

Thermochemistry of Molecular Complexes. 5. Molecular Complexes of I₂ with Ethylbenzenes and *n*-Alkylbenzenes

IAN DREPAUL and JEFFREY A. JOENS*

Department of Chemistry, Florida International University, Miami, Florida 33199, U.S.A.

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Abstract. The enthalpies of formation and equilibrium constants are reported for molecular complexes of I₂ with five ethylbenzene and nine *n*-alkylbenzene donor molecules in CCl₄. The wavelength of maximum absorbance for each complex is also reported. For ethylbenzene donor molecules, the formation enthalpy and equilibrium constant for the complexes depend strongly on the number of ethyl groups attached to the benzene ring, but only weakly on the position of the groups. For the *n*-alkylbenzene donor molecules, both the formation enthalpy and equilibrium constant for complex formation are independent of the length of the alkyl chain. These results are consistent with previous observations on weak complexes of I₂ with substituted benzene donors.

Key words: Iodine complex, enthalpy of formation.

1. Introduction

The study of molecular complexes has many applications in chemistry. Information from such studies can be used to investigate the relationship between complex formation and the rate and mechanism of chemical reactions [1–3], to develop general methods for measuring the strengths of Lewis acids and bases [4–6], and to help to understand the forces involved in weak interactions between molecules [7, 8].

Morales and coworkers have developed a procedure for measuring the enthalpy of formation and formation constant for weak molecular complexes in solution [9]. Their method has been validated by showing the results obtained by their procedure for methylbenzene–iodine complexes are in accord with previous results for these complexes [10]. This has made it possible to study the extremely weak complexes that form between halogenated benzene derivatives and iodine [9, 11], and complexes between chloromethylbenzenes and iodine [12], leading to the development of general rules for the formation enthalpy for such complexes.

The purpose of the present paper is to extend the study of weak complexes of benzene derivatives and iodine to two additional types of donor molecules.

* Author for correspondence.

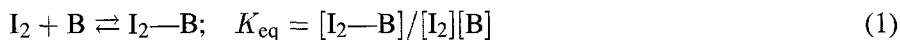
Results are presented for the enthalpy of formation and formation constant for five complexes between ethylbenzenes and iodine, and an additional nine complexes between *n*-alkylbenzenes and iodine. The wavelength of maximum absorbance for each complex is also given. The results are compared with previous results for complexes of benzene derivatives with I₂.

2. Experimental

Donor molecules were purchased from Aldrich at the following minimum purity: ethylbenzene (99+%), 1,3-diethylbenzene (99%), 1,4-diethylbenzene (96%), 1,2,4-triethylbenzene (97%), 1,3,5-triethylbenzene (98%), *n*-propylbenzene (98%), *n*-butylbenzene (99+%), *n*-pentylbenzene (99%), 1-phenylhexane (97%), 1-phenylheptane (99%), 1-phenyloctane (99%), 1-phenylnonane (99%), 1-phenyldodecane (99%), and 1-phenyltridecane (99%). Compound purity was checked by UV-visible spectroscopy and/or GC and GC/MSD. 1-Phenyloctane, 1-phenyldodecane, and 1-phenyltridecane were further purified by recrystallization at low temperature from hexane 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 molecule in carbon tetrachloride were prepared 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 300–360 nm. Wavelengths were selected to minimize absorbance from the donor molecule and to obtain a large 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 solution density with temperature.

The formation of the molecular complex between iodine and a donor molecule is given by the reaction



where B is the donor molecule (a Lewis base) and I₂—B is the molecular complex. An apparent value for the enthalpy change for reaction (1), Δ*H*_{app}, is defined by the equation

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

where *A*_{DA} is the absorbance of the complex, and is found from the slope of a plot of ln *A*_{DA} vs 1/*T*. If Δ*H*_{app} is plotted against donor molecule concentration under conditions where [B] ≫ [I₂], it can be shown [9] that the slope and intercept of the

plot are related to the enthalpy of reaction, ΔH , and the equilibrium constant for complex formation, K_{eq} by the expressions

$$\text{slope} = -K_{\text{eq}}(\Delta H) \quad (3)$$

$$\text{intercept} = \Delta H. \quad (4)$$

To find λ_{max} , the wavelength of maximum absorbance of a 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 a solution of donor molecule, at the same concentration as in the sample cuvette, in the reference cuvette. Because all of the donor molecules used in the present study possess a strong absorption band in the region 250–320 nm, which overlaps the absorption band of the molecular complex, low concentrations of donor molecules (< 10 mM) were used in the determination of λ_{max} .

Further details concerning the experimental method are given in [9].

3. Results and Discussion

Experimental values for the enthalpy of formation, equilibrium constant, and wavelength of maximum absorbance for complexes of various donor molecules with molecular iodine are given in Table I. Results are based on six to ten separate measurements for each complex. Error limits for the formation enthalpies and equilibrium constants are given at the 95% confidence limits. For the complexes for which previous results have been reported there is generally good agreement between the present results and earlier measurements.

For the ethylbenzene–iodine complexes, the enthalpy of formation is, to a first approximation, a function of the number of ethyl groups attached to the benzene ring. This behavior has previously been observed for methylbenzene [10] and halogenated benzene [9, 11] donor molecules. The magnitude of the change in the formation enthalpy is approximately 1.0 kJ/mole per ethyl group added to the benzene ring, similar to the value 1.09 kJ/mole previously found for substitution by methyl groups [10]. The equilibrium constant for complex formation also increases with the number of ethyl groups attached to the benzene ring.

The *n*-alkylbenzene–iodine complexes studied in the present work include ten *n*-alkylbenzene donors ranging from ethylbenzene to 1-phenyltridecane. Both the enthalpy of formation and equilibrium constant for complex formation are reported for all compounds except 1-phenyldodecane and 1-phenyltridecane, where problems with reproducibility of the experimental results made it impossible to obtain a value for the formation constant for the complex. For the *n*-alkylbenzene donors both the enthalpy of formation and the equilibrium constant for complex formation were found to be independent of the length of the alkyl chain. It thus appears that steric hindrance for long chain aliphatic groups attached to the benzene ring does

TABLE I. Enthalpies of formation, formation constants, and wavelength maxima for donor-I₂ molecular complexes.

Donor	ΔH (kJ/mole) ^{a,b}	K (L/mole) ^{a,b}	λ_{\max} (nm)
ethylbenzene	8.59 ± 0.18	0.17 ± 0.05 (0.23) ^c	300.8
1,3-diethylbenzene	9.91 ± 0.17	0.28 ± 0.06	317.6
1,4-diethylbenzene	9.50 ± 0.09	0.32 ± 0.05	304.4
1,2,4-triethylbenzene	10.61 ± 0.10	0.34 ± 0.05	323.0
1,3,5-triethylbenzene	11.26 ± 0.15 (11.0) ^d	0.37 ± 0.11 (0.54) ^d	335.9
<i>n</i> -propylbenzene	8.64 ± 0.14	0.20 ± 0.07 (0.23) ^c	303.1
<i>n</i> -butylbenzene	8.56 ± 0.15	0.17 ± 0.05 (0.19) ^c	303.8
<i>n</i> -pentylbenzene	8.72 ± 0.10	0.17 ± 0.03 (0.20) ^c	303.7
1-phenylhexane	8.72 ± 0.21	0.29 ± 0.09 (0.17) ^c	300.2
1-phenylheptane	8.73 ± 0.07	0.22 ± 0.03 (0.17) ^c	305.2
1-phenyloctane	8.69 ± 0.13	0.23 ± 0.07	303.8
1-phenylnonane	8.79 ± 0.08	0.22 ± 0.03	300.6
1-phenyldodecane	8.0 ± 1.0		302.1
1-phenyltridecane	8.4 ± 1.0		300.6

^a Error limits at the 95% confidence limits.

^b Literature values in parentheses.

^c Ref. [13].

^d Ref. [14].

not significantly affect either the enthalpy of formation or the equilibrium constant for complex formation.

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