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Complexation and Separation of Alkylaromatics with Copper(I) Trifluoromethanesulfonate

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Complexation and Separation of Alkylaromatics with Copper(I) Trifluoromethanesulfonate

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Abstract

A novel mode of complexation of aromatics has been observed in the case of copper(I) triflate. Further, it has been found that in the solid the spatial demands of the inorganic matrix dictates a unique stability ordering of the alkylaromatics based on their shape more than on their π-basicity. This property can be the basis of an efficient means of separating isomers; for instance, in isolating *p*-xylene from the other eight-carbon arenes. Brief attention is focused upon the mechanism of the ligand exchange reaction via which the separating ability is manifested.

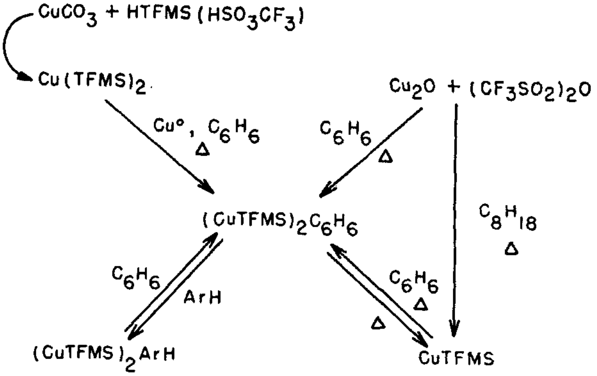
INTRODUCTION

In the effort to exploit the well-known capability of the copper(I) ion to complex unsaturated hydrocarbons, workers have sought appropriate counterions which would confer upon the system the desired stability, solubility, activity, and selectivity. These anions have typically derived from strong acids, since such conjugate bases are necessarily weak and hopefully coordinatively passive. Trifluoromethanesulfonic acid ("triflic" or "trimsylate" acid for short—HSO_3CF_3) has recently become readily available and presents an obvious fulfillment of the requisite properties for such a copper(I) agent. While we were pursuing this investigation, two other reports appeared on the subject (*1*, *2*); however, no details of the preparative and aromatic complexing properties of the system have been presented and are herein described.

RESULTS AND DISCUSSION

One of the favorable properties of the parent acid, aside from its extreme strength, is its nonoxidizing character (*3*). However, this same stability also implies that the copper salts are not accessible via simple reaction of the metal with the acid. The copper(II) salt is simply preparable via copper(II) carbonate. To prepare the copper(I) salt one must either reduce the copper(II) salt or react cuprous oxide with the acid or its anhydride, preferably in a passive diluent such as *n*-octane. Copper trifluoromethanesulfonate (CuTFMS) thus obtained is a maroon powder somewhat unstable in the atmosphere. In a sealed capillary tube the material decomposes above 300°C concomitantly with the appearance of crystals of copper. If, alternatively, in the preparation of CuTFMS one uses benzene rather than a paraffin, a light microcrystalline solid results which has the composition $(CuTFMS)_2C_6H_6$. Exhaustive heating of the bare salt in benzene or reduction of the copper(II) salt in benzene likewise affords this same complex (Scheme 1).

Benzene need not be the medium, and it has been found that any alkylaromatic will serve as the ligand if initially present during the formation of the salt, or if the complex of CuTFMS with benzene is subsequently treated with that alkylaromatic. The stoichiometry of the complex is invariably two salt units per aromatic in the case of nonheterocyclic single ring aromatics. [With polynuclear aromatics or *n*-donating heterocycles other stoichiometries are sometimes observed and will be separately reported. This ratio has not been previously found for copper(I) aromatic complexes.] The structure of the benzene complex has been reported (*4*)



SCHEME 1. Pathways to $(CuTFMS)_2C_6H_6$.

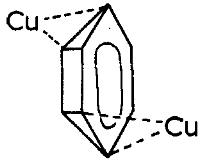


FIG. 1. Detail of the structure of $(CuTFMS)_2C_6H_6$.

and was found to involve bonding of two copper(I) ions to two alternate carbon-carbon bonds of the ring (without significantly inducing bond alternation) from opposite faces of the ring (see Fig. 1). The aromatic served to bind polymeric ladder-like chains of the CuTFMS together into sheets between which a van der Waals region exists.

The aromatic complexes are of low solubility in their respective neat liquids, and are even less soluble in paraffins. They are all quite sensitive to the atmosphere, and in a sealed tube they typically dissociate to the bare salt and regenerate the free aromatic at temperatures approximately 20 to 50° above the boiling point of the aromatic.

The ligand exchange reaction, in which one aromatic is substituted for another, is effected most simply if a paraffinic slurry of one complex is treated with an excess of the second aromatic. Equilibria such as are generalized in the following equation are thus established:

$$\underset{\text{(solid)}}{(\mathrm{CuTFMS})_2\mathrm{ArH}} + \mathrm{Ar'H} \underset{K_{eq}}{\overset{\text{paraffin}}{\rightleftharpoons}} \underset{\text{(solid)}}{(\mathrm{CuTFMS})_2\mathrm{Ar'H}} + \mathrm{ArH} \qquad (1)$$

A convenient means of expressing the equilibrium constants for a series of aromatics was found in the method described by Fetterly (5) who was dealing with urea clathrates. The equilibrium constant K_{eq} is actually a ratio of the dissociation constants (K_d) of the two complexes present. Thus in Eq. (1), K_{eq} may be equated with $K_{d_{\mathrm{ArH}}}/K_{d_{\mathrm{Ar'H}}}$. The absolute value of these dissociation constants is difficult to measure since their values are very low and extremely sensitive to solvent impurities. These evaluations are further complicated by the finding that the solubilities of the complexes in paraffins are of a similar order of magnitude to the dissociation, i.e., $\sim 10^{-4}$ M. Additionally, as discussed below, it is questionable that a true equilibrium is established in the absence of a substituting aromatic. However, the ratio $K_{d_{\mathrm{ArH}}}/K_{d_{\mathrm{Ar'H}}} = K_{eq}$ is readily measured using a ternary phase diagram (Fig. 2) and the relation

$$K_{eq} = K_{d_{\mathrm{ArH}}}/K_{d_{\mathrm{Ar'H}}} = \frac{X_{\mathrm{Ar'H}}Y_{\mathrm{ArH}}}{X_{\mathrm{ArH}}Y_{\mathrm{Ar'H}}} = \alpha_{\mathrm{ArH/Ar'H}}$$

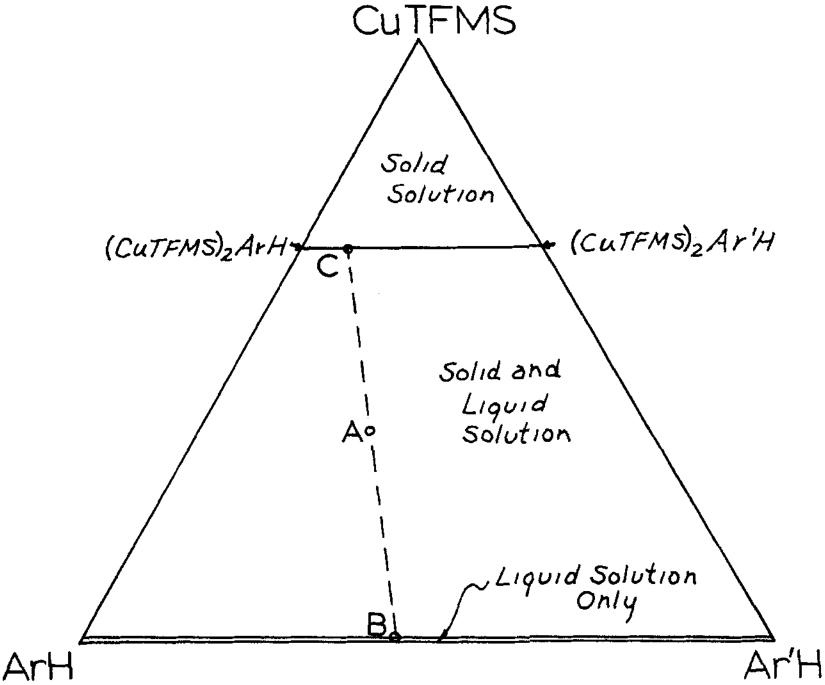


FIG. 2. General ternary phase diagram. A: Initial composition. B: Composition in liquid phase at equilibrium. C: Implied composition in solid phase.

X is the mole fraction of the component in the solid phase and Y is the mole fraction in the supernatant phase.

If several aromatic components are present, the designation α may be used in its usual sense as a separation factor. Experimentally, then, all that is needed to evaluate K_{eq} is the initial overall composition and the equilibrium composition of the supernatant phase—easily obtainable from gas chromatography. These two points yield the solid composition from the tie-line on the phase diagram. Since solubility of the complexes is so low, the single phase liquid solution region of the phase diagram is nearly nonexistent, and in reality the base of the triangle can be used for Point B.

The assumptions implicit in this approach are (a) that a solid solution exists, rather than discrete phases; (b) that the same stoichiometry holds for the complexes; and (c) since a paraffin diluent was used to expedite formation of a tractable supernatant (for GC analysis), it is assumed that the actual quaternary component system is suitably approximated by a ternary phase diagram.

As a reference complex, the benzene adduct was arbitrarily assigned the value K_d of unity—in other words, all values are referred to the benzene complex. Therefore the values of K_{eq} reported are greater than 1 for complexes more stable than benzene, and less than 1 for those of lower stability. Table 1 summarizes the K_{eq} (or α) values thus obtained. In actual practice the benzene complex was usually used, since it seemed to have a stability of intermediate order, and also since it was the most available. It was shown, however, that the values were valid by cross checking some complexes against one another. Furthermore, the equilibrium constants held, starting on either side of the chemical equation. Although the equilibrium could be attained in various paraffins, the rate of approach was solvent dependent, and *n*-pentane was usually used because it afforded the quickest attainment of equilibrium.

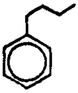
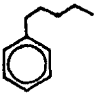
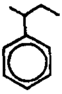
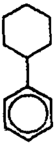
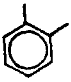
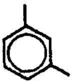
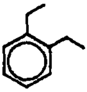
It is immediately evident that the stability ordering does not follow previously established patterns of π-basicity, which correlate with electron richness of the π-system, and roughly increases with the number of alkyl substituents on the rings (*6*). This, of course, is not to say that the bonding between the ring and the metal is not of the typical σ-π type (*7*), but rather that the predominating factors dictating the comparative stability are found elsewhere—more than likely from the geometrical spacial constraints of the solid-state structure of the agent.

It is also apparent from the values of α that the bulk size of substituent, although a factor, is of subordinate significance compared to shape and to placement on the ring. Thus cyclohexylbenzene is far more stable than *n*-pentylbenzene, and *para*-substituted isomers are generally more stable than *ortho* and *meta* analogs in the three representative cases. The immediate proximity of a second aromatic ring seems to enhance the stability, possibly via an electronic contribution to the π-system.

Although little effort has been expended to illuminate the precise mechanism of the substitution, several pertinent observations suggest that it may involve a direct solid phase reaction. Despite the marginal solubility of the benzene complex in pentane ($\leqslant$40 mg/10 ml), the exchange with *p*-xylene proceeds with facility ($t_{1/2} < 1.5$ min). The ability of a dry bed of the benzene complex to undergo exchange when subjected to vapors of the xylenes further corroborates the hypothesis that intermediate steps involving solution need not be invoked. Additionally the slow formation of the complex from bare CuTFMS and benzene almost certainly rules out its intermediacy. Hence a picture emerges of the

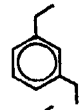
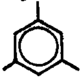
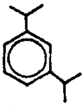
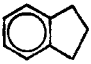
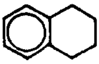
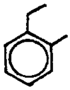
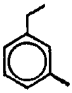
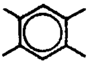
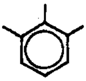
TABLE 1

Selectivity Factors (α) for Alkylaromatics[a]

Aromatic	α (benzene = 1)
	0.70
	0.08
	0.04
	0.05
	0.02
	0.02
	0.9
	1.24
	0.46
	16.0
	1.9

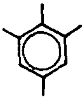
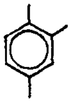
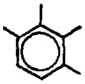
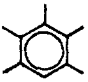
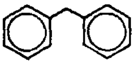
(continued)

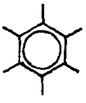
TABLE 1 (*continued*)

	0.3
	6.5
	0.03
	0.04
	5.1
	1.1
	0.9
	0.4
	0.2
	2.1
	0.01
	3.4
	1.4

(*continued*)

TABLE 1 (*continued*)

	0.05
	1.2
	0.6
	0.4
	25.0
	43.0
	3.0

[a] Unsuccessful attempts were made on  and  due to solubility problems and the fact that for very low α values (<0.01) the dissociation of benzene from the complex negates the veracity of the result.

exchange in which the inorganic backbone remains intact, possibly with aromatics diffusing in and out by way of the van der Waals space between the sheets.

Efforts to measure the enthalpy of the interaction either from a slurry or gas–solid derived dependence of ln K_d on reciprocal temperature were unsuccessful owing to an apparent hysteresis and/or rate effect. It seems that in a substitution reaction sequence there are never very many vacancies in the lattice, since one aromatic can with facility replace another. However, in an experiment during which no ligand replaces those diffusing out, it may be that long-lived vacancies, or local accumulations of vacancies, lead to a gradual irreversible degradation of the lattice, with oxygens filling the sites left open, and a local return to the nonreactive bare CuTFMS configuration results. It will be recalled that this substance is complexed only after exhaustive heating in neat aromatic. Inactive CuTFMS likely has a three-dimensional polymeric structure which must be broken down and reorganized before the aromatic structure can result.

What is actually observed when the vapor pressure of the solid benzene complex or the activity of benzene in a hydrocarbon slurry is measured, is a slow increase without attainment of an equilibrium value. Furthermore, on lowering the temperature no clear response such as would be expected in a true equilibrium situation is seen.

As a demonstration of the practical application of the complex, Fig. 3 illustrates the changes in the composition of a typical eight-carbon aromatic fraction (20% ethyl benzene, 20% *o*-xylene, 20% *p*-xylene, and 40% *m*-xylene) with time when the benzene complex was contacted in a pentane slurry. The *p*-xylene rich (~ 80%) complex can be either destructively decomposed using aqueous cyanide or other materials, or the complexed aromatics can be exchanged off, regenerating active agent.

Other difficult separations are also suggested by the α values and could be carried out in the same way, or in variations. For instance, it has

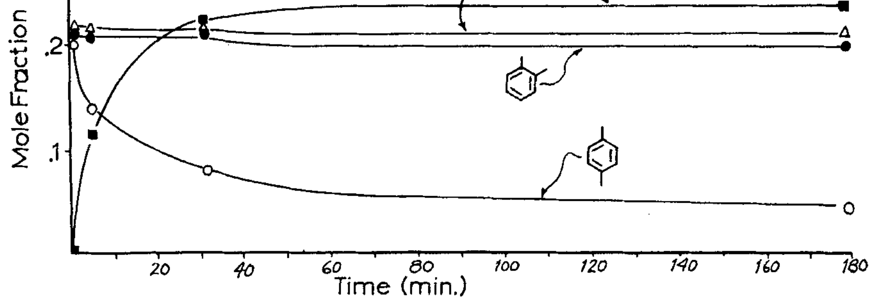


FIG. 3. Change in the composition of the supernatant of a slurry of $(CuTFMS)_2C_6H_6$ (2.4 g) in pentane with 1.2 g blend composed of ethylbenzene (20%), *o*-xylene (20%), *m*-xylene (40%), and *p*-xylene (20%).

been mentioned that the gas–solid reaction also works, and in the case of the xylenes very similar α's were found when a dry bed of $(CuTFMS)_2C_6H_6$ was treated with a nitrogen stream saturated with the isomeric eight-carbon aromatics.

EXPERIMENTAL

Since most of the preparations followed certain general procedures, only representative examples will be presented. Solvents were distilled and heart cuts used. Reagents, unless otherwise specified, were used as received from suppliers. Melting and decomposition points were taken on a standard Mel-Temp device and are corrected. All work was performed under a blanket of nitrogen or in a dry box. Gas chromatography was carried out on an Aerograph 1520 instrument. Whenever the xylenes were examined, a 6 ft × 0.125 in. stainless steel column of 10% Benton 34, 10% diisodecylphthalate on Chromasorb W was used, operating at 75 to 125°, usually with a programmer. Copper analyses were performed using a standard iodometric titration technique.

Preparation of Copper(I) Trifluoromethanesulfonate

In 50 ml octane and 35 g trifluoromethanesulfonic acid anhydride, 16.7 g cuprous oxide was added and the mixture slowly brought to reflux (first 85°, then 125°) overnight. The resulting maroon slurry was filtered and dried, leaving 44.4 g (90%) dark red powder, dec. (sealed tube) 300–305°.

Analysis. Calculated for $CuSO_3CF_3$: C, 5.65; Cu, 29.9; S, 15.05. Found: C, 5.36; Cu, 30.0; S, 14.12. This same composition could also be obtained by heating the aromatic complexes in a vacuum extensively or in a high boiling paraffin such as octane.

Di(copper(I) Trifluoromethanesulfonate) Benzene Complex

From the Bare Salt. In a Soxhlet apparatus loaded with 2.0 g CuTFMS, benzene was refluxed for 24 hr. From the benzene extracts, 1.8 g light tan solid was isolated, copper analysis 23.7%. (A complete analysis is given following the next preparation.)

From Cuprous Oxide. Into 250 ml benzene, 127 g (0.45 *m*) trifluoromethanesulfonic acid anhydride and 48.2 g (0.338 *m*) cuprous oxide were added. The mixture was brought to reflux for 1 day, cooled, and filtered in a dry box. White microcrystals (155 g, 0.31 *m*) were thus recovered which darken in a sealed capillary tube at ~ 125 °C.

Analysis. Calculated for $Cu_2S_2O_2C_8H_6F_6$: C, 19.10; H, 1.20; Cu, 25.10; S, 12.75. Found: C, 18.83; H, 1.19; Cu, 24.50; S, 12.96.

Di(copper(I) Trifluoromethanesulfonate) *p*-Xylene Complex from the Copper(II) Salt and Cu^0

This method is most useful for higher boiling aromatics: Copper(II) trifluoromethanesulfonate was prepared from basic cupric carbonate and the acid. This salt (3.0 g) and 1.0 g copper powder were added to 40 ml *p*-xylene and the mixture refluxed 36 hr and filtered hot. From the cooling filtrate, 0.80 g solid crystallized which was identical to the substance obtained from slurrying the benzene complex (previous preparation) in excess *p*-xylene.

Analysis. Calculated for $Cu_2S_2O_6C_{10}H_{10}F_6$: C, 22.6; H, 1.9; Cu, 23.9. Found: C, 22.0; H, 2.1; Cu, 23.5.

Generally, the route used to prepare most of the aromatic complexes was to use the preformed benzene complex by slurrying in neat aromatic, heating to drive off the benzene, and cooling, an example of which follows. However, the other means are also applicable (i.e., cuprous oxide with the acid or anhydride or cupric TFMS and copper powder and extended heating in the neat aromatic).

Preparation of the Tetralin Complex from the Benzene Complex

To 10 ml tetralin was added 2.5 g $(CuTFMS)_2C_6H_6$ and the slurry stirred at room temperature for 1 hr. It was then filtered, washed with pentane, and dried in a dry box. There resulted 1.6 g light tan solids, having a copper analysis of 23.0% [$(CuTFMS)_2C_{10}H_{12}$ requires 22.85% Cu]. The same material (although of a better crystalline nature) was obtained either from the reaction in Tetralin of cuprous oxide and TFMS anhydride, or from reaction of $Cu(TFMS)_2$ and copper powder in refluxing Tetralin (dec 160°). If the exchange route is used to prepare a complex of lower stability than the benzene complex, it is preferable to use a large excess of the neat aromatic and to heat the reaction. Once formed, it is convenient to test the purity of a new complex (besides analyzing for copper) by decomposing some of it between dilute nitric acid and pentane, and shooting some of the pentane solution resulting into a GC. This will provide an assay for complexed aromatic.

Determination of α for *o*-Xylene

To 5.0 ml *n*-octane, 2.0 g $(CuTFMS)_2C_6H_6$, 0.6 ml *o*-xylene, and 0.3 ml benzene was added and the slurry was stirred at room temperature. Samples were withdrawn periodically until no further change in the composition of the supernatant was seen. At equilibrium the aromatic content of the supernatant was 59.5% benzene, 40.5% *o*-xylene. Using a ternary diagram as described in the text, the $\alpha_{o\text{-xylene}}$ was calculated to be 1.20. In many cases, the α value was checked by starting with several compositions or by using the complex of both aromatics.

Acknowledgments

The author is grateful to E. J. Fuller for enlightening discussions and to Raymond Kelly for his able technical assistance.

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