-dichlorotoluene	7	4.35 ± 0.32	280
2,6-dichlorotoluene	6	4.67 ± 0.14	279
3,4-dichlorotoluene	6	5.12 ± 0.31	279
2-chloro-*m*-xylene	8	7.62 ± 0.20	304
2-chloro-*p*-xylene	6	6.70 ± 0.23	298
4-chloro-*o*-xylene	7	6.97 ± 0.12	278
2,4,5,6-tetrachloro-*m*-xylene	6	2.8 ± 0.9	278

[a] Number of measurements.

[b] Error range reported at 95% confidence limits.

[c] Wavelength of maximum absorbance by the complex.

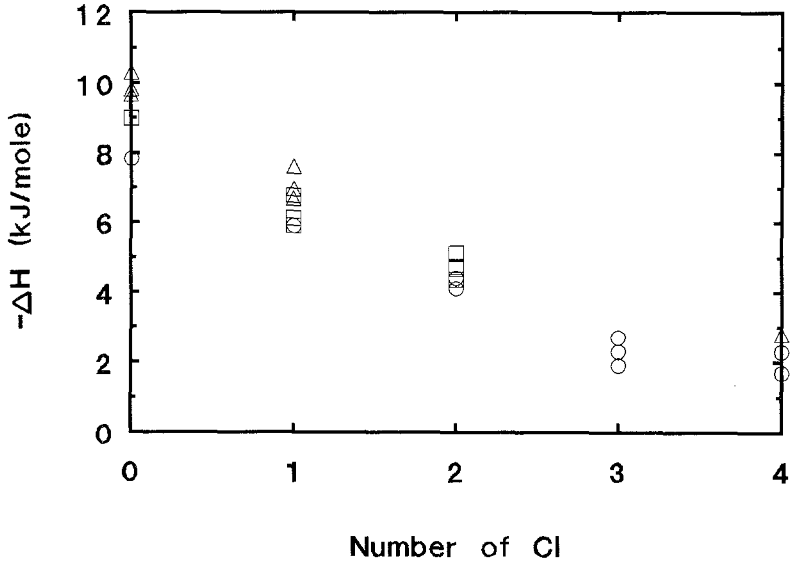

Fig. 1. Plot of $-\Delta H$ vs. number of Cl groups for benzene derivatives containing (○) zero, (□) one, and (△) two methyl groups. Data are taken from the present results and [8, 9].

molecular complexes such as those formed in the present study, it is not possible to determine the value for the equilibrium constant for complex formation. Based on previous experimental work [8–10], it can be determined that $K_{eq} < 0.20\ M^{-1}$ for all of the complexes in the present study.

A plot of the enthalpy of formation for molecular complexes of iodine with chlorinated benzene derivatives containing zero, one, and two methyl groups is given in Figure 1. Data are taken from the present results and previous experiments [8, 9]. As has been noted for cases of substitution by a single type of substituent, the formation enthalpy appears to depend strongly on the number of methyl and/or chlorine groups attached to the benzene ring, and to have only a weak dependence on the position of the substituent groups on the ring. If this behavior is true in general, then it should be possible to predict the enthalpy of formation of complexes of iodine with substituted benzene donor molecules based on a limited number of experimental measurements.

The wavelength for maximum absorption of the molecular complexes formed in this study has also been reported in Table I. Based on the relationship between the ionization potential of the donor molecule and the formation enthalpy and wavelength of maximum absorbance of the corresponding molecular complex [1, 4, 11], the wavelength of maximum absorbance is expected to increase as the magnitude of the formation enthalpy increases. The present data are consistent with this expectation with the exception of two donors, 4-chlorotoluene and 4-chloro-*o*-xylene, both of which have a smaller than expected wavelength of maximum absorbance. The reason for the discrepancy for these two donor molecules is not known.

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