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# The Heats of Dissociation of 2:1 and 1:1 Molecular Complexes Formed between Toluene and Copper(I) Tetrachloroaluminate

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Vapor pressure–phase composition studies have been carried out on toluene–$CuAlCl_4$ systems at 0°. The results indicate the existence of 2:1 and 1:1 toluene–$CuAlCl_4$ molecular complexes. The dissociation vapor pressures of these two complexes have been measured over a range of temperatures. The heats of dissociation, $\Delta H_D$, for the two processes

$$2(\text{toluene})\cdot CuAlCl_4(l) \rightleftharpoons \text{toluene}\cdot CuAlCl_4(s) + \text{toluene}(g) \quad (1)$$

$$\text{toluene}\cdot CuAlCl_4(s) \rightleftharpoons CuAlCl_4(s) + \text{toluene}(g) \quad (2)$$

have been found to be 9.58 ± 0.21 and 11.4 ± 0.33 kcal/mol for equilibria 1 and 2, respectively. The $\Delta H_D$ value obtained for process 1 is very close to $\Delta H_{vap}$ of neat toluene and suggests that the toluene molecules in the 2:1 complex are functioning essentially as molecules of solvation. The heat of dissociation of toluene from the 1:1 complex (process 2) is more in line with the energetics of known metal–aromatic molecule $\pi$ complexes. This paper also serves to introduce a new, reliable, and fast analytical technique for measuring a wide range of colligative properties of air- and moisture-sensitive compounds in solution.

The term molecular complex has been used to describe a wide range of products formed by the association of two or more molecules. The strength of intermolecular interaction varies greatly and has been related to the ionization potential of the donor and the electron affinity of the acceptor.[1] As extreme examples one can compare the strong dative bond formed between trimethylamine and dimethylberyllium[2] which is stable in the gas phase up to at least 180° with the very weakly interacting self-complexes of benzene.[3] Between these two extremes exist the interesting donor–acceptor complexes formed by the interaction of aromatic and olefinic molecules with a variety of metal complexes.[4–7] These $\pi$ complexes are often too unstable to be isolated and exist only in solution in equilibrium with their components. The formation and utility of molecular complexes between numerous aromatic and olefinic hydrocarbons and Cu(I) salts have been known for some time.[8] The majority of these Cu(I) complexes are unstable but the crystal structure of one such complex, namely, $C_6H_6\cdot CuAlCl_4$, has been reported.[9] This benzene complex contains a Cu(I) atom in a distorted tetrahedral environment containing three Cu–Cl bonds with the Cl atoms being supplied by three $AlCl_4^-$ tetrahedra. The fourth coordination site of Cu(I) was shown to be occupied by a $\pi$ interaction with the nearest C–C bond of the complexed benzene molecule. The crystal structure indicates that the $\pi$ bond arises by the very specific interaction of Cu(I) with one double bond in an isolated Kekule-type resonance structure of the complexed benzene molecule. The bonding in the asymmetric 1:1 complex, as opposed to that of a symmetric $C_6$ $\pi$ complex, has been adequately described by Mulliken[10,11] as arising from the use of an empty 4s orbital of copper as an electron acceptor and the filled $e_1$ molecular orbital of benzene as the donor. A small bonding contribution may also be derived by back-donation of electron density from filled 3d orbitals of copper to an empty $e_2$ molecular orbital of benzene.[12] In an attempt at elucidating the energetics of the interaction giving rise to the unique mode of complexation of aromatic molecules by $CuAlCl_4$, the vapor pressure of several toluene–$CuAlCl_4$ compositions has been measured as a function of temperature. The results of this study form the basis of the present report.

## Experimental Section

All sample preparations were carried out in an inert-atmosphere enclosure which employed a nitrogen atmosphere. Solvents were carefully dried and degassed by standard techniques. Anhydrous $CuAlCl_4$ was prepared by slurrying a slight excess of CuCl with resublimed $AlCl_3$ in either a toluene or benzene solvent system.[9] The colorless $CuAlCl_4$–aromatic complex solution was filtered and the filtrate reduced to dryness at 50–60° and $10^{-4}$ mm. $CuAlCl_4$ prepared free of aromatic solvent by this procedure is obtained as a white, extremely air-sensitive solid. Total chemical analyses were performed on $CuAlCl_4$ and were found to be in good agreement with its stoichiometry. Analytical samples for the vapor pressure measurements were prepared by two methods. (1) The desired $CuAlCl_4$–toluene molar composition was loaded into a 25-ml equilibration vessel equipped with a 6-mm Teflon vacuum stopcock to which was fitted a 14/35 standard taper male joint. (2) A series of $CuAlCl_4$–toluene compositions was continuously prepared by vacuum distilling portions of toluene, reweighing the vessel, and recalculating the new solution composition. The analytical solutions were thoroughly degassed by repetitive freeze–thaw techniques before performing the vapor pressure measurements.

The vapor pressure above the $CuAlCl_4$–toluene complexes was measured as a function of temperature. The equilibration vessels were kept at constant temperature in a common dewar flask, employing well-stirred chilled water. Bath temperatures were measured with a calibrated thermometer to the nearest 0.1°. The vapor pressure measurements were performed on an electronic pressure meter in which a change in pressure deflects a metal diaphragm, causing a change in electrical capacity that is measured by a sensitive bridge circuit.[13] The total pressure above the solutions was differentially determined by connecting the solution equilibration vessel to one side of the diaphragm with the other side pumped to $10^{-5}$ mm. The range of the

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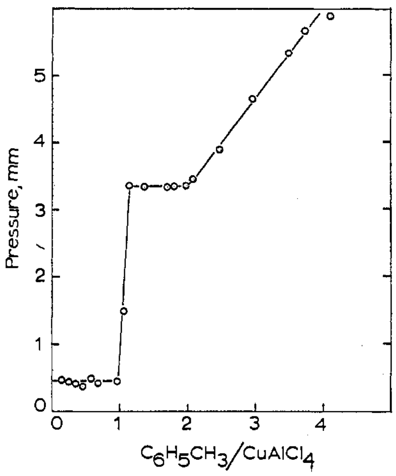

Figure 1.—Vapor pressure–composition diagram for the toluene–$CuAlCl_4$ system at 0°. Initial solution contained 4.9049 g of $CuAlCl_4$ dissolved in 7.9807 g of toluene.

pressure head was 0–300 mm, readable to $10^{-2}$ mm. The pressure above the solution was recorded after allowing at least 15 min to reach equilibrium at each successive temperature. The pressure readings were reproducible to 0.02 mm. The solution was kept at temperatures below ambient to avoid condensation in the manifold lines and measuring system. The extremely air-sensitive analytical solutions remained colorless throughout the vapor pressure measurements.

## Results

The results of a vapor pressure study of various toluene–$CuAlCl_4$ compositions at 0° are graphically shown in Figure 1. The two pressure plateaus in the mole fraction ranges of toluene:$CuAlCl_4$ from 2.0 to 1.0 and 1.0 to 0.0 are clearly attributable to the following two equilibria involving respectively a liquid 2:1 and a solid 1:1 molecular complex

$$2(\text{toluene})\cdot CuAlCl_4(l) \rightleftharpoons \text{toluene}\cdot CuAlCl_4(s) + \text{toluene}(g) \quad (1)$$

$$\text{toluene}\cdot CuAlCl_4(s) \rightleftharpoons CuAlCl_4(s) + \text{toluene}(g) \quad (2)$$

Dissociation vapor pressures were found to be 3.34 and 0.40 mm, respectively, for the 2:1 and 1:1 toluene–$CuAlCl_4$ molecular complexes at 0°. The discrete dissociation vapor pressure of the heretofore unknown 2:1 complex is constant over a wide composition range and suggests that both molecules are held within the primary coordination sphere of the Cu(I) cation. The 2:1 and 1:1 composition regions gave rise to two distinct physical modifications. Through the major portion of the 2:1 pressure plateau a colorless viscous liquid exists, while the 1:1 pressure plateau is characterized by a white granular powder. The dissociation vapor pressure of the 2:1 molecular complex is roughly 10 times greater than that found for the 1:1 molecular complex. This strongly suggests that considerable molecular rearrangement has occurred after the removal of one toluene molecule from the initial liquid 2:1 molecular complex. The nature of the physical rearrangement leading to a more tightly complexed toluene molecule in the case of the solid 1:1 molecular complex will be discussed in a later section.

The existence of the previously unknown 2:1 molecular complex was further substantiated by the following observation. If the linear, high toluene–$CuAlCl_4$ mole fraction region of the curve is extended, it crosses the zero axis at approximately 0.60 mm. Thus, the pressure drop experienced by the pure solvent would be less than the measured pressure in the dilute region of the curve by this value. If it is further assumed that, in this dilute region, 2 mol of toluene is removed by each mole of $CuAlCl_4$ present, then an average molecular weight of 405 is obtained by employing Raoult's law. Therefore, it seems reasonable to formulate the complex with the toluene:$CuAlCl_4$ mole fraction of 2.0 as $2C_7H_8\cdot CuAlCl_4$ (calculated mol wt 416) ($C_7H_8$ = toluene throughout).

The constant vapor pressure observed in the 2:1 and 1:1 toluene:$CuAlCl_4$ composition regions prompted us to study the thermal dependence of the dissociation vapor pressure of the two individual complexes in an attempt to assign $\Delta H$ of dissociation values to the processes described by eq 1 and 2. The vapor pressure above a 1.87 toluene–$CuAlCl_4$ mole fraction complex was measured as a function of temperature. The results of these measurements are presented in Table I. The temperature was changed as listed in Table I and it can be seen from the data that the vapor pressure of the 1.87 mole fraction system was completely reversible. The vapor pressure measured at 0° (3.40 mm) was in good agreement with that found (3.34 mm) in the vapor pressure–composition study reported above, in which a different complex preparation was employed (see Figure 1). A 0.83 mole fraction toluene–$CuAlCl_4$ complex was prepared by carefully removing toluene from the 1.87 mole fraction complex with reduced pressure. The vapor pressure above the 0.83 mole fraction complex as a function of temperature is also listed in Table I. At 0° a vapor pressure of 0.46 mm was measured. This is in good agreement with a value of 0.40 mm found in an earlier study of a 1:1 mole fraction complex (see Figure 1). The data in Table I show that the vapor pressure of the 0.83 mole fraction system is also reversible with temperature.

Table I

Vapor Pressure of 2:1 and 1:1 Toluene–$CuAlCl_4$ Complexes as a Function of Temperature

| 1.87 mole fraction | | 0.83 mole fraction | | Pure toluene | |
|---|---|---|---|---|---|
| Temp, °C | Pressure, mm | Temp, °C | Pressure, mm | Temp, °C | Pressure, mm |
| 0.0 | 3.40 | 12.4 | 1.38 | 17.9 | 21.40 |
| 18.2 | 8.37 | 9.5 | 1.17 | 11.4 | 14.82 |
| 21.1 | 9.90 | 6.2 | 0.94 | 14.2 | 16.35 |
| 15.2 | 6.97 | 1.2 | 0.63 | 7.6 | 12.04 |
| 12.2 | 5.85 | 0.0 | 0.46 | 4.4 | 9.54 |
| 7.5 | 4.47 | 3.9 | 0.78 | 2.0 | 8.67 |
| 3.6 | 4.16 | 17.9 | 1.86 | 9.4 | 12.84 |
| 10.6 | 5.42 | 14.9 | 1.66 | 15.1 | 17.85 |
| 14.2 | 6.53 | 12.7 | 1.44 | 6.6 | 10.70 |
| 17.4 | 7.94 | 7.1 | 1.02 | | |
| 6.2 | 4.12 | | | | |

## Discussion

The heats of dissociation, $\Delta H_D$ (as described by eq 1 and 2), of 2:1 and 1:1 toluene–$CuAlCl_4$ molecular complexes were obtained from the slope of plots of ln $P$ *vs.* $1/T$ (see Figures 2 and 3). $\Delta H_D$ values of 9.58 ± 0.21 and 11.4 ± 0.33 kcal/mol were obtained for processes 1 and 2, respectively. Thus a $\Delta\Delta H_D$ of 1.82 ± 0.27 kcal/mol between the dissociation energy of the first and second toluene molecules suggests that the toluene molecules in the 2:1 complex are not as strongly bonded to the Cu(I) center as is the toluene molecule in the 1:1 complex.

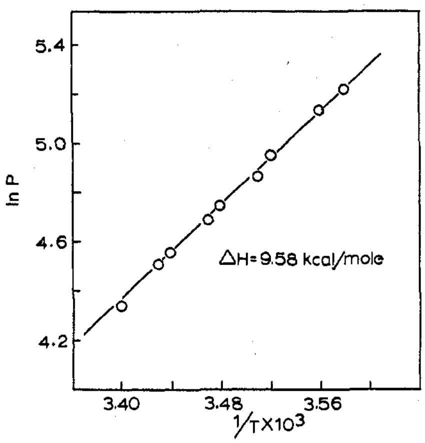

Figure 2.—Plot of ln $P$ vs. $1/T$ for a 1.87 toluene–$CuAlCl_4$ mole fraction complex. The starting solution contained 10.3202 g of $CuAlCl_4$ dissolved in 7.6509 g of toluene.

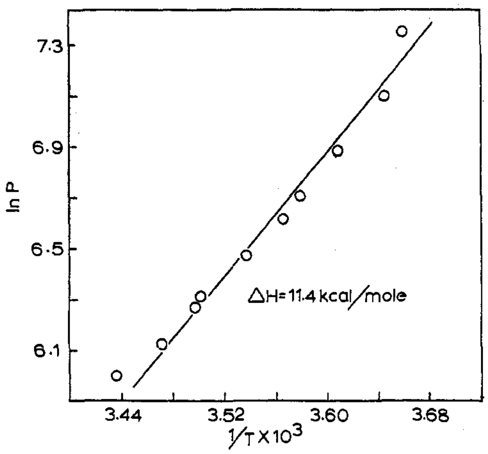

Figure 3.—Plot of ln $P$ vs. $1/T$ for a 0.83 toluene–$CuAlCl_4$ mole fraction complex.

The vapor pressure of toluene as a function of temperature is included in Table I for comparative purposes. Our measured values compare well with those calculated from the analytical expression[14] $\log P = -0.05223/Ta + b$, where $a = 39.198$ and $b = 8.330$. From ln $P$ vs. $1/T$ plots, $\Delta H_{vap}$ for neat toluene was calculated to be 9.37 ± 0.02 and 9.04 ± 0.15 kcal/mol, respectively, from the analytically and experimentally derived vapor pressures. As a further check on the accuracy of the present analytical procedure, our value of 9.04 kcal/mol for $\Delta H_{vap}$ of neat toluene can be compared to a value of 8.87 kcal/mol obtained from vapor pressure measurements with a precision U-tube manometer.[15]

The small difference between the heat of dissociation of a toluene molecule from the 2:1 molecular complex and the heat of vaporization of neat toluene, 0.54 ± 0.18 kcal/mol, suggests that the toluene molecules are only weakly bonded. Thus an input of 0.54 kcal/mol of heat would be required to overcome the binding energy of toluene to the Cu(I) atom in the 2:1 complex. Although weak, the Cu(I)–toluene interaction is sufficient to give rise to a discrete 2:1 molecular complex as shown by the flat plateau in the 1–2 mole fraction region of the toluene–$CuAlCl_4$ vapor pressure–composition curve (see Figure 1). The apparent low $\Delta H_D$ value for process 1 is completely acceptable as the formation of many molecular complexes is accompanied by only small changes in enthalpy.[16] For example, the heats of dissociation of the well-studied molecular complexes formed between iodine and aromatic molecules fall in the range of 0.1–2.0 kcal/mol.[17]

The removal of toluene from the 1:1 molecular complex is more difficult than removal of toluene from the 2:1 molecular complex. Removal of toluene from the 1:1 molecular complex requires the addition of 2.36 ± 0.24 kcal/mol of energy [$\Delta H_D$(process 2) − $\Delta H_{vap}$(toluene)] to rupture the charge-transfer interaction in the more tightly bonded 1:1 molecular complex. This binding energy is comparable in magnitude to the difference between the heat of dissociation and the heat of vaporization of the aromatic molecule found for 2:1 molecular complexes of $AlBr_3$ with toluene and *m*-xylene. Values of 2.3 and 1.6 kcal/mol were found, respectively, for the toluene and *m*-xylene complexes of $AlBr_3$.[18] In making this comparison, we have assumed that the Cu(I) and Al atoms are both $\pi$ complexed to the aromatic molecules. Binding energy comparisons with more closely related systems such as Ag(I)–aromatic molecule complexes cannot be made because the heats of dissociation of complexes of this type have not been reported. In light of the present work, binding energy values of 50[19] and 15.7[20] kcal/mol for the charge-transfer interaction between Ag(I) and benzene, which were calculated using crystal energy arguments, appear too high.

In the present paper we have observed that toluene forms both 1:1 and 2:1 molecular complexes with $CuAlCl_4$. It appears reasonable to speculate that the 1:1 molecular complex is formed by breaking one of the four Cu(I)–bridging chloride bonds in the polymeric $CuAlCl_4$ crystal lattice and replacing it with a Cu(I)–toluene interaction. By analogy with the structure of $C_6H_6 \cdot CuAlCl_4$,[9] the solid 1:1 toluene–$CuAlCl_4$ complex probably contains a polymeric pleated sheet network of $CuAlCl_4$ units with Cu(I)–toluene linkages protruding from the sheet. The major Cu(I)–toluene interaction most likely results from the overlap of an empty 4s orbital on Cu(I) with a filled $e_1$ type molecular orbital of toluene. Thus $\Delta H_D$ found for the 1:1 molecular complex is essentially the energy required to break this donor–acceptor interaction. This number should prove useful, especially to spectroscopists who are interested in relating the theory of charge-transfer spectra to intermolecular bond strengths.[21,22]

The addition of a second molecule of toluene to each $[C_7H_8 \cdot CuAlCl_4]_x$ unit in the 1:1 polymeric solid complex results in the production of a liquid 2:1 complex. This process is best thought of as a solvation process (additional Cu(I)–bridging chloride bonds are broken) producing a monomeric, $2C_7H_8 \cdot CuAlCl_4$, 2:1 complex.

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The existence of a discrete 2:1 molecular complex, aside from the vapor pressure–composition study, is further supported by molecular weight measurements which gave a value consistent with the species $2C_7H_8 \cdot CuAlCl_4$ when $CuAlCl_4$ is dissolved in toluene. An infrared study carried out on the liquid 2:1 complex[23] indicates the presence of two chemically different toluene molecules complexed to the Cu(I) center.

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# Inner-Sphere Mechanisms of Oxidation. II.[1] Stoichiometry and Kinetics of the Manganese(III) Oxidation of Thiocyanate, Thiourea, and Some Alkylthioureas in Acid Perchlorate Solution

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The kinetics of the rapid manganese(III) oxidation of excess thiourea, *N,N'*-dimethylthiourea, *N,N'*-diethylthiourea, and *N,N'*-ethylenethiourea have been studied in a stopped-flow apparatus over a range of acidities and temperatures at ionic strength 4.0 *M*. Although the reaction with $SCN^-$ was too fast to be followed by this method at 25° ($k_{obsd} \geq 3 \times 10^5$ $M^{-1}$ sec$^{-1}$ at $[H^+] = 1.00$ *M* and ionic strength 4 *M*), the stoichiometry of reaction with excess $SCN^-$ was the same as that measured with the thioureas in the presence of excess manganese(III), *viz.*, $\Delta[Mn(III)]/\Delta[\text{reductant}] = 1$, corresponding to the formation of S–S bonded products in each case. Evidence is presented for changes in the state of protonation and possibly the extent of tautomerism of alkylthiourea molecules over the experimental acidity range. By using the rate parameters for reaction of $Mn^{3+}_{aq}$ and $MnOH^{2+}_{aq}$ with monoprotonated thiourea as a basis, the rate constants for reactions of $MnOH^{2+}_{aq}$ with the monoprotonated alkylthiourea species are derived. Comparison of these rate constants with those for other reductants suggests an inner-sphere mechanism, with substitution at the manganese(III) center as the rate-determining process.

## Introduction

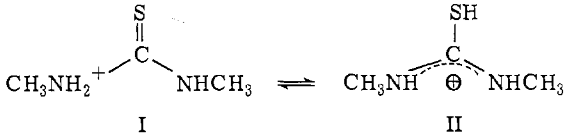
The rates of complexation and oxidation of thiocyanate and its derivatives may depend on whether or not attack takes place at the nitrogen or sulfur atoms of the molecule. For example, in this work it is shown that the rate of complexation of iron(III) by thiocyanate is considerably decreased by the presence of manganese(II), presumably because of the removal of free $NCS^-$ in the form of an N-bonded $MnNCS^+$ complex under these conditions. In addition, the inner-sphere oxidations of free thiocyanate by iron(III)[2] (in acetonitrile) and cobalt(III)[3] (in acid perchlorate solution) produce S–S bonded $(SCN)_2$, whereas the much slower oxidations of the inert, N-bonded complex $Co(NH_3)_5NCS^{2+}$ by $H_2O_2$[4] and cerium(IV)[5] produce $Co(NH_3)_5CN^{2+}$ (*via* isomerization of $Co(NH_3)_5NC^{2+}$), $Co(NH_3)_6^{3+}$, and $SO_4^{2-}$, rather than S–S bonded products.

Thiourea and the symmetrical alkylthioureas are converted to the corresponding disulfides in analogous reactions with cerium(IV)[6] and cobalt(III),[7] which might thus be construed as evidence for attack at nitrogen atoms rather than sulfur in these molecules.

The aquomanganese(III) cation $Mn^{3+}_{aq}$ is a strong

$$Mn^{3+}_{aq} \rightleftharpoons MnOH^{2+}_{aq} + H^+_{aq} \quad K_h \qquad (1)$$

acid in aqueous perchlorate media, with $K_h = 0.93$ *M* at 25° and ionic strength 1–4 *M*,[8] and this factor is important in determining the acid dependence of oxidation reactions of the Mn(III)–Mn(II) couple. Although thiourea molecules are believed to be monoprotonated[9] under the strongly acidic conditions where manganese(III) species are stable, the predominant molecular forms in solution have been the subject of debate.[10] For example, the tautomeric forms of the monoprotonated *N,N'*-dimethylthiourea species might be written



(2)

The observation of a disulfide product does not necessarily distinguish between these two forms even if they yield different oxidation products, since they might be rapidly interconvertible with reactions to disulfide being the fastest oxidation processes. Very rapid oxidation of II might conceivably lead to a situa-

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