Stability Constants for Iodine-Aromatic Complexes in Cyclohexane

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The stability constants for the iodine complexes with eight aromatic compounds in cyclohexane solvent at 25° have been determined spectroscopically. In general, the values are a little larger in cyclohexane than in n-hexane and considerably larger than in CCl_4. Values for ethylbenzene and o-dichlorobenzene, not previously reported in any solvent, are of the expected order of magnitude.

MANY investigators (*2, 4, 6, 7, 8*) have speculated on the nature of iodine-aromatic complexes. Since Benesi and Hildebrand (*2*) devised a method of determining stability constants for the complexes from ultraviolet spectra, many such constants have been determined. Nearly all of these have been with CCl_4 as the solvent. Since the relative magnitudes of the stability constants play an important part in the various theories it was felt further investigation of the solvent effect was needed.

The most extensive list of compounds studied is that of Keefer and Andrews (*7*). Most of their stability constants are given in liters per mole. Most other investigators have given the stability constants in mole fraction units. These cannot be compared directly without partial molar volume data. However, for dilute solutions K_c (liters per mole) can be calculated from K_N (reciprocal mole fraction) by multiplying the latter by $M_1/1000d_1$ where M_1 and d_1 refer to the molecular weight and density of the solvent.

There is some indication that K_c is more constant from solvent to solvent than is K_N. For example, Benesi and Hildebrand (*2*) found values of K_N for the benzene complex at 22° C. to be 1.72 and 1.15 in CCl_4 and *n*-heptane, respectively, which when converted to K_c for dilute solutions become 0.167 and 0.168, respectively. C. van de Stolpe (*9*) reports a value of K_N for this complex in *n*-hexane of 1.21 which when converted to K_c for dilute solution becomes 0.158. These are all in good agreement with the value of K_c found by Keefer and Andrews (*7*) 0.15 in CCl_4 at 25° C.

Cyclohexane was chosen in this study for a solvent since no cycloalkanes have been used for these complexes. Hastings, Franklin, Schiller, and Matsen (*5*) showed that I_2 forms a complex with cyclohexane. Using *n*-hexane, which they believed approached inertness, as a solvent they calculated K_c for the I_2-cyclohexane complex to be 0.0127. However, Evans (*3*) showed the *n*-hexane was not completely inert to I_2. He showed that perfluoroheptane is inert to I_2 and using this as a solvent he attempted to determine the stability constant by the Benesi and Hildebrand method. The intercept of the plot was almost exactly zero from which he concluded that the complex was either a very weak one with a very high extinction coefficient or a collision complex.

At any rate the interaction of I_2 with cyclohexane appears to be small compared to that between I_2 and aromatic compounds such that no serious competition for I_2 between cyclohexane and the aromatic compounds exists and that all the I_2 not complexed with the aromatic compound may be considered free I_2.

EXPERIMENTAL

Materials. Iodine (Fisher Certified Reagent) was resublimed and stored over anhydrous $Mg(ClO_4)_2$.

Cyclohexane (Matheson, Coleman and Bell) was passed through a 4-foot column of activated alumina, then fractionally distilled through a packed column, with the middle one third being saved. It was optically clear when checked against distilled water from 240 to 340 mμ.

Benzene (Fisher Certified Reagent) was shaken repeatedly with concentrated H_2SO_4 until the acid layer remained colorless, washed with distilled water, refluxed 6 hours over anhydrous CaO, and fractionally distilled through a packed column, with the middle one third being saved.

Chlorobenzene (Matheson, Coleman and Bell) was purified by the same procedure used for benzene.

Toluene (Baker Reagent) was shaken repeatedly with concentrated H_2SO_4 until the acid layer remained colorless, washed with distilled water, shaken 3 times with 10% NaOH, washed again with distilled water, dried by refluxing 6 hours over anhydrous P_2O_5, and fractionally distilled through a packed column, with the middle one third being saved.

o-Dichlorobenzene (Eastman Practical) was dried over anhydrous CaO and fractionally distilled through an adiabatic 4-foot packed column at high reflux ratio. The fraction distilling at 177.0° C. (731 mm. of Hg) was collected.

o-Xylene (Eastman White Label) was initially purified by several fractional freezings, then refluxed over CaO and fractionally distilled, with the middle one third being saved.

Ethylbenzene (Eastman White Label) was shaken repeatedly with concentrated H_2SO_4 until the acid layer remained colorless, washed with distilled water, 10% Na_2CO_3, distilled water, and dried over anhydrous CaO for 2 days. It was then fractionally distilled from metallic sodium, the middle one third being saved.

Bromobenzene (Eastman Practical) was purified in the same manner as was chlorobenzene.

Biphenyl (Eastman White Label) was recrystallized several times from cyclohexane and dried in a vacuum desiccator.

All refractive indices and densities checked with the best values in the literature.

Absorption Measurements. All absorption curves were made using a Beckman ratio recording spectrophotometer Model DK-2 equipped with a hydrogen discharge tube. The cell compartment was equipped to provide a constant temperature of 25.0° ± 0.1° C. Matched 1.0-cm. cells were used in all determinations.

The absorptivities of iodine (ϵ_I) and the aromatic compound or donor (ϵ_D) in cyclohexane were determined at the wave length chosen for the calculations. Absorption curves for the mixed solutions of iodine and the aromatic compound of varying concentrations in cyclohexane were determined over the range of 280 to 340 mμ. In order to minimize the absorbance correction for the uncomplexed donor, except for benzene, toluene, and ethylbenzene, the wave lengths chosen for equilibria calculations were not those of the maxima in the complex absorption curves but were arbitrarily chosen ones.

Calculations. Equilibrium constants were calculated by means of Equation 1.

$$C_D = \frac{\epsilon_c C_I C_D}{A_T - \epsilon_D C_D - \epsilon_I C_I} - 1/K,\ C_D \gg C_I,\ C_c;\ \text{and}\ \epsilon_c \gg \epsilon_I, \epsilon_D \quad (1)$$

where C_D and C_I are concentrations in moles per liter of total donor and total iodine, respectively; C_c is concentration of the complex; ϵ_D, ϵ_I, and ϵ_c are absorptivities of the donor, iodine, and the complex at the wave length chosen; A_T is total absorbance (cell thickness equal 1 cm.); and K is the stability constant in liters per mole. A plot of C_D *vs.*

$$\frac{C_I C_D}{A_T - \epsilon_D C_D - \epsilon_I C_I}$$

gives a straight line whose slope is ϵ_c and whose intercept is $1/K$. The best straight line was obtained by the method of least squares.

Table I. Stability Constants for Iodine-Aromatic Complexes in Cyclohexane at 25° C.

$C_I \times 10^4$ Mole/Liter	C_D Mole/Liter	A_T	K_c Liter/Mole
Benzene, 290 mμ, $\epsilon_D = 0.0054$, $\epsilon_I = 75.6$, $\epsilon_c = 13{,}550$			
0.869	8.341	0.798	0.207
1.738	6.951	1.482	0.223
1.521	3.244	0.854	0.206
2.028	2.438	0.960	0.211
2.535	1.622	0.906	0.212
3.042	0.811	0.642	0.216
	From least-squares intercept		0.212
Toluene, 300 mμ, $\epsilon_D = 0.0084$, $\epsilon_I = 55.5$, $\epsilon_c = 11{,}560$			
0.869	6.808	0.725	0.285
1.738	5.673	1.313	0.294
2.607	4.539	1.807	0.307
2.028	1.981	0.878	0.287
2.535	1.321	0.843	0.293
3.041	0.660	0.589	0.291
	From least-squares intercept		0.293
Ethylbenzene, 302 mμ, $\epsilon_D = 0.0058$, $\epsilon_I = 52.1$, $\epsilon_c = 12{,}490$			
1.481	5.734	1.163	0.269
1.481	2.389	0.731	0.260
2.592	2.230	1.211	0.259
3.457	1.673	1.340	0.261
4.321	1.115	1.263	0.266
5.185	0.558	0.885	0.273
	From least-squares intercept		0.263
o-Xylene, 320 mμ, $\epsilon_D = 0.0125$, $\epsilon_I = 26.0$, $\epsilon_c = 9{,}950$			
1.481	5.543	1.100	0.415
1.481	2.310	0.739	0.398
2.592	2.156	1.223	0.397
3.457	1.617	1.392	0.406
4.321	1.078	1.347	0.412
5.185	0.539	0.968	0.418
	From least-squares intercept		0.407
Chlorobenzene, 300 mμ, $\epsilon_D = 0.0029$, $\epsilon_I = 55.5$, $\epsilon_c = 9{,}510$			
0.869	6.969	0.367	0.101
1.738	5.808	0.636	0.101
2.607	4.646	0.818	0.101
3.476	3.485	0.879	0.099
4.345	2.323	0.804	0.099
5.214	1.162	0.559	0.102
	From least-squares intercept		0.101
Bromobenzene, 300 mμ, $\epsilon_D = 0.0694$, $\epsilon_I = 55.5$, $\epsilon_c = 10{,}240$			
1.481	7.066	1.217	0.127
2.963	5.888	1.728	0.128
2.222	2.355	0.695	0.126
3.457	2.061	0.894	0.127
3.704	1.178	0.600	0.128
8.888	1.178	1.321	0.128
	From least-squares intercept		0.127
o-Dichlorobenzene, 310 mμ, $\epsilon_D = 0.00364$, $\epsilon_I = 38.6$, $\epsilon_c = 15{,}370$			
1.481	7.064	0.384	0.0260
2.963	5.887	0.628	0.0255
4.444	4.710	0.769	0.0256
5.926	3.532	0.799	0.0259
7.407	2.355	0.687	0.0257
8.888	1.178	0.441	0.0257
	From least-squares intercept		0.0257
Biphenyl, 340 mμ, $\epsilon_D = 0.0299$, $\epsilon_I = 15.4$, $\epsilon_c = 5{,}520$			
1.481	1.032	0.253	0.357
2.963	0.860	0.417	0.360
4.444	0.688	0.510	0.356
5.927	0.516	0.530	0.354
7.407	0.344	0.470	0.358
8.888	0.172	0.304	0.359
	From least-squares intercept		0.357

RESULTS

Table I shows the stability constants of each of the iodine-aromatic complexes. In order to illustrate the constancy of K_c at different concentrations ϵ_c is calculated from the slope of a plot of Equation 1 and this value is substituted into Equation 1 to calculate K_c for each point. It is noted that generally K_c is constant over a wide range of concentrations within 2 or 3 percent.

Table II gives a comparison of the values in cyclohexane with those in *n*-hexane and CCl_4. In general, the stability constants in cyclohexane are a little larger than in *n*-hexane and are considerably larger than in CCl_4 although for bromobenzene and biphenyl this solvent effect is not noted. Values for ethylbenzene and *o*-dichlorobenzene in other solvents are not available. However, Keefer and Andrews (*7*) obtained identical stability constants for iodine monochloride complexes of toluene and ethylbenzene in CCl_4.

Table II. Comparison of Stability Constants of Iodine-Aromatic Complexes in Various Solvents at 25° C.

	K_c, Lit./Mole		
	Cyclohexane	*n*-Hexane	CCl_4
Benzene	0.212	0.16[a] (*9*)	0.15 (*7*), 0.17[a] (*2*)
Toluene	0.293	0.293[a] (*9*)	0.16 (*7*)
Ethylbenzene	0.263	. . .	. . .
o-Xylene	0.407	0.386[a] (*9*)	0.27 (*7*)
Chlorobenzene	0.101	0.088[a] (*9*)	. . .
Bromobenzene	0.127	. . .	0.13 (*7*)
o-Dichlorobenzene	0.0257	. . .	. . .
Biphenyl	0.357	. . .	0.37 (*1*)

[a] Calculated from K_N for dilute solution case.

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