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HYDROCARBON SEPARATION USING LIGAND EXCHANGE REACTIONS

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INTRODUCTION

Organometallic complexes bridge the gap between organic and inorganic chemistry or for that matter, between the world of the living and non-living. Life on this planet may well have been initiated by the interaction of coordinated ligands of complexed metal ions. The abundance of carbon monoxide, ammonia and a "hot soup" of metal ions in the absence of oxidizing agents make it entirely feasible that organic molecules first became synthesized in this manner. The presence of organometallic complex molecules in the life stream of plants and animals attest to the fact of their necessity in life sustaining processes.

Today we find that organometallic compounds are of ever increasing importance in the "life stream" of the Chemical Processing Industry. Homogeneous catalytic processes based on coordination compounds are becoming well established in the Industry as primary synthesis routes. Many of our present processes which are operating inefficiently will be replaced, in the future, with processes which convert raw material to finished product at greater selectivity and yields. It is only logical that companion purification processes based on coordination compounds of metal complexes will be developed to replace conventional systems. The motivation for development of such processes is primarily economics; but improved product quality, higher efficiency and reduced

pollution through lower energy requirements are often cited as justification for doing research on any separation-purification problem.

It is well known that certain metal ions of complexes in anhydrous solutions form coordinated compounds with the π -bonds of aromatics and olefins. The chemical bonds which are formed between the metal ion and the hydrocarbon are often weak enough to allow exchange or displacement reactions with compounds of similar type in equilibrium with the complex solution. A process of this nature is a powerful tool for separating compounds which have π -bonds from those which do not. For example, in hydrocarbon systems, since the metal ion can react only with an olefin or an aromatic, saturated hydrocarbons are rejected and extraction selectivity approaches infinity. In addition, aliphatic olefins are selectively extracted from aromatics. No simple organic solvent can make such a separation, economically.

Areas where ligand exchange extraction techniques have proved useful are in the extraction of aromatics from non-aromatics, olefins from aromatics, olefins from paraffins, olefins from other olefins and carbon monoxide from other gases. One of the most unique separations is that of extracting cis olefins from trans olefin isomers. Another is the extraction of vinyl substituted aromatics from other close boiling aromatics. These ligand exchange processes involve very low orders of energy requirements while yielding purities and recoveries of desired species difficult or impossible to attain by conventional physical processes.

Since Zeise's observation in 1827^[1] that ethylene formed a solid compound with certain platinum salts, many investigators have studied the reaction of unsaturated hydrocarbons with a variety of inorganic salts. However, practical application of these compounds has been limited. Cuprous ammonium acetate complex, which is used to recover butadiene from crude C₄ streams, is a classic example of a practical commercial application.

In 1946, Anderson^[2] described the effect of olefin substitution on complex stability. Kharasch^[3] reported a generally applicable method of replacing benzonitrile residues of PdCl_2 with mono, di and oligo olefins. This latter reaction was of considerable interest to the authors in that it presented the potential opportunity for developing highly specific techniques for separating olefins from mixed hydrocarbon streams. The relative stabilities of various olefin complexes of palladium salts have been determined by Sparke^[4]. Featherstone and Sorrie^[5] have discussed the effect of silver salt concentration on coordination of olefins and the effect of hydrocarbon structure on complex stability in some detail. Winstein and Lucas^[6] studied the coordination of silver ion with unsaturated compounds and noted that solid silver complexes were formed with biallyl and cyclopentadiene.

Silver nitrate has been used extensively in analytical chemistry for the quantitative determination of olefins in saturated hydrocarbons after being patented by Horsley in 1928. Bonding energies of olefins and diolefins with silver complexes have been measured by H. W. Quinn and coworkers^[7,8,9]; J. G. Traynham and J. R. Olechowski^[10] and J. W. Kraus and E. W. Stern^[11]. Olah and Quinn improved the preparation of silver tetrafluoroborate^[12] in 1960 and since that time it has been used in aqueous and non-aqueous extraction studies. William Featherstone of Imperial Chemical Industries has patented a process for extracting styrene from ethylbenzene using aqueous silver tetrafluoroborate^[13]. Krekeler, Hischbeck and Schwenk reported to the Sixth World Petroleum Congress^[14] the advantages of silver tetrafluoroborate and ethanolamine-copper-nitrate complexes for ethylene and propylene recovery.

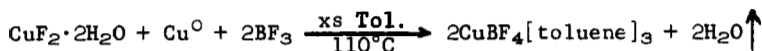
The preparation of cuprous tetrafluoroborate complex has been described by J. C. Warf^[15]. Unlike the silver complex which can be prepared in anhydrous crystal form, the copper complex must be prepared in the presence of coordinating ligands and cannot be isolated as a stable salt.

D. A. McCaulay^[16] has described the preparation and use of a cuprous tetrafluoroborate aromatic complex for extracting aromatics from non-aromatics. McCaulay's complex contained two aromatic molecules per copper ion.

Our investigation has improved the preparation of some cuprous and silver complexes and established their composition. We have extended these improved complex compositions to greater potential utilization. Ligand exchange techniques have made possible the practical application of these complexes to industrial separation problems.

EXPERIMENTAL

Cuprous tetrafluoroborate is best prepared by the method of Warf^[15] with only slight modification of his original technique. Cupric fluoride and powdered copper metal are reacted with BF_3 in an excess of refluxing toluene:



In this preparative technique, gaseous BF_3 is continuously passed into a flask equipped with an agitator and a reflux condenser. Water is continuously removed from the reflux condensate in a water trap. When the dispersed solids become dissolved, the reaction mixture is cooled to room temperature. The complex phase is separated from the excess toluene and centrifuged to remove suspended solids. The complex is usually a pale yellow, clear, slightly viscous liquid; but extended dehydration by azeotropic refluxing yields a toluene complex which is easily crystallized by lowering the solution temperature to 0°C or by adding hexane. However, the complex composition is not altered with respect to the number of coordinated toluene ligands.

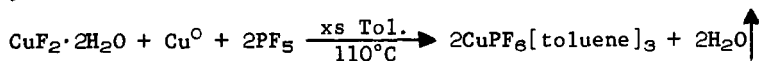
Other aromatics may be used instead of toluene in these preparations, but there are practical limitations. The reaction is slower in refluxing benzene [80°C] and dehydration is not as efficient. Complex yields are low when xylenes are used possibly

because of thermal instability or lower BF_3 solubility. Toluene provides the optimum reflux temperature for complex preparation. Mixtures of benzene with toluene and toluene with xylenes have been used in these preparations with good success but mixed aromatic ligands are not desirable. The mixed ligands complicate complex analysis in analytical separations and evaluations.

The complex prepared in pure toluene was analyzed and found to contain three toluene ligands. The complex also contained from 0.25 to 0.5 ligands of water depending on how much dehydration occurred during preparation. $\text{CuBF}_4[\text{toluene}]_3$ liquid complex has a density of 1.22 to 1.26 grams per cc at 25°C . Its calculated molecular weight is 426.48. Freezing point determination shows no definite crystallization point, but the complex becomes glassy around -70°C .

The cuprous tetrafluoroborate complex is sensitive to oxygen and disproportionates on contact with moisture. Water ligands can be added to the anhydrous complex by exchange from hydrated copper salts [e.g., $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$] without causing complex decomposition.

Cuprous hexafluorophosphate was prepared in the apparatus described above in much the same manner as the fluoroborate complex. Phosphorous pentafluoride was reacted with cupric fluoride dihydrate and finely divided copper metal in excess toluene.

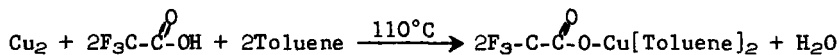


Synthesis of this complex suffers from the highly competitive hydrolysis reaction;



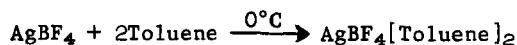
Cuprous hexafluorophosphate toluene complex is a white crystalline solid at room temperature and disproportionates rapidly upon exposure to water vapor. The complex slowly decomposes on standing in sealed bottles at room temperature. It is soluble in excess toluene and in sulfolane when heated to 80° .

Cuprous trifluoroacetate was prepared by adding trifluoroacetic acid to Cu_2O in refluxing toluene.



The reaction is essentially instantaneous and does not require an induction period as does the CuBF_4 synthesis. While the reaction proceeds well at room temperature, the preparation is conducted at 110°C to remove the generated water.

Silver tetrafluoroborate complex can be conveniently purchased in either anhydrous or aqueous form. Aromatic coordination complexes were prepared by adding anhydrous AgBF_4 to the desired aromatic chilled to 0°C .



The silver tetrafluoroborate complex was also prepared from AgF and BF_3 in nitromethane according to the method of Olah and Quinn^[17] and in liquid sulfur dioxide as reported by Russell and Sharp^[18]. The sulfur dioxide solvent produced better results than did nitromethane. Pure silver fluoride was prepared from Ag_2CO_3 and aqueous HF by the method of Andersen and Bak^[19].

Cuprous tetrafluoroborate complex was found to be superior to other complexes in its ability to coordinate π -bonds. After initial evaluation, study of AgBF_4 , CuPF_6 and cuprous trifluoroacetate complexes was discontinued. Cuprous tetrafluoroborate complex could coordinate three or four ligands, while the other complexes could coordinate with only two ligands. CuPF_6 was very unstable due to sensitivity of its anion to hydrolysis. Cuprous trifluoroacetate was miscible in all proportions with all hydrocarbons and most organic solvents. Immiscibility did occur in some nitrile solvents, but at the expense of considerable coordination capacity. For these reasons, the bulk of our investigations concerned cuprous tetrafluoroborate complex and this discussion will be directed toward the results of that investigation.

The structure of cuprous tetrafluoroborate complex is dictated by the electronic configuration of the cuprous ion. The outer electron shell consists of filled $3d$ electron orbitals, empty $4s$ and empty $4p$ orbitals. The cuprous ion can accept 2

electrons at the $4s$ level and 6 at the $4p$ level for a total of 8 electrons. Hence, a coordination number of 4 and the closed configuration of krypton is assumed. Theoretically, the cuprous ion can coordinate with 4 ligands each of which donate 2 electrons to form the coordination bonds. These bonds are probably formed through the empty sp^3 hybrid atomic orbitals of the cuprous ion and the π molecular orbitals of the donor groups [aromatics, olefins, etc.]. The sp^3 hybrid orbitals are oriented in space in a manner which would give the ligands of the coordination compound a tetrahedral spacial configuration. The tetrahedral configuration for the cuprous ion is assumed with bonds formed at the apices from the electron rich π -bond of the donor group. Most likely the tetrahedron is distorted when polar ligands such as water, etc. are coordinated in conjunction with hydrocarbon ligands.

The current view of bonding between π bonds and metal ions was advanced by M. J. S. Dewar in 1946^[20] and elucidated by Chatt and Duncanson in 1953^[21]. Their views have been helpful in the interpretation of the bonding of ligands to the cuprous ion of the cuprous tetrafluoroborate complex.

Something should be said about the fluoroborate anion and its stability. BF_3 has a trigonal planar structure and the bonding energy of each boron-fluoride bond is about 140 kilocalories. The BF_4 anion has a tetrahedral structure and being equal each boron-fluoride bond has a bonding energy of 150 to 158 kilocalories per mole. Therefore, the BF_4 anion gains 40 to 70 kilocalories per mole upon formation. It is believed that the cuprous ion tetrahedron and the fluoroborate tetrahedron exist in the anhydrous solution as an ion pair. The toluene-cuprous tetrafluoroborate complex is extremely stable in the absence of air and moisture and has a very long shelf life when sealed in glass.

General Reactions of $CuBF_4$ Complex

For the purpose of orientation, the bonding energy of coordination compounds is compared to those of other physical separation

processes in Figure 1. The ligand bonding energy of coordination compounds ranges from about 2 to 20 kilocalories per mole. This energy range spans the scale from weak solution effects to the adsorption of hydrocarbons on crystal surfaces such as zeolites or silica gels. The upper energy range approaches that of weak molecular co-valent bonds. Ligand to metal ion bond distance varies from 2 to 2.5 Ångstroms. Thus it can be seen that coordination compounds occupy an enviable position and may be classified as liquid adsorbents as opposed to solid adsorbents or super selective solvents when compared to conventional selective solvents.

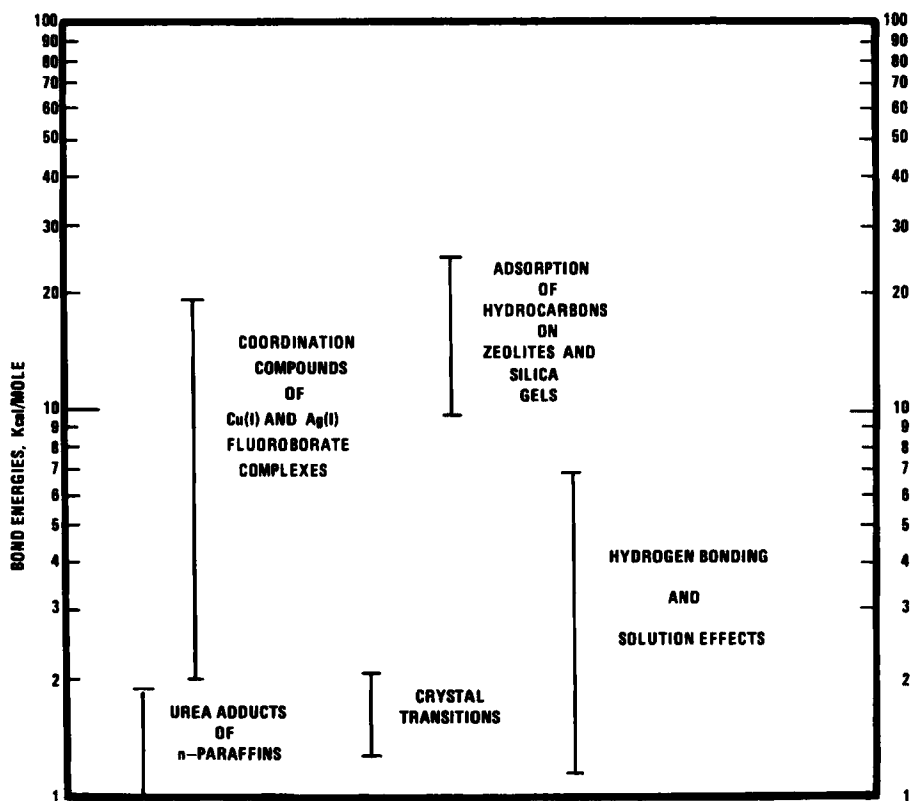
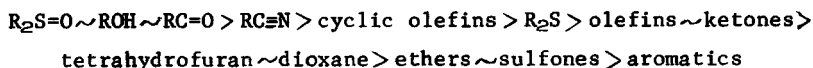


FIGURE 1.

Some association energies for single bond formation.

As prepared the $\text{CuBF}_4[\text{Tol}]_3$ complex is not very stable because aromatics are relatively poor complex stabilizers.

Cuprous ion stabilization can be increased by adding ligands with stronger coordination power than aromatics. Ligands such as olefins, ketones, sulfones, ethers, dioxane or tetrahydrofuran are very good stabilizers. These compounds are listed in order of decreasing coordination strength as determined by ligand displacement studies.



It can be seen that aromatics are displaced by sulfones, ethers, etc. and that these compounds are in turn displaced by olefins. Nitriles completely displaced all hydrocarbons and all other organic compounds studied.

Sulfoxides, alcohols, aldehydes and amines cause copper ion disproportionation when added directly to the $\text{CuBF}_4[\text{Tol}]_3$ complex.

As shown there are ligands which stabilize the CuBF_4 complex and still allow ligand exchange reactions to take place. Olefins and aromatics or olefins and some organic compounds were found to exchange very rapidly when brought into contact with the complex. Sulfolane, for example, was found to be a very good reaction solvent because it functioned both as a stabilizing ligand and mutual solvent which did not interfere with exchanging ligands.

Cyclic olefins form coordination compounds which are too stable to allow ligand exchange reactions to proceed at reasonable rates. It is possible that the shape of the cyclic olefin combines with its crystal structure to make it resistant to ligand exchange. Nitriles were the only compounds in the test series capable of exchanging the cyclic olefin coordinated ligands.

When arranged on the bond energy scale as shown in Figure 2 it can be seen that the bond energy of ligands preferred in ligand exchange reactions ranges from about 8 to 12 kilocalories per mole. Olefins, CO, vinylaromatics and sulfolane ligand bond energies fall, conveniently, in this range. These ligands all have very

small differences in bonding energy and were selected to demonstrate the performance of the CuBF_4 complex in making selective separations.

The effect of molecular geometry on ligand bond energy is shown by the range covered by various substituted aromatics. This will be discussed in detail later.

Olefins are more strongly coordinated than aromatics and are exchangeable with other olefins. The only driving force for this exchange reaction is concentration. An excess of the displacing olefin in the hydrocarbon phase will shift the concentration of

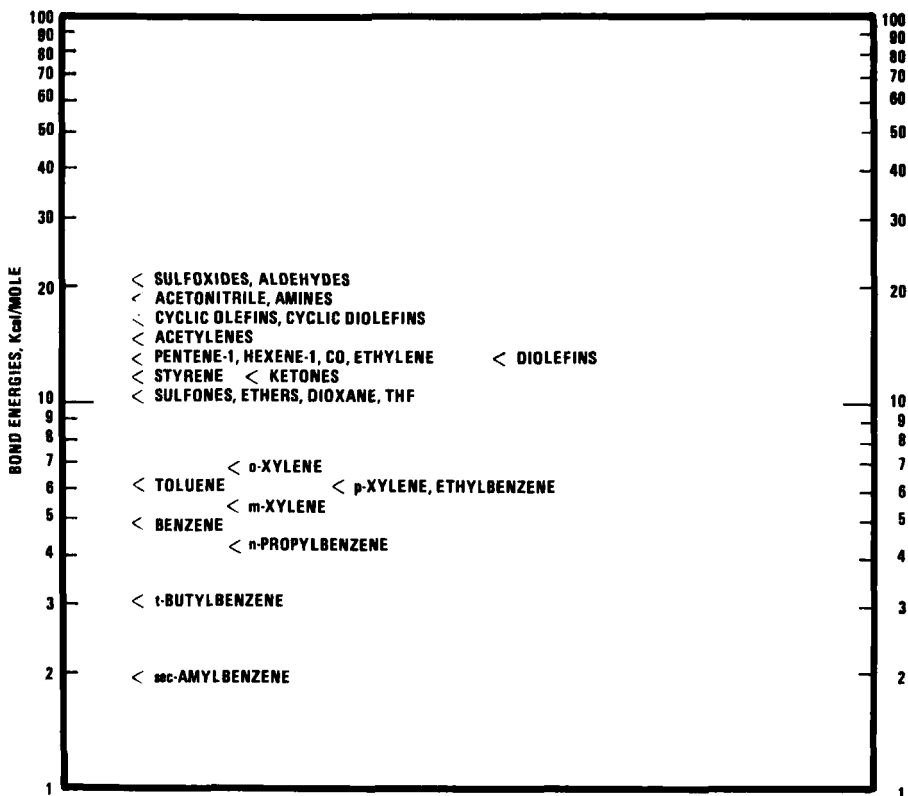


FIGURE 2.

Bond energies for some ligands on CuBF_4 complexes.

the coordinate species in the complex phase until an equilibrium composition is attained. This equilibrium concentration is dependent upon the strength of the bond formed between the olefin and the copper atom. The bond energy is closely related to molecular weight [vapor pressure, activity] and molecular configuration [accessibility of the double bond] which determines the bond length. The association energies of olefin-metal complex bonds are comparable to those of chemisorbed molecules on catalyst surfaces, zeolites and silica gel.

Cyclic olefins are more strongly bonded to CuBF_4 complex than aliphatic olefins. They form crystalline gel or polymeric complexes in various colors [e.g., brown, purple, violet, blue, etc.]. Cyclohexene complex is purple and slowly crystallizes after the initial gel formation. The 4-methylcyclohexene complex is dark blue and slightly soluble in toluene. It is more of a viscous liquid than a gel. Cyclopentene forms a brown, gel complex which slowly crystallizes. Cyclic olefin- CuBF_4 complex bonds are the strongest formed by hydrocarbons and can only be broken by compounds forming bonds through nitrogen or some oxygen atoms.

Vinylcyclohexene and dicyclopentadiene form polymeric complexes, and bonding strength appears to be about the same as cyclic olefins. Vinylcyclohexene complex is a very tacky, polymeric gel which is insoluble in hydrocarbons. Dicyclopentadiene complex is a very hard amorphous solid which is also insoluble in hydrocarbons.

The bond strength for hydrocarbons may be arranged in the order of decreasing strength as follows:

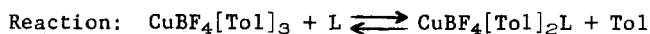
Cyclic diolefin \sim cyclic olefins $>$ acetylenes $>$ aliphatic
diolefins \sim aliphatic monolefins $>$ aromatics $>$ cyclic
and aliphatic paraffins.

It is believed, but not proven, that saturated molecules do not form coordination compounds with complexes. But, they are soluble to some extent in most complexes and are given the lowest order in the series of bond strength since solubility implies some secondary association.

These compounds were arranged in order by equilibrium studies and measurement of heats of reaction for a few key compounds which are shown in Table I. The heats of reaction are for the exchange of one given ligand for one toluene ligand. The binding energy of the toluene ligand was taken to be 6 kilocalories per mole as measured by reacting toluene with solid AgBF_4 and this amount of energy must be added to the value shown to obtain the total ligand binding energy. The values obtained in our laboratory compare well with those obtained by Christensen and Izatt of Brigham Young University [private communication]. The value given for CO was calculated from thermal dissociation curves at constant CO loading which will be discussed later. CO is very similar to ethylene or propylene in its bonding characteristics.

This binding energy is for the first ligand to exchange. We have evidence which leads us to believe that each additional ligand is bound less strongly. This is reflected in vapor pressure measurement and thermal stability curves for various coordination compounds.

TABLE I
Heats of Reaction for CuBF_4 Toluene Complex



<u>Ligand, L</u>	<u>ΔH, Kcal/mole for Reaction</u>	
	<u>Our Work</u>	<u>Others</u> [*]
Acetonitrile	-9.9	-11.0
Pentene-1, Hexene-1	-5.5	- 6.0
Styrene	-4.2	- 4.3
Sulfolane	-4.0	- 3.8
Carbon Monoxide	-5.4	-

^{*}J. J. Christensen and R. M. Izatt, B.Y.U., Provo, Utah
Private Communication

The apparatus used in our heat of reaction measurements, as shown in Figure 3, was a small cell with evacuated walls which was mounted inside a second vacuum bottle for double insulation. The cell was equipped with a heater, stirrer, capillary tube and thermal sensor. A toluene solution of $\text{CuBF}_4[\text{toluene}]_3$ was charged to the cell and vigorously agitated. A measured impulse of electrical energy was passed through the heater coil and the response of the sensing diode was recorded. A quantity of reactant was injected through the capillary with a micro-syringe and the recorder deflection was again noted. By comparing this deflection with the calibration heat, the heat of reaction was calculated.

In the displacement reactions shown in Table II, $\text{CuBF}_4[\text{toluene}]_3$ complex was reacted with various organic compounds and the resulting coordination compound was, in turn, reacted with an

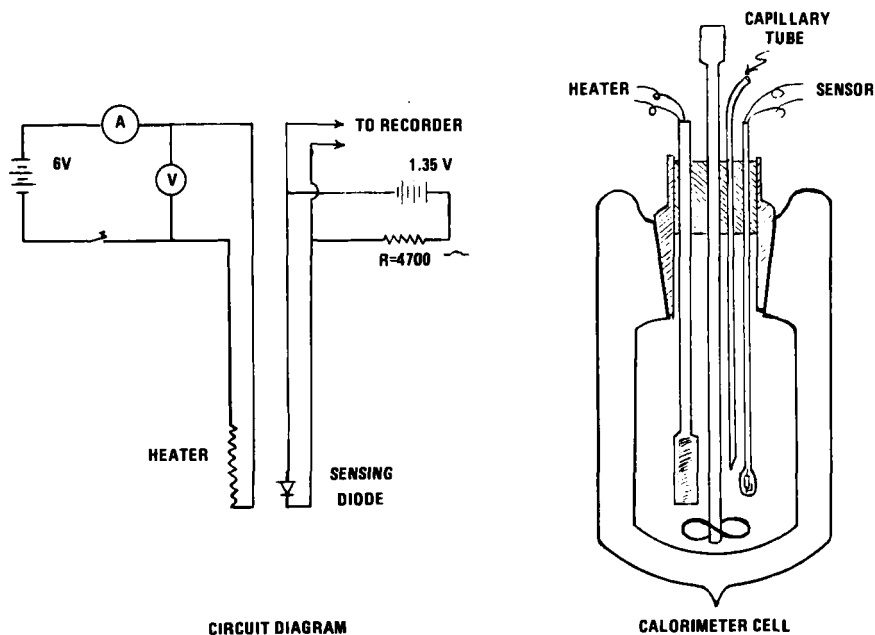


FIGURE 3.

Apparatus for measurement of reaction enthalpies.

TABLE II
Reaction of Compounds With CuBF_4 .Toluene Complex

<u>Compound</u>	<u>Resulting Reaction</u>	<u>Addition of Olefin</u>
Sulfolane	Stable, yellow solution	Olefin coordinated
Tetrahydrofuran	Orange precipitate plus light green solution	Olefin coordinated, precipitate dissolved
Dimethyl sulfoxide	Heated reaction, Cu mirror, black precipitate plus green solution	Insoluble, no coordination
Dioxane	Heated reaction, white gel, violet solution	Olefin coordinated, gel dissolved, color changed
Tri-n-butylphosphate	Complete decomposition of complex Cu mirror, black precipitate	
Dimethyl sulfone	Same as sulfolane	Olefin coordinated
Ethoxysulfolane	Same as sulfolane	Olefin coordinated
N-Methylmorpholine	Mixture of brown and orange precipitate plus clear hydrocarbon layer	
Acetic anhydride	Blue and lavender precipitate plus violet colored complex solution	

TABLE II [Cont'd.]
Reaction of Compounds With CuBF_4 -Toluene Complex

<u>Compound</u>	<u>Resulting Action</u>	<u>Addition of Olefin</u>
Acetic anhydride [Cont'd.]	plus clear hydro- carbon phase	
Carbon disulfide	Brown viscous com- plex plus hydro- carbon layer	
Diethyl disulfide	Light green stable complex plus hydro- carbon layer	
Diphenyl sulfide	Slowly reacts to form white crystals [liquid point $\sim 60^\circ\text{C}$], decomposed by water	Olefin reacted at 45°C to form stable liquid complex
Nitrobenzene	Deep red, liquid complex	Olefin coordinated and solution became colorless

olefin, usually pentene-1 or hexene-1, to determine if ligand exchange would occur.

CuBF_4 will form coordination compounds with organic compounds containing nitrogen, oxygen or sulfur atoms. When two functional groups are available in the same molecule, the one that forms the strongest bond will dominate the reaction. Generally, nitrogen forms the strongest bond with $\text{Cu}[\text{I}]$ cation followed by sulfur and oxygen. This order does not always apply when different arrangements of the atoms are possible. For example, sulfoxide, sulfone and sulfate groups have different bonding strengths. Some compounds, such as aldehydes, alcohols and amines destroy the complex.

DAVIS AND MAKIN

One compound of special interest is diphenyl sulfide because of its unusual and unique behavior with CuBF_4 . Addition of small quantities of diphenyl sulfide to $\text{CuBF}_4[\text{toluene}]_3$ forms a liquid compound, and toluene is displaced forming a separate phase. Introducing additional diphenyl sulfide to the complex has no immediate effect. Then, after a short induction period, crystals begin to form at a rapid rate, starting from numerous points throughout the solution. Crystal formation, which is accompanied by noticeable heat evolution, continues until the entire solution solidifies. The diphenyl sulfide complex liquifies when heated to 60°C and recrystallizes upon cooling. Aliphatic olefins are not soluble in this complex until it is heated to about 45°C . Cyclic olefins are soluble at room temperature.

It is suspected that in those reactions which gave green products, the reagent contained traces of peroxide and, in fact, the cuprous complex has been used to detect peroxides in olefins. It can be generally stated that the complex can coordinate a large variety of compounds containing sulfur and/or oxygen and still exchange with olefins. Obviously, more work is needed in this area to better define the reactions of organic compounds with CuBF_4 . Physical properties and structural determinations would be beneficial to the understanding of related CuBF_4 complexes.

The reaction of $\text{CuBF}_4[\text{toluene}]_3$ complex with various nitriles is shown in Table III.

As stated previously, the cuprous complex reacts with nitriles to form very stable coordination compounds. When fully coordinated with four nitrile ligands the complex is unable to react with olefins. However, when only one nitrile ligand is coordinated, the complex is able to exchange other ligands and its stability is much improved. The benzonitrile and phenylacetonitrile complexes are stable in air and water. It should be noted that the stability of the phenylacetonitrile cuprous complex is due to its non-wetting characteristic. The methoxypropionitrile coordination compound is liquid and moderately soluble in water. The cuprous ion appears to be stable, but there is some doubt about the BF_4^- anion stability.

TABLE III
Reaction of Nitriles With CuBF_4 -Toluene Complex

<u>Compound</u>	<u>Resulting Reaction</u>	<u>Addition of Olefin</u>
Acetonitrile	White crystals, un- stable in air or water	Olefin not reactive
Benzonitrile	Liquid complex, stable in air and water	Olefin not reactive
Phenylacetonitrile	White crystals, stable in air, insoluble in water, decomposed in MeOH-water mixtures	Olefin not reactive
Methoxypropionitrile	Liquid complex, stable in air, moderately sol- uble in water and Cu^+ retained but BF_4^- stability in doubt	Olefin not reactive

The crystalline acetonitrile derivative of the $\text{CuBF}_4[\text{toluene}]_3$ complex was extensively studied because of its stability and homogeneous composition. Elemental analysis confirmed the composition to be $\text{CuBF}_4[\text{CH}_3\text{CN}]_4$.

The $\text{CuBF}_4[\text{CH}_3\text{CN}]_4$ coordination compound is a colorless crystalline material of moderate stability. It slowly turns green in air and is not readily decomposed by water. It has a melting point of 161 to 171°C by sealed tube tests. Some decomposition was suspected at this temperature, since the compound recrystallized at a lower temperature and changes in its physical appearance were noted. Its density was determined by floatation to be 1.466 gm/cc at 24°C. X-ray analysis showed the crystal to be monoclinic with unit cell dimensions of 24.64 Å x 20.92 Å x 8.55 Å [$V_c=4407.6 \text{ Å}^3$]. Molecular weight of the unit cell was calculated to be 955 amu. A unit cell containing 3 molecular weight units of $\text{CuBF}_4[\text{CH}_3\text{CN}]_4$

would have a molecular weight of 942 amu. The stability of this coordination compound indicates that copper has a tetrahedral spacial arrangement.

The stability and well defined composition of the acetonitrile coordination compound suggested acetonitrile could be used as a reagent to determine CuBF_4 complex concentration in unknown solutions. The reaction of acetonitrile with CuBF_4 complex yields an insoluble crystalline phase which serves as an indicator. We were able to confirm complete composition of complexes containing mixed ligands by titration with acetonitrile followed by VPC analysis of the displaced ligands.

The exchange reaction of $\text{CuBF}_4[\text{toluene}]_3$ complex with various hydrocarbons is shown in Table IV. Our purpose was to compare the

TABLE IV
Reaction of Hydrocarbons With $\text{CuBF}_4[\text{Tol}]_3$ Complexes

<u>Olefins</u>	<u>"Wet" $\text{CuBF}_4[\text{Tol}]_3$</u>	<u>"Dry" $\text{CuBF}_4[\text{Tol}]_3$</u>
Ethylene	immiscible liquid	crystalline
Propylene	" "	"
Butene-1	" "	miscible liquid
Pentene-1	" "	" "
Hexene-1	" "	" "
Heptene-1	miscible liquid	" "
Dodecene-1	" "	solid at 0°C
Tetradecene-1	" "	solid at 21°C
Hexadecene-1	" "	solid at 32°C
<u>Aromatics</u>		
Toluene	immiscible liquid	crystallizes from solution
Benzene	" "	miscible liquid
Ethylbenzene	" "	" "
o-Xylene	" "	crystallizes from solution
m-Xylene	" "	miscible liquid
p-Xylene	" "	" "
Mesitylene	solid	crystallizes from solution

type of phases formed with "wet" and "dry" complexes. The "wet" complex can accept ligands up to hexene before complete miscibility occurs, while the "dry" complex becomes miscible upon coordinating with butene-1. The water ligand on the "wet" complex appears to control the complex miscibility with hydrocarbons. The dry complex does not form an immiscible liquid phase with hydrocarbons as it forms only crystalline or miscible liquid phases. If two liquid phases are desired, a ligand from the group of organic compounds just discussed may be added to the system. Addition of a paraffinic hydrocarbon to the system can achieve the same result in some cases involving low molecular weight olefins.

The "dry" complex appears to be less stable in storage than the "wet" complex and does not offer any advantages in performance or capacity. Since it is more difficult to prepare, the "wet" complex was preferred in most of our investigations.

Various systems used to test the selectivity of the CuBF_4 complex for separating hydrocarbons are shown in Table V. The broad classes of olefin-aromatic, olefin-olefin and olefin-paraffin systems were tested first by liquid-liquid contact in small vials to obtain an estimate of the β -factor. The β -factor is a measure of the relative selectivity of the complex for one component as determined from concentration distribution between the two liquid phases. The relative selectivity is analogous to relative volatility in vapor-liquid systems. It was noted that the separation factors were very large compared to those obtained with common organic solvents. In some cases the separations obtained were impossible by ordinary physical methods. The pentene-1, toluene equilibrium indicates the olefin is coordinated 2:1 over the aromatic. Styrene coordinates 10:1 over ethylbenzene which has to compete with toluene for the coordination site and probably occupies the weakest position. Olefin-olefin equilibria indicate that terminal olefins are coordinated more strongly than those with internal unsaturation.

Olefins with a *cis* configuration are coordinated almost as strongly as terminal olefins. Molecular weight seems to have

TABLE V
Hydrocarbon Separations With CuBF₄ Complex

<u>System</u>	<u>β factor</u>
<u>Olefin-Aromatic</u>	
Pentene-1; Toluene	2.33
Styrene; Ethylbenzene	~10.00
<u>Olefin-Olefin</u>	
Pentene-1; c-Pentene-2	1.41
Pentene-1; t-Pentene-2	4.39
c-Pentene-2; t-Pentene-2	3.11
Hexene-1; Pentene-1	1.00
<u>Olefin-Paraffin</u>	
Pentene-1; Hexane	1/16
Hexene-1; Heptane	1/10
Dodecene-1; Dodecane	1/190

little effect on coordination unless it produces a miscible system. Since paraffins have no π -bonds with which to form a coordination bond, the olefin-paraffin systems provide the most spectacular β -factors. It was observed that these separation factors can vary considerably with the ratio of olefin to complex.

These initial equilibria studies indicate very low volatilities for high vapor pressure ligands. This hypothesis was checked by measuring the evaporation rates of pentene-1 and toluene from an excess of sulfolane with and without CuBF₄ complex present. The results of these tests are shown in Figure 4. At 100 mm Hg and 25°C, pentene-1 evaporated from the sulfolane solvent in about two hours. Toluene concentration dropped sharply and leveled off. In the system containing CuBF₄ complex, initial concentrations of both toluene and pentene-1 were much higher. Over the 18 hour test period, pentene-1 concentration changed very little while the toluene concentration decreased to less than that of the olefin.

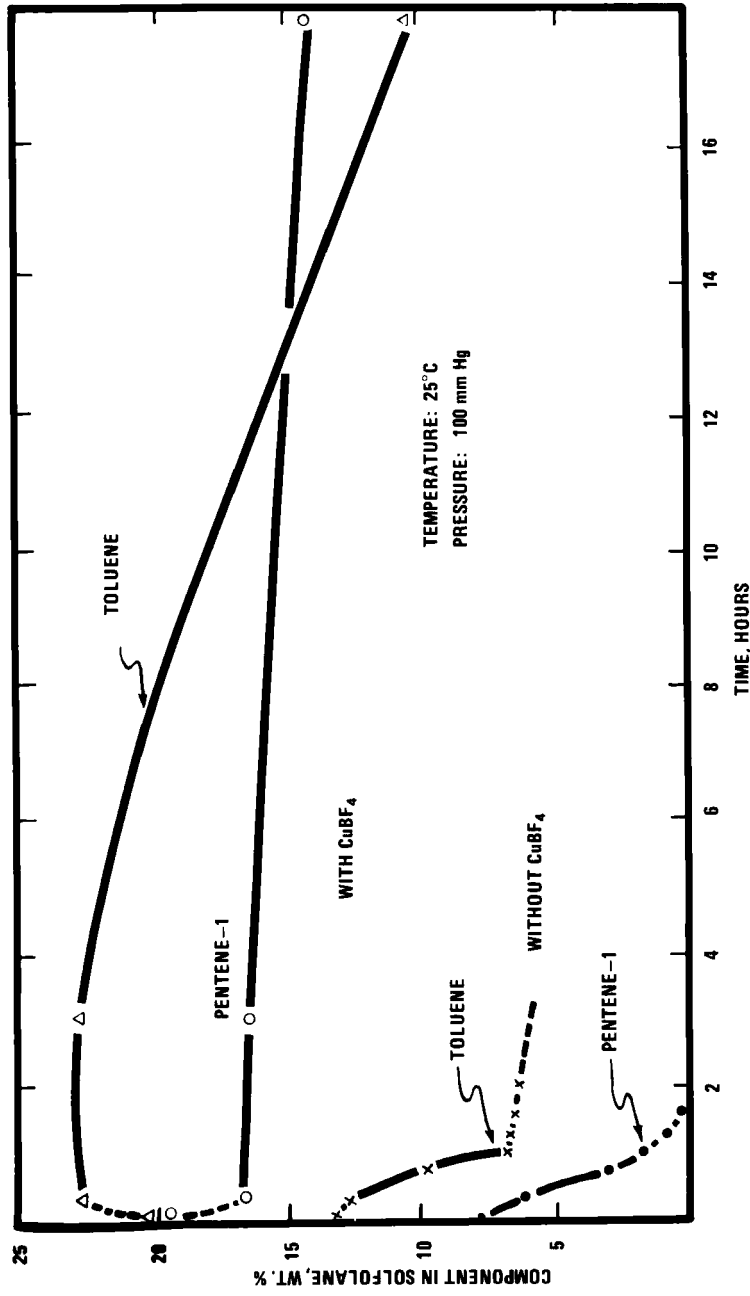


FIGURE 4.
Volatility of pentene-1 and toluene in sulfolane.

It must be concluded from this experiment that olefin bonding with CuBF_4 is much stronger than solvent effects and that the residual toluene molecule is also strongly bonded to the copper ion. These results also show that the olefin-complex bond is stronger than the aromatic-complex bond since the volatilities of pentene-1 and toluene were reversed. That is, toluene [b.p. 110°C] was more volatile than pentene-1 [b.p. 30°C] in the CuBF_4 -sulfolane system.

Thermal dissociation studies of olefin complexes have shown that the ethylene- CuBF_4 complex begins to dissociate at about 50°C , while the propylene complex dissociates at about 70°C . The pentene-1 complex was only slightly dissociated at the boiling point of toluene. Higher temperature [$>110^\circ\text{C}$] leads to thermal decomposition of CuBF_4 , so thermal regeneration techniques are not applicable to most separation processes employing coordination complexes of this type. However, pentene-1 is easily displaced from the complex by ethylene. One olefin is displaced by another by mass action, and this appears to be the only means capable of producing a substantial mass transfer in high molecular weight olefin complexes. When an olefin complex is contacted with excess olefin of different molecular weight, the composition of the olefin complex will come to equilibrium favoring the olefin that is in excess. A number of such contacts will cause displacement of substantially all the original olefin. This is illustrated by the data in Figure 5.

The CuBF_4 complex was saturated with pentene-1 and then contacted with hexene-1 in a number of successive extractions to demonstrate pentene displacement by ligand exchange.

An amount of hexene-1 equal to the amount of coordinated pentene-1 was added to the complex. At equilibrium, the ratio of the distribution coefficients were 1 to 1. The complex showed little or no preference for hexene-1 over pentene-1. The resulting first stage exchange was about 50% hexene-1 and 50% pentene-1 coordinated with the complex. Two successive exchanges with hexene-1 were made in the same manner. Extrapolation of these three equi-

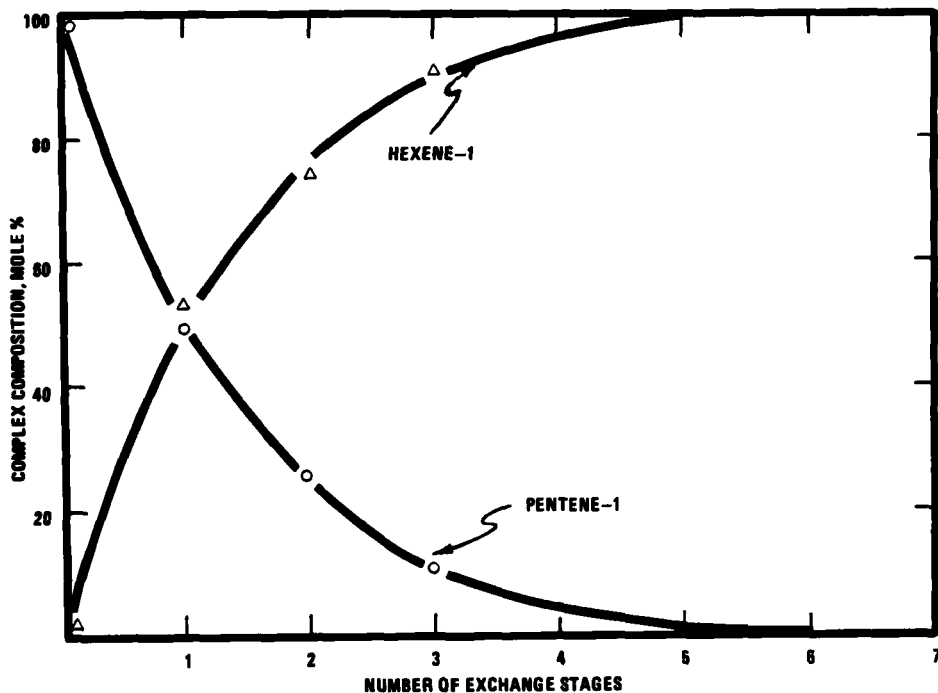


FIGURE 5.

Change in pentene-1 CuBF_4 complex composition by hexene-1 exchange.

librium exchange data points indicate that in about 6 stages the exchange would be complete.

In practice the coordinated olefin would be exchanged with propylene or ethylene to release the pentene. The low molecular weight olefin would then be recycled to contact the high molecular weight olefin at a temperature which would cause the low molecular weight olefin coordination complex to dissociate. Equilibrium would then be shifted in favor of the high molecular weight olefin coordination.

A quantitative measure of the separation of pentene-1 from pentene-2 isomers is shown in Table VI. An olefin to complex mole ratio of 6 to 1 was used in order to impose maximum competition for

TABLE VI
Separation of Pentene-1 and Pentene-2 Isomers With CuBF₄ Complex

Analysis of Resulting Phases

<u>Component, wt. %</u>	<u>Feed</u>	<u>Raffinate</u>	<u>Complex</u>	<u>β-Factors</u>
Pentene-1	31.27	27.64	45.27	2.61
tr-Pentene-2	31.93	37.01	13.80	0.27
cis-Pentene-2	36.80	35.34	40.93	1.27

available coordination sites. The complex selectivity for pentene-1 over the trans isomer is nearly 10:1 and over the cis isomer 2:1. Selectivity for cis-pentene-2 over trans-pentene-2 is about 4:1. The separation of these two isomers is most difficult to perform by physical means because molecular differences are small and their boiling points differ by only 0.6°C. This illustrates just how selective these coordination complexes really are.

The data in Figure 6 show the effect of olefin to complex mole ratios on selectivity for cis-pentene-2 over trans-pentene-2. The β -factor decreases rapidly when the mole ratio of olefin to complex drops below 3:1 where the trans isomer does not have to compete for the coordination site. The β -factor approaches 1 at a mole ratio of 1.5 to 1. This is equivalent to 1.5 ligands per copper ion. Normally, olefin loadings vary from about 1.5 to 2.5 coordinated ligands per copper ion.

Olefin-paraffin separation was demonstrated using pentene-1 and n-hexane as model compounds. The resulting complex performance is shown in Table VII. A feed mixture of 60% pentene-1 and 40% n-hexane produced a complex containing 78% pentene-1 relative to the n-hexane content. The solubilized n-hexane can be removed by paraffin or aromatic wash. Pentene loading in the complex was 1.91 ligands per copper ion while toluene occupied 1.16 ligands per copper ion for a total of 3.06 ligands. In a second test using a 92% pentene-1, 8% n-hexane feed, a complex was obtained containing 99.4% pentene-1 relative to n-hexane. The complex contained 2.85

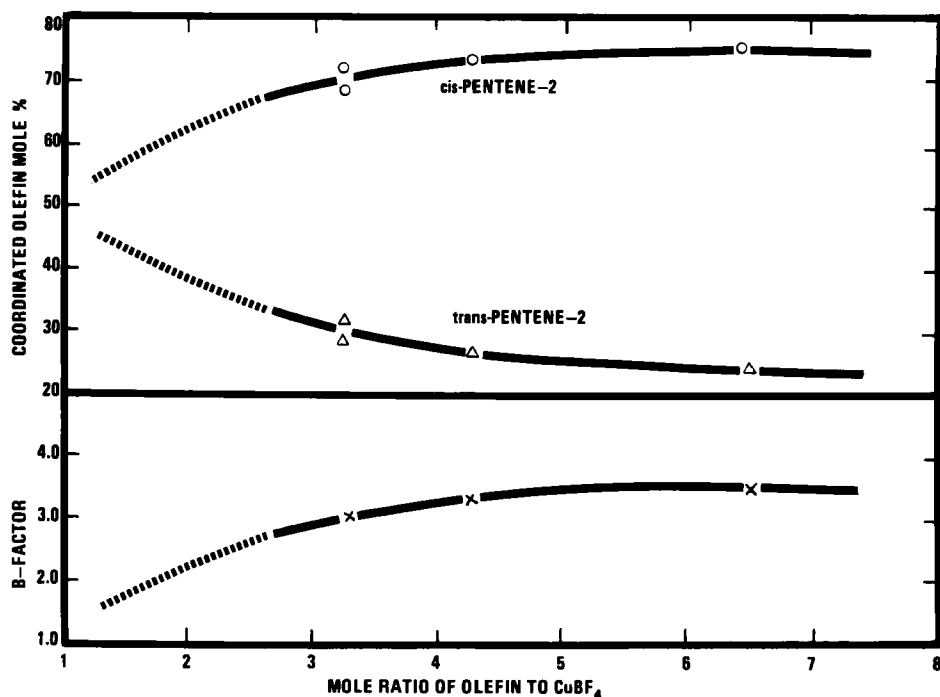


FIGURE 6.

Separation of pentene-2 isomers with CuBF_4 complex.

TABLE VII

Separation of Pentene-1 From n-Hexane With $\text{CuBF}_4[\text{Tol}]_3$

Component	Feed	Raffinate		Complex		Moles per mole of CuBF_4
	gms	Wt. %	gms	Wt. %	gms	
Pentene-1	3.0	25.0	1.27	48.2	1.78	1.91
Hexane	2.0	29.1	1.48	13.7	0.51	-
Toluene	3.7	45.2	2.38	38.1	1.41	1.15
CuBF_4	<u>2.0</u>	-	-	-	<u>2.0</u>	-
	10.8		5.10		5.70	3.06

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ligands of pentene-1, while toluene was reduced to 0.54 ligand sites. A total of 3.39 ligand sites per copper ion were occupied. These examples represent a single equilibrium contact and not the ultimate purity of product which could be obtained by washing undesirable components from the complex phase.

High molecular weight olefins are also coordinated by the CuBF_4 complex. Data for a C_{12} normal olefin, normal paraffin system is presented in Table VIII. The feed mixture containing 14.5% olefin was separated into a 95.2% paraffinic raffinate and an 89.9% olefinic extract in a single stage. In many applications, this single stage upgrading of the olefin concentrate would be sufficient for production of a useful intermediate. Complex capacity for the C_{12} olefin was about 18% by weight compared to about 30% for pentene-1 in the C_5 olefin complex.

Extraction of long chain olefins presents a solubility problem, in that these ligands cause the complex phase to be partially miscible with the hydrocarbon phase. Copper loss becomes significant due to this increased solubility. The effectiveness of sulfolane in controlling complex solubility is shown in Figure 7. With no sulfolane present in the complex, copper loss to the hydrocarbon phase was about 9% of that available. By adding 1 mole of sulfolane per mole of complex, this loss was reduced to 0.9% - 9,000 ppm, and when 3 moles of sulfolane were added the loss was reduced to about 2 ppm. Sulfolane has about the same density as the copper complex and they are completely miscible, and, as mentioned earlier, sulfolane does not interfere with ligand exchange.

TABLE VIII
Example of C_{12} Paraffin-Olefin Separation

<u>Component</u>	<u>Feed</u>		<u>Raffinate</u>		<u>Complex Phase</u>	
	<u>Wt. %</u>	<u>Grams</u>	<u>Wt. %</u>	<u>Grams</u>	<u>Wt. %</u>	<u>Grams</u>
<u>n-Paraffin</u>	85.5	85.5	95.2	81.5	10.1	0.9
<u>n-Olefin</u>	14.5	<u>14.5</u>	4.8	<u>4.2</u>	89.9	<u>8.2</u>
		100.0		85.7		9.1

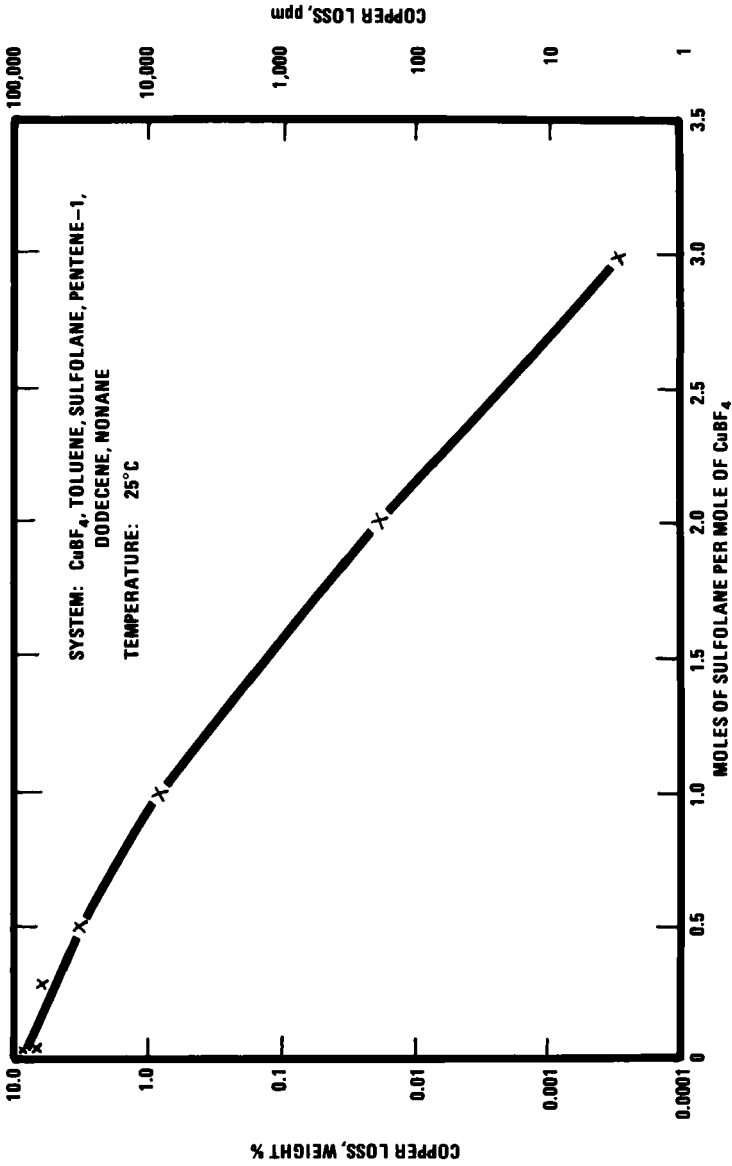


FIGURE 7.

Effect of sulfolane ligands on CuBF_4 solubility in hydrocarbons.

The extraction of vinyl aromatics from other aromatics was demonstrated using styrene and ethylbenzene as model compounds. The number of stages required to extract all the styrene from an ethylbenzene mixture is shown in Figure 8. In five equilibrium contact stages, 99% of the styrene was extracted, with 50% of the styrene being extracted in the first stage. In the second stage the complex extracted about 50% of the remaining styrene. This trend was followed in the third and fourth stages.

Styrene purity in the complex phase was increased by extracting the ethylbenzene with a paraffin as shown in Figure 9. In four stages of wash, styrene purity increased from 76% to 99% while the complex loading decreased from 2.2 moles of styrene per mole of CuBF_4 to about 1.5 moles per mole. The recovery of styrene by this technique requires an extraction cycle, a wash cycle and a ligand exchange cycle. In the ligand exchange cycle, a low boiling olefin

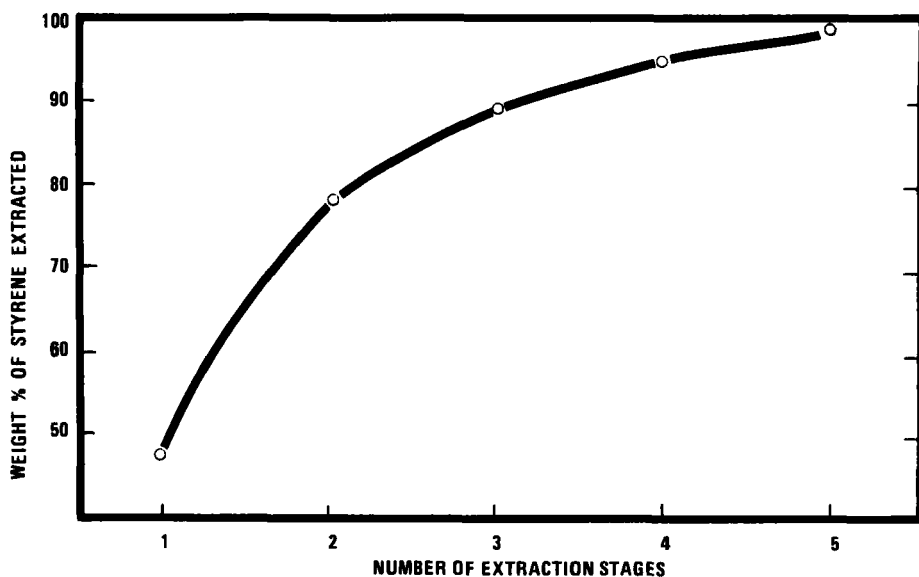


FIGURE 8.

Styrene extraction from ethylbenzene with CuBF_4 .

is used to displace the styrene from the complex which is recycled to the styrene extraction cycle. The low boiling olefin is distilled from the styrene product. A process of this sort allows the direct extraction of styrene from cracked oil streams.

Equilibrium studies involving the Cu[I] toluene complex with other aromatics show a definite order and coordination preference exists which is based to a large extent on molecular geometry but is also strongly influenced by the presence of electron releasing groups as shown in Table IX. The order of decreasing coordination strength is as follows:

o-xylene > mesitylene > p-xylene > ethylbenzene > toluene
 m-xylene > benzene > n-propylbenzene > tert-butylbenzene
 tri-ethylbenzene > sec-amylbenzene

Since electron releasing groups are preferred over benzene one would suspect that electrical properties of the molecule are a factor in selective coordination with the complex. However, no distinct correlation of selectivity with dielectric constant, dipole moment or basicity was found.

[1] Order of decreasing dielectric constant:

o-xylene > m-xylene > toluene > benzene > p-xylene

[2] Order of decreasing dipole moment:

o-xylene > toluene > m-xylene > p-xylene > benzene

[3] Order of decreasing basicity toward $\text{HF} \cdot \text{BF}_3$:

Mesitylene > m-xylene > o-xylene > p-xylene > toluene

There is little advantage in applying coordination compounds to the separation of aromatics because the equilibrium ratios differ by such a small degree. However, the C_8 aromatics meta- and para-xylene are separated from ortho-xylene at 0°C . At this temperature, ortho-xylene coordination compound crystallizes from solution. The enrichment of ortho-xylene over the meta-, para-xylenes is about 3:1 per stage. The same type of equilibrium was obtained for the ethylbenzene, o-xylene system.

CuBF_4 complex was applied to the separation of aromatics from paraffins and naphthenes. The results are shown in Table X. The

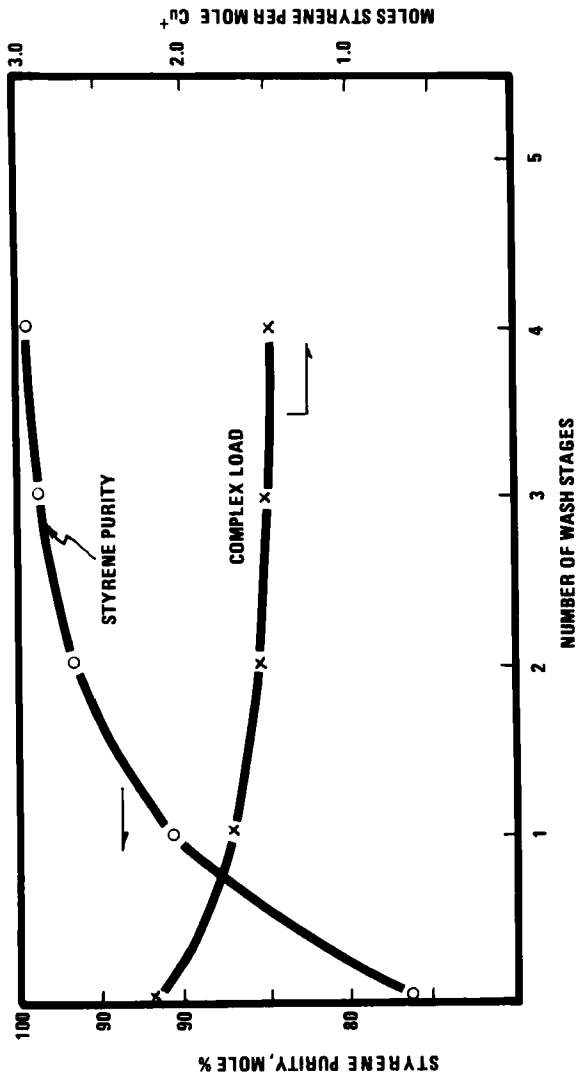


FIGURE 9.
Styrene purity in the complex phase.

TABLE IX
Binary Equilibrium Distribution of Aromatics in CuBF₄

<u>Components</u>	<u>Raffinate</u>	<u>Complex</u>	<u>Distribution</u> <u>Coefficient,</u>	
			<u>K</u>	<u>β-Factor</u>
Toluene	55.4	48.4	1.146	1.326
<u>o</u> -Xylene	44.6	51.6	0.864	
Toluene	52.7	47.8	1.102	1.215
Mesitylene	47.3	52.2	0.907	
Toluene	53.4	50.4	1.060	1.129
<u>p</u> -Xylene	46.6	49.6	0.939	
Toluene	54.5	54.2	1.005	1.011
Ethylbenzene	45.5	45.8	0.994	
Toluene	51.7	53.9	0.962	0.918
<u>m</u> -Xylene	48.3	46.1	1.048	
Toluene	43.1	46.7	0.923	0.864
Benzene	56.9	53.3	1.068	
Toluene	51.9	62.5	0.831	0.635
<u>n</u> -Propylbenzene	48.1	37.5	1.309	
Toluene	55.5	68.2	0.814	0.582
tert-Butylbenzene	44.5	31.8	1.399	
Toluene	57.9	73.4	0.789	0.501
tri-Ethylbenzene	42.1	26.6	1.573	
Toluene	51.2	74.9	0.684	0.350
sec-Amylbenzene	48.8	25.1	1.953	

technique used in this separation utilizes a solid CuBF₄[CO]₃ coordination compound which is thermally decomposed in a mixture of aromatics and paraffins. A liquid aromatic complex results and the CO escapes from the liquid phase. The aromatics are recovered from the complex when CO is again brought into contact with the complex

TABLE X
Aromatics Recovery With $\text{CuBF}_4[\text{CO}]_3$

<u>Components, wt. %</u>	<u>Feed</u>	<u>Raffinate</u>	<u>Complex</u>
Benzene	44.1	35.9	32.8
Toluene	26.5	39.0	46.8
Ethylbenzene	7.0	7.2	5.6
p + m-Xylene	7.9	6.8	7.8
o-Xylene	3.0	2.2	3.5
C ₉ Aromatics	2.7	2.2	3.2
Paraffins	8.8	6.7	0.5
Grams HC	86.0	45.0	41.0
Grams CuBF_4	25.0	-	25.0

causing it to crystallize leaving an aromatic liquid phase. This separation is essentially single stage contact for the extraction cycle and the regeneration cycle. A paraffin wash between these cycles did not improve the aromatic extract purity. The driving force for this separation is the low energy phase change - liquid to solid and vice versa.

The $\text{CuBF}_4[\text{CO}]_3$ is of interest in other separations, such as the extraction of CO from hydrogen and carbon dioxide to obtain pure CO for hydroformylation reactions. Thermal dissociation curves for the CO complex in equilibrium with toluene are shown in Figure 10. The curves are designated 1.0, 2.0, and 3.0 moles of CO per mole of CuBF_4 complex, which does not necessarily correspond to the number of CO ligands on the complex. Some molecules of complex may have three ligands, while others may have only one or none. Thus, the curves are based on averages. The heats of reaction were calculated for these curves assuming that some order of equilibrium was achieved. The values obtained were 11.4, 7.3 and 4.7 kilocalories per mole for the respective CO loadings of 1.0, 2.0 and 3.0 moles per mole of complex. These values indicate that

two of the CO ligands would be easily removed while the third would be more difficult and the last traces very difficult to remove. This is quite analogous to the recovery of compounds adsorbed on molecular sieves. Solid phases are present in the system upon addition of about two moles of CO per mole of CuBF_4 complex which complicates the equilibrium. A change of state in this direction increases the complex stability as would be expected. At any rate, the recovery of CO by this technique has worked well in the laboratory and preliminary estimates suggest that it could be at least competitive with low temperature distillation.

SUMMARY AND CONCLUSIONS

New technology is needed to achieve highly specific separations that are impossible or impractical to achieve by conventional physical processes such as distillation and extraction. Also needed for ecology reasons are processes that involve very low energy requirements. Chemical complexes satisfy the requirement of specificity. Choice of agent and reaction conditions can provide a very effective tool for sorting complex hydrocarbon mixtures on the basis of structure.

Low energy prerequisites are more difficult to attain. However, incorporating phase change analogous to liquid-liquid extraction and pseudo chemical or chemical compound formation includes the benefits sought. The cuprous and silver complexes of olefins provide the chemical leverage needed, and by taking advantage of differences in relative stability of various olefin complexes to exchange one hydrocarbon for another, the low energy target appears attainable.

Olefin exchange reactions and olefin separation processes utilizing cuprous tetrafluoroborate complexes appear feasible. Equilibrium studies indicate steric factors are most important in the strength of the bond formed between the complex and the olefin. Competition for the coordination sites on the copper [I] ion is

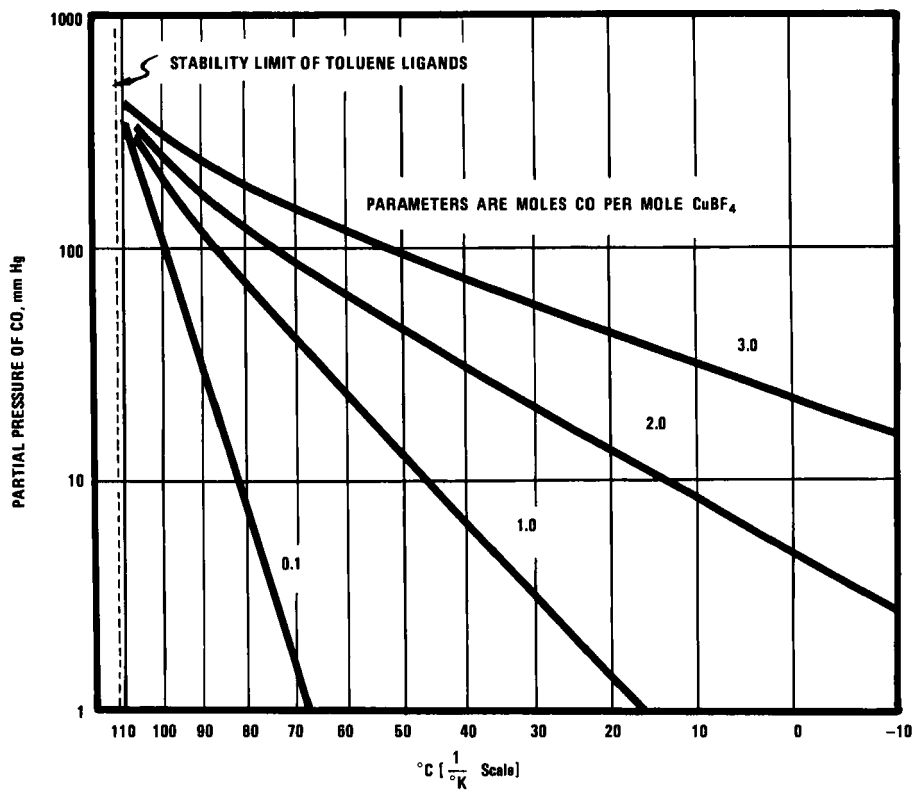


FIGURE 10.
Stability of CuBF_4 toluene-CO coordination complex.

largely controlled by copper availability - or the ratio of olefin to copper ion. If the ratio of olefin to copper ion is large, then the most stable olefin species will dominate the complex. If the ratio of olefin to copper ion is low, the less stable olefin isomer is not rejected so strongly and little or no preference for the more stable isomer is shown.

Most likely, the complex would not be applied to the separation of olefin isomers except in special cases; but rather more generally to the extraction of olefins from paraffins, vinyl aromatics from aromatics and carbon monoxide from other gases. These processes offer the greatest potential for success with fewer associated problems to hinder direct application.

Aromatic separation with CuBF_4 complex has been only slightly investigated, but data which have been obtained strongly suggest such processes are workable. Separation of aromatics from paraffins with CO complexes is novel and equilibrium is easily shifted toward aromatic coordination by increasing the temperature. The aromatics are recovered from the complex by increasing CO pressure at lower temperature which favors CO coordination.

Selective crystallization of certain aromatics from aromatic mixtures [esp. o-xylene from xylene isomers] with excellent enrichment was observed. Toluene, ortho xylene and mesitylene are the only aromatics which have been noted to form crystalline complexes with CuBF_4 . Screening has been limited to the cited systems and special cases of potential application may exist with polycyclic aromatics, for example.

CuBF_4 complex may not be the ultimate complex of choice for a specific separations process, but it has served well in the demonstration of exchange reactions. Although a more stable complex is desirable, a more stable complex may neither be as reactive nor have the desired physical properties. In any case, $\text{Cu}[\text{I}]$ has proven to be a suitable cation, and the BF_4 anion is equally suited to its role in the complex.

Interest and activity in the field of coordination chemistry of complexes has mounted in the last few years as evidenced by publications, patents and private consultation. For the most part, this activity is confined to homogeneous catalysis. Although our research has been confined to problems related to separations, the uses for nonaqueous CuBF_4 complexes are not necessarily limited to this field. The diversity of the Chemical Processing Industry may offer many application possibilities for CoBF_4 complexes of which we are not yet aware.

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REFERENCES

1. W. C. Zeise, Pogg Ann., 21, 497 [1831].
2. J. S. Anderson, J. Chem. Soc., 1042 [1936].
3. M. S. Kharasch, R. C. Seyler and F. R. Mayo, J. Am. Chem. Soc., 60, 882 [1938].
4. M. B. Sparke, L. Turner and A. J. M. Wenham, J. Catal., 4, 332 [1965].
5. W. Featherstone and A. J. S. Sorrie, J. Chem. Soc., 5235 [1964].

6. S. Winstein and H. J. Lucas, J. Am. Chem. Soc., 60, 836 [1938].
7. H. W. Quinn and D. N. Glew, Can. J. Chem., 40, 1103 [1962].
8. H. W. Quinn, Can. J. Chem., 45, 1329 [1967].
9. H. W. Quinn and D. N. Glew, Can. J. Chem., 44, 2663 [1966].
10. J. G. Traynham and J. R. Olechowski, J. Am. Chem. Soc., 81, 571 [1959].
11. J. W. Kraus and E. W. Stern, J. Am. Chem. Soc., 84, 2893 [1962].
12. G. A. Olah and H. W. Quinn, J. Inorg. Nucl. Chem., 14, 295 [1960].
13. W. Featherstone, Imperial Chemical Industries, U.S. Patent 3,347,948 [1967].
14. W. Krekeler, J. Hischbeck and U. Schwenk, Sixth World Petroleum Congress, Frankfurt/Main, June 1963.
15. J. C. Warf, J. Am. Chem. Soc., 47, 3702 [1952].
16. D. A. McCaulay, Standard Oil of Indiana, U. S. Patent 2,953,589 [1960].
17. G. A. Olah and H. W. Quinn, J. Inorg. and Nucl. Chem., 14, 295 [1960].
18. D. R. Russell and D. W. A. Sharp, J. Chem. Soc., 4689 [1961].
19. F. A. Andersen and B. Bak, Acta. Chem. Scand., 7, 236 [1953].
20. M. J. S. Dewar, J. Chem. Soc., 406 [1946].
21. J. Chatt and L. A. Duncanson, J. Chem. Soc., 2939 [1953].