

A CALORIMETRIC STUDY OF THE RELATIVE DONOR STRENGTH OF BENZENE, TOLUENE AND THE XYLENES

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SUMMARY

Log K , ΔH° and ΔS° values have been calorimetrically determined for the reactions forming salt:aromatic complexes between Al_2Br_6 , NaAlBr_4 , or CuAlBr_4 with benzene or xylene in toluene solvent and for Al_2Br_6 with toluene in benzene solvent. The results indicate that benzene is a stronger electron donor than toluene for these metal salts.

INTRODUCTION

It has long been recognized that aromatic hydrocarbons are weak bases¹ and the equilibrium constants for the interaction of the various methyl substituted benzenes with a wide variety of electron acceptors have been determined. In general, it has been concluded that the electron donor strength of the benzene ring increases with the number of methyl substituents²⁻⁸. Two previous calorimetric studies on the donor strength of aromatic hydrocarbons have been reported. McGlashan⁹ and coworkers have determined the enthalpies of mixing of carbon tetrachloride with benzene, toluene, *p*-xylene and mesitylene. It was found that while the equilibrium constant for complex formation increases in the order benzene < toluene < *p*-xylene < mesitylene the magnitude of the (negative) enthalpy change for the formation of the complexes decreases in the same order. Arnett *et al.*¹⁰ have reported ΔH° values for the complexation of benzene, toluene and mesitylene with *p*-fluorophenol in carbon tetrachloride. Their results indicate the enthalpy of formation is identical for the benzene and toluene complexes and 0.3 kcal/mole more exothermic for the mesitylene complex.

We have calorimetrically determined equilibrium constant and enthalpy change values for the interaction of various AlBr_3 salts with benzene, toluene and the xylenes. The relative electron donor strength of these aromatic hydrocarbons is discussed in terms of the enthalpy change values obtained.

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MATERIALS

Reagent grade AlBr_3 (Alfa Inorganics) was further purified by distillation in a nitrogen atmosphere. Reagent grade NaBr (Baker "Analyzed") was dried at 120°C for 24 hours in a vacuum oven prior to use. The CuBr used was prepared according to previously described procedures¹¹. The NaAlBr_4 and CuAlBr_4 solutions were prepared by dissolving stoichiometric amounts of AlBr_3 and either NaBr or CuBr in the appropriate solvent. The toluene and benzene solvents (Matheson, Coleman and Bell "analyzed" reagent) were refluxed for several hours over sodium metal and distilled in a nitrogen atmosphere. The xylenes (Eastman Kodak "white label" reagent) were used without further purification. All purified reagents were stored and solutions prepared in a dry box nitrogen atmosphere and the calorimetric runs were made under a nitrogen atmosphere.

EXPERIMENTAL

All runs were made using a Tronac Inc. constant temperature environment titration calorimeter. Runs were made by titrating toluene solutions of each of the salts with toluene solutions of benzene, *o*-, *p*-, and *m*-xylene and by titrating a benzene solution of Al_2Br_6 with a benzene solution of toluene. Heat of dilution runs in each case were made by titration into the solvent. Four duplicate runs were made. The heat capacities of the benzene and toluene solvents were measured electrically. The resulting values were 0.354 ± 0.001 and 0.343 ± 0.002 cal/ $^\circ\text{C}$ per ml at 25°C for benzene and toluene, respectively. The uncertainty is expressed as the standard deviation among four runs.

CALCULATIONS

The method of data analysis has been previously described¹². The equilibrium constant and enthalpy change values were calculated from the thermometric titration data using a least squares variable metric method for minimization previously described¹³. A UNIVAC 1108 computer was used in the analysis of the data.

RESULTS

The $\log K$, ΔH° and ΔS° values calculated from the thermometric titration data are summarized in Table I. The values in Table I refer to the molal concentration scale. Density data used to convert from molarity to molality were taken from the literature¹⁴. The thermometric titration data from which the values in Table I were calculated are available*.

*The thermometric titration data from which the results given in Table I were calculated have been deposited with the National Auxiliary Publications Service (NAPS) of the American Society for Information Science (ASIS) as document number 1174. A microfilm or photoprint copy may be obtained from NAPS c/o CCM Information Sciences, Inc. 22 W. 34 St., New York, N.Y., 10001.

TABLE I

Log K , ΔH° AND ΔS° VALUES FOR THE REACTION $M + nX \rightleftharpoons MX_n$ IN TOLUENE AT 25°C

The uncertainties are expressed as the standard deviation among runs

M	X	n	$\log K$	ΔH° (kcal/mole)	ΔS° (gibbs/mole)	
Al_2Br_6	<i>p</i> -Xylene	1	0.42 ± 0.04	-1.70 ± 0.1	-3.8 ± 0.3	
		2	0.40 ± 0.1	-7.0 ± 1	-22 ± 3	
	<i>o</i> -Xylene	1	0.46 ± 0.09	-1.0 ± 0.2	-1.4 ± 0.6	
		2	0.8 ± 0.2	-4.7 ± 0.7	-12 ± 2	
	<i>m</i> -Xylene	1	0.53 ± 0.1	-1.3 ± 0.2	-2.0 ± 0.6	
		2	0.58 ± 0.1	-2.0 ± 0.2	-4.3 ± 0.6	
	Benzene	1	0.51 ± 0.07	-1.39 ± 0.09	-2.4 ± 0.3	
		2	0.39 ± 0.1	-8.2 ± 1	-26 ± 3	
	Toluene ^a	1	0.04 ± 0.1	0.2 ± 0.4	0.8 ± 1	
		2	0.98 ± 0.1	-0.3 ± 0.2	3.7 ± 0.6	
$NaAlBr_4$	<i>p</i> -Xylene	1	0.33 ± 0.08	-0.89 ± 0.03	-1.5 ± 0.3	
		2	0.38 ± 0.05	-3.2 ± 0.3	-9.2 ± 0.9	
	<i>o</i> -Xylene	1	0.44 ± 0.09	-0.89 ± 0.1	-1.0 ± 0.3	
		2	0.57 ± 0.09	-2.7 ± 0.3	-6.7 ± 0.9	
	<i>m</i> -Xylene	1	0.46 ± 0.07	-0.74 ± 0.06	-0.4 ± 0.3	
		2	0.50 ± 0.1	-0.71 ± 0.1	-0.2 ± 0.3	
	Benzene	1	0.39 ± 0.1	-1.11 ± 0.08	-2.0 ± 0.3	
		2	0.42 ± 0.1	-3.2 ± 0.2	-9.0 ± 0.6	
	$CuAlBr_4$	<i>p</i> -Xylene	1	0.38 ± 0.09	-0.49 ± 0.07	0.0 ± 0.3
			2	0.51 ± 0.1	-1.77 ± 0.1	-3.7 ± 0.3
<i>o</i> -Xylene		1	0.24 ± 0.05	-0.35 ± 0.04	-0.1 ± 0.2	
		2	0.35 ± 0.07	-0.5 ± 0.2	-0.3 ± 0.6	
<i>m</i> -Xylene		1	0.19 ± 0.06	-0.34 ± 0.1	-0.3 ± 0.3	
		2	0.41 ± 0.05	-0.26 ± 0.05	0.9 ± 0.2	
Benzene		1	0.03 ± 0.08	-1.28 ± 0.1	-4.2 ± 0.3	
		2	0.16 ± 0.07	-1.70 ± 0.1	-5.1 ± 0.3	

^aSolvent is benzene.

DISCUSSION

There are no previously reported values with which the results of the present study can be compared. The equilibrium constants given in Table I were calculated assuming that Al_2Br_6 exists as a dimer in aromatic solvents^{4,6,15} and that $NaAlBr_4$ and $CuAlBr_4$ are both monomeric¹⁶⁻¹⁸. The existence of metal complexes containing two aromatic molecules for each central metal group has been reported for aluminum trihalides^{3,6,15}. The existence of complexes containing two aromatic molecules is consistent with the calorimetric data. The data were not considered accurate enough to reliably check for the formation of small amounts of 3:1 complexes.

The magnitude of the ΔH° values given in Table I indicate that the electron donor strength of benzene is comparable to that of the xylenes and that both form stronger complexes than toluene. The thermometric titration curves in Fig. 1 for the

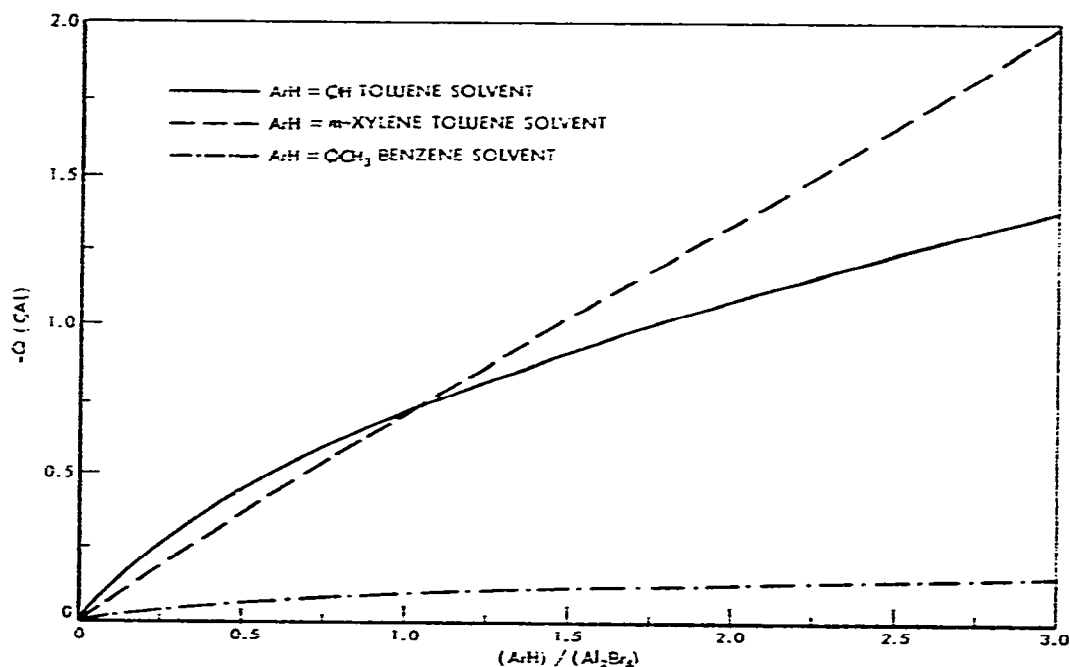


Fig. 1. Plot of $(ArH)/(Al_2Br_6)$ vs. Q for the titration of 50 ml of a 0.05 F Al_2Br_6 solution with a 3.00 F ArH solution.

titration of Al_2Br_6 solution in toluene with benzene and *m*-xylene and for the titration of an equivalent Al_2Br_6 solution in benzene with toluene, clearly shows this difference in donor strengths. Since the three systems were not studied in a common solvent the relative magnitudes of the ΔH° and ΔS° values cannot be directly determined from the present results. The ΔH° values in Table I also indicate that the donor strength of the xylenes increases in the order *m*-xylene < *o*-xylene < *p*-xylene and that the strength of the interaction for all the aromatics increases in the order $CuAlBr_4 < NaAlBr_4 < Al_2Br_6$. The order of donor strengths for toluene and the xylenes²⁻⁶ and for complexation with the salts³ is in agreement with conclusions drawn from most previous equilibrium studies. However, the conclusion that benzene is a stronger donor than toluene is in variance with conclusions drawn from equilibrium studies where the acceptor is Al_2Br_6 ⁴, tetracyanoethylene⁵, hexafluorobenzene⁷ or CCl_4 ⁹. When CCl_4 is the acceptor, heats of mixing data have shown⁹ that while the equilibrium constants for the formation of the 1:1 complexes increase in the order benzene < toluene < *p*-xylene < mesitylene, the corresponding ΔH° values increase in opposite order, *i.e.* mesitylene < *p*-xylene < toluene < benzene. Calorimetric data in CCl_4 solvent where *p*-fluorophenol is the acceptor¹⁰ indicate the ΔH° values for benzene and toluene are nearly identical and the ΔH° value for mesitylene is 0.3 kcal/

mole more exothermic. Thus, these results indicate very little difference in the electron donor properties of benzene and toluene for *p*-fluorophenol. The corresponding equilibrium constants were not reported. In the cases of both Al_2Br_6 and CCl_4 the equilibrium constants do not parallel the enthalpy change values. Thus, in general it would appear unwise to draw conclusions on relative donor strengths from equilibrium data alone^{9,19,*}, particularly for weak complexes where the magnitudes of the ΔH° and ΔS° values are often comparable and both enthalpy and entropy terms contribute significantly to the magnitude of the equilibrium constant. Moreover, recent theoretical calculations on bonding in aromatic-halogen and aromatic-TCNE complexes²¹ indicate that the bond energies may be comparable for benzene and *p*-xylene in these complexes. Accurate calorimetric data on these systems would, therefore, be of interest.

If it is assumed that the interaction between toluene (T) and benzene (B) complexes of Al_2Br_6 in either toluene or benzene solvents involves the simple displacement of one aromatic molecule by another, then the $\log K$, ΔH° and ΔS° values for the process



should be equal in either solvent system. Comparisons of thermodynamic data to study structural effects have validity only for the mole fraction scale²². The thermodynamic quantities calculated for reaction (1) in either toluene or benzene on a mole fraction scale²² are given in Table II. The values given in Table II indicate that

TABLE II

CALCULATED ΔG° , ΔH° AND $-T\Delta S^\circ$ VALUES FOR THE REACTION $\text{Al}_2\text{Br}_6(\text{T})_2 + 2\text{B} = \text{Al}_2\text{Br}_6(\text{B})_2 + 2\text{T}$

Solvent	ΔG° (kcal/mole)	ΔH° (kcal/mole)	$-T\Delta S^\circ$ (kcal/mole)
Benzene	4.4	0.3	4.1
Toluene	-3.3	-8.2	4.9

solvation effects are very important in the interactions. In both solvents the magnitude of the entropy change is the same and the difference in the ΔG° values arises from the difference in the ΔH° values in the two solvents. This difference may be explained two ways. The magnitude of the ΔH° values is consistent with the picture that the complexes are strongly solvated, particularly in benzene. Thus the interaction of benzene with Al_2Br_6 in toluene solvent is strongly exothermic since the stronger donor benzene

* ΔH° values have been calculated from the variation of $\log K$ with T for the interaction of various methyl benzenes with Al_2Br_6 ⁴, TCNE⁵ and hexafluorobenzene⁷. In all cases the reported ΔH values parallel the changes in the equilibrium constants but the differences in the ΔH values in going from benzene to toluene to xylene is small, usually a few tenths of a kcal/mole. In view of the large uncertainties involved in calculating enthalpy change values from equilibrium constants determined over a small temperature range²⁰, the accuracy of these ΔH values is probably not great and the results are therefore uncertain.

is replacing the weaker donor toluene. In benzene the complex is already strongly solvated by benzene and the tendency for benzene to replace the coordinated toluene species is greatly reduced. The data may be explained also by assuming that in benzene the toluene solute cannot replace the coordinated benzene molecules and the $\log K$, ΔH° and ΔS° values are for the formation of weak outer-sphere toluene complexes. There is no way to distinguish between these two possibilities on the basis of the present thermodynamic data.

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