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OLEFIN RECOVERY PROCESS

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ABSTRACT OF THE DISCLOSURE

Olefinic hydrocarbons such as ethylene are separated from mixtures of same with other materials by absorption on and desorption from a copper complex resulting from the reaction of (1) a copper II salt of a weak ligand such as copper II fluoborate, (2) a carboxylic acid such as acetic acid, and (3) a reducing agent such as metallic copper.

This invention relates to a process for removal of olefins from mixtures with other materials and more particularly pertains to the isolation of olefins from mixtures of same with other materials by absorption of the olefins on a particular type of copper complex.

The use of copper salts and complexes for olefin absorption is well known to those skilled in the art. British Pat. No. 1,053,802 discloses the recovery of carbon monoxide and olefins from a gaseous mixture by absorption in and desorption from an aqueous solution of monoethanolamine and mono- and divalent copper, 5–20% by weight of the copper being in divalent form. In this prior art process absorption is said to occur at a temperature in the range of from 0 to 30° C. and desorption occurs at temperatures not exceeding 60° C. The conditions employed in this prior process are different from the instant process, and the copper complex employed in the instant process has not been disclosed previously for this purpose.

Olefin absorption employing $AgBF_3OH$ as the absorbent is described in British Pat. No. 1,046,416. It is necessary to use a twelve-molar concentration of the $AgBF_3OH$ to obtain stoichiometric absorption of the olefin. A direct comparison of the instant process with that of British Pat. No. 1,046,416 shows a ten-fold increase on a molar basis in the olefin absorption ability of the instant copper complex over that of the $AgBF_3OH$ at 85° C.

The use of a copper complex containing a copper-to-copper bond as well as the ability of this complexing agent to reversibly absorb olefins in the order of one magnitude or more higher than that previously reported for copper compounds is indeed unexpected.

The present process is applicable to the separation oı unsaturated hydrocarbons, preferably olefinic hydrocarbons having from 2 to 20 carbon atoms and more preferably monoolefins having from 2 to 20 carbon atoms and diolefins having from 4 to 20 carbon atoms from mixtures containing same. The olefins are selectively absorbed on the copper complex and subsequently may be desorbed and isolated by the process of this invention.

The absorption-desorption of olefins, according to the process of this invention, can be carried out continuously or batch-wise and the same copper complex can be employed for numerous absorption-desorption cycles with no noticeable deleterious effect on the activity of the complex. Moreover, the absorption-desorption can be carried out on olefin mixtures which are either in the liquid phase or gas phase.

The copper complex useful in the process of this invention is thought to be composed of copper in the I and II valence states and the Cu^+ and Cu^{++} are bonded together. The exact structure of the copper complex is not known with any degree of certainty, but the complex can be best characterized and identified by its manner of preparation as hereinafter described.

The copper complex employed in this invention is the reaction product of three essential components. The first essential reaction component is a copper II salt of a weak ligand such as copper II fluoborate, copper II perchlorate, copper II tetraphenylborate and less preferred is copper II sulfate. The second essential reaction component is a carboxylic acid or material which will readily yield a carboxylic acid such as an anhydride. Useful carboxylic acids or their anhydrides include those mono- and polycarboxylic acids which form a Cu II salt having a magnetic moment in the range of 1.2 to 1.6 and preferably 1.36 to 1.44 BM (Bohr Magnetic units) as determined at about room temperature by the procedure described in Chemical Reviews, vol. 64, 98–128 (1964). The copper II acetate BM at 295° K., for example, is 1.39 by this method. Carboxylic acids and anhydrides useful in this invention are those composed of from 2 to 20 carbon atoms and most preferred are monocarboxylic acids having from 2 to 20 carbon atoms such as acetic acid, propionic acid, the butyric acids, benzoic acid, phenyl acetic acid, lauric acid, myristic acid and the like. The third essential reaction component required in the preparation of the copper complex used in the instant process is a reducing agent. Although practically any known reducing agent will work, it is preferred to use a metal such as copper or nickel or electric current.

In the preparation of the copper complex, the foregoing three essential reaction components are allowed to react under substantially anhydrous condition in the substantial absence of oxygen. There is nothing critical about the order of addition of the foregoing three components in the reaction to form the copper complex. The complex will form from interaction of the three essential reaction components at low, ordinary temperatures or at elevated temperatures in the range of 0° C. or less up to about 230° C. The absorption efficiency of the complex usually will be markedly decreased when the complex is subjected to temperatures in the range of 230–250° C. or higher.

The three essential components required in the preparation of the copper complex will react over a wide range of molar proportions of each component. It is contemplated to use an excess of one or two of the three essential components in relation to the third essential component. Thus, the copper II salt of a weak ligand can be in molar excess, the carboxylic acid can be in molar excess and the reducing agent can be in molar excess, each in relation to at least one of the other two components.

The copper complex of this invention can be used as a catalyst in the instant olefin absorption-desorption process per se, in solution, on a solid carrier, or in any other form desired. The copper complex is soluble in polar organic solvents such as alcohols, ethers, carboxylic acids, carboxylic acid anhydrides, nitroalkanes, sulfolane and the like.

The univalent-divalent copper complex useful in the present process forms a strong purple coloration in certain solvents. Solvents suitable for forming this complex must be sufficiently polar to dissolve the copper complex and yet be inert. Specific acceptable solvents for the copper complex include nitromethane, 2-butanol, p-dioxane, diisopropyl ether, acetic anhydride, acetic acid, ethanol, sulfolane and many others. The purple coloration of the complex in a solvent exhibits a very strong absorption band at 500 to 513 millimicrons which is in the center of a region attributed either to an electron transfer complex between the metal and its ligand or a binuclear complex with the meal atoms in two different oxidation states.

This color formation does not take place with either univalent or divalent copper, $CuBF_4$ or $Cu(BF_4)_2$, in an organic solvent. Electron-spin resonance indicates the univalent-divalent complex has a single unshared electron that is delocalized between two equivalent nuclei and is capable of reaction with p-π electrons of olefins. On reaction with olefins (absorption) which preferably is carried out under substantially anhydrous conditions and in the substantial absence of molecular oxygen, a colorless complex is formed which upon decomposition with heat or vacuum (desorption) yields the free olefin and the purple colored complex again.

The recovery of olefins from mixtures containing the same is carried out by contacting the mixture containing the olefin with the copper complex in the range of about 25–85° C. and preferably 70–85° C. when done at or near atmospheric pressure. The absorption can be carried out at higher or lower temperatures depending upon the pressure employed. The absorbed olefin can be desorbed under substantially anhydrous conditions at atmospheric pressure at a temperature in the range of 100–200° C., depending on the olefin. The desorption temperature may be higher if higher pressures are employed, but it is preferred to remain below about 230° C. in the desorption step because of the lack of stability of the complex in the higher temperature range.

The copper complex employed in the process of this invention is believed to contain copper which can be considered to be in the 3/2 valence state on the average. This complex is nearly ten times more efficient as an absorption agent for monoolefins than univalent silver salts and is far superior to the known mono- or divalent copper salts sometimes used for this purpose.

The process of this invention is particularly useful for the recovery of olefins from hydrocarbon mixtures of same with paraffins, alicyclic hydrocarbons and aromatic hydrocarbons. Olefins can be selectively isolated by our process from complex hydrocarbon mixtures produced in petroleum refining processes including cracking, isomerization, alkylation, dealkylation, hydrodealkylation, hydroforming, aromatization and the like, which processes may be catalytic or non-catalytic in nature.

The process of this invention is particularly applicable to the recovery of ethylene or propylene from various gas streams. As has been mentioned earlier, the exact conditions for optimum absorption or desorption are dependent upon the olefin to be recovered. Absorption of ethylene, for instance, can be carried out at temperatures up to about 85° C. at about atmospheric pressure. The thermal stability of the complex containing the absorbed olefin up to that temperature implies that a stoichiometric coordination compound is formed. Above this temperature the coordination compound decomposes with loss of ethylene. Optimum desorption temperature is in range of 120° C.

In the case of ethylene, initial absorption increases with an increase in absorption temperature in the range of from about 0° to about 85° C. and increase in the concentration of the complex. The copper complex may be used preferably in solution in concentrations of from about 0.1 to 2 molar, although the use of higher or lower concentrations is contemplated within the scope of this invention.

The process of this invention will be further illustrated in the following examples wherein the amounts of ingredients are expressed in parts by weight unless otherwise indicated.

EXAMPLE I

A copper complex was prepared from copper fluoborate, acetic anhydride and copper. A two-molar solution of the complex was prepared by heating 1000 ml. of acetic anhydride to 85–90° C. with stirring and then adding 474 g. of copper fluoborate at such a rate as to maintain the temperature between 90 and 100° C. When the addition was complete, the solution was cooled and aged for 24 hours. To the resulting two-molar solution were added 40 g. of electrolytically purified metallic copper. A one-molar complex was then prepared by diluting the resulting mixture with an equal volume of acetic acid containing 10% acetic anhydride. A 0.2 molar mixture of complex was also prepared by diluting one volume of the two-molar mixture described above with nine volumes of dry acetic acid.

Eighty-five ml. of the copper complex solution described above were placed in an enclosed glass reactor equipped with magnetic stirrer, gas inlet tube extending well below the liquid level of the contents of the reactor and a gas outlet tube located near the top of the reactor. An additional 3 grams of electrolytic grade copper metal were added to this copper complex solution, stirring was commenced and the mixture was heated to 70–80° C. The mixture was given a one-minute flush with helium before the absorption and desorption steps. The flushing serves to remove residual gases from the void spaces in the reaction apparatus. A gaseous mixture of ethylene, propane and nitrogen was produced by passing each gas through a rotameter into a common flow-control blender where the gases were ratioed and mixed. The pressure of the gases into the rotameter was 17 p.s.i.g., but the pressure of the blended gases was reduced to 5 p.s.i.g. in the blender. Absorption was carried out by introducing as feed a fraction of the blended gas mixture (26.4 to 29.6 cc./min.) into the reaction mixture through the gas inlet tube. Samples of the feed gas were taken from the feed line at intervals for analysis of the composition. The exhaust gas from the gas outlet tube was passed through a liquids trap and was analyzed periodically for its composition. All gas analyses were made with a Fisher Gas Partitioner, System D.

Desorption was carried out after stopping the flow or feed gases and slowly raising the temperature of the copper complex solution to 120° C. while analyzing the exhaust gases.

The results of a four and one-half hour absorption run under the foregoing conditions are given in Table I.

TABLE I

Percent by volume of exhaust gas components	Time, hours						
	1.0	2.0	2.5	3.0	3.5	4.0	4.5
Propane	57.5	57.0	56.5	55.5	54.5	53.0	51.0
Nitrogen	39.4	39.2	39.0	38.5	38.0	37.5	37.0
Ethylene	0.8	2.0	3.2	4.3	6.0	8.2	10.9
Total	97.7	98.2	98.7	98.3	98.5	98.7	98.9
Feed gas:							
Propane	41.0	-------	40.5	-------	-------	39.8	-------
Nitrogen	28.0	-------	28.3	-------	-------	28.8	-------
Ethylene	32.5	-------	32.5	-------	-------	31.6	-------
Total	101.5	-------	101.3	-------	-------	100.2	-------

The results of desorption of absorbed gases as carried out in the foregoing manner are given in Table II. Table II gives the analysis of desorbed gases with correction for vaporized solvent.

TABLE II

Percent by volume of desorbed gas components	Solution temperature, ° C.								
	109	110	111	112	113	114	115	118	120
Ethylene	85.0	92.3	95.1	97.4	98.7	99.1	99.6	99.8	99.8
Propane	14.7	7.4	4.4	2.2	0.9	0.5	0.2	0.1	0.1
Nitrogen	0.4	0.4	0.4	0.4	0.4	0.5	0.2	0.1	0.1
Total	100.1	100.1	99.9	100.0	100.0	100.1	100.0	100.0	100.0

EXAMPLE II

The procedure of Example I was followed using a gaseous mixture of propane, propylene and nitrogen. The absorption results are given in Table III.

TABLE III

Percent by volume of exhaust gas components	Time, hours				
	1.0	2.0	2.5	3.0	4.0
Propane	68.0	67.0	66.8	66.5	65.5
Nitrogen	32.0	32.5	32.5	32.5	32.5
Propylene	0.2	0.5	0.7	0.8	1.2
Total	100.2	100.0	100.0	99.8	99.2
Feed gas composition:					
Propane	57.5		57.5		57.4
Nitrogen	28.5		28.9		28.9
Propylene	18.5		18.5		18.6
Total	104.5		104.9		104.9

The results of the desorption step are given in Table IV.

TABLE IV

Percent by volume of desorbed gas components	Bath temperature, ° C.					
	99	102	108	114	120	123
Propane	75.8	75.2	72.8	66.0	3.4	0.2
Nitrogen	16.8	16.2	13.9	9.6	5.1	3.0
Propylene	6.6	7.7	11.2	19.6	87.2	95.0
CO_2	0.8	1.0	1.9	4.8	4.3	1.8
Total	100.0	100.1	99.8	100.0	100.0	100.0

EXAMPLE III

The procedures of Example I were repeated using a feed gas mixture of ethylene, propylene and nitrogen. The results of the absorption are given in Table V.

TABLE V

Percent by volume of exhaust gas components	Time, hours			
	1.0	2.0	2.5	3.0
Nitrogen	90.5	77.5	60.0	42.5
Propylene	1.0	10.5	24.5	36.0
Ethylene	0.5	6.0	12.7	20.2
Total	92.0	94.0	97.2	98.7
Feed gas:				
Nitrogen	30.0		29.6	
Propylene	40.5		40.6	
Ethylene	31.2		31.3	
Total	101.7		101.5	

Results of the desorption are given in Table VI.

TABLE VI

Percent by volume of desorbed gas components	Temperature, ° C.				
	91	100	106	112	118
Propylene	60.2	58.8	56.5	55.5	52.6
Ethylene	38.5	37.4	36.9	38.3	45.5
Nitrogen	1.0	3.2	5.7	4.8	0.6
CO_2	0.2	0.5	0.8	1.5	1.3
Total	99.9	99.9	99.9	100.1	100.0

EXAMPLE IV

The procedures of Example I were repeated using a feed mixture of ethylene, butene-1 and nitrogen. Results of the absorption are given in Table VII.

TABLE VII

Percent by volume of exhaust gas components	Time, hours			
	1.0	2.0	2.5	4.0
Nitrogen	89.0	58.8	37.5	25.5
Butene-1	2.5	21.0	31.5	36.5
Ethylene	2.2	22.5	33.0	33.5
Total	93.7	102.3	102.0	95.5
Feed gas:				
Nitrogen	27.0		27.0	27.0
Butene-1	45.0		44.9	44.6
Ethylene	32.2		32.3	32.2
Total	104.2		104.2	103.8

Desorption results are given in Table VIII.

TABLE VIII

Percent by volume of desorbed gas components	Temperature, ° C.					
	104	108	114	116	118	120
Butene-1	56.3	57.5	56.8	58.0	60.3	63.3
Ethylene	42.0	42.2	42.8	41.8	39.4	36.4
Nitrogen	1.8	0.4	0.4	0.2	0.2	0.2
Total	100.1	100.1	100.0	100.0	99.9	99.9

EXAMPLE V

This example will illustrate the separation of an olefin, cyclohexene, from a saturated hydrocarbon, cyclohexane, in the liquid phase by means of the catalyst of this invention. 125 ml. of the one molar solution of the copper complex described in Example I containing 5 grams of fine copper shot were employed. To this solution were added 50 grams of a mixture of 20% by weight of cyclohexene and 80% by weight of cyclohexane, and air was excluded from the reaction mixture. The resulting mixture was stirred and heated to 65° C. for 25 minutes. Heating was discontinued, and the mixture was stirred at ambient temperature overnight. The mixture was then placed in a separation flask and the two layers were separated. The bottom layer contained the copper complex solution, and the upper layer was primarily cyclohexane with a trace of complex to impart a light blue color.

Distillation of the bottom layer described above resulted in the fractions shown in Table IX.

TABLE IX

Distillation flask Temperature, ° C.:	Weight ratio of cyclohexene/cyclohexane in distillate
84	0.164
85	0.182
91	0.227
95.1	0.292
100	0.358
106.5	0.445
116.5	0.855
121.5	1.55
121.5	6.28
121.5	52.5

Although the boiling points of pure cyclohexane, 81.4° C., and cyclohexene, 83° C., are quite close together, the bulk of the cyclohexene from this mixture was recovered at a much higher temperature. Table IX shows that the major part of the cyclohexane comes off at 84–90° C. solution temperature, while the concentration of the cyclohexene in the distillate does not become significant until the solution temperature reaches 121.5° C. This represents a temperature separation of about 35° C., compared with the normal 1.6° C. separation for mixtures of pure cyclohexane and cyclohexene.

EXAMPLE VI

This example demonstrates the separation of a diolefin butadiene-1,3, from mixtures of butadiene-1,3 and isobutane by the process of this invention.

Eighty-five mls. of one molar catalyst solution described in Example I containing three grams of copper metal were placed in the reactor. A gaseous mixture of 42% (by volume) of butadiene-1,3, 41.2% isobutane and 16.3% nitrogen was bubbled into the catalyst solution at a rate of 46 ml. per minute. The gas effluent from the reactor was periodically analyzed. The results of these analyses are given in Table X.

TABLE X

Reaction time, hours	Effluent analyses (volume) Percent butadiene	Percent isobutane	Percent N_2	Degree of saturation of catalyst solution	Ratio (volume) butadiene/ isobutane
0.33	0.0	6.8	30.8	16.7	0.2
1.0	2.5	67.5	28.4	49.8	0.6
1.33	7.8	64.2	27.2	64.3	0.78
1.67	18.8	58.5	24.2	76.6	0.93
2.0	23.2	53.2	21.3	85.0	1.03
2.33	30.5	48.8	19.0	91.0	1.10
2.67	35.4	45.2	17.2	95.0	1.15
3.0	37.8	44.0	16.8	97.2	1.18
3.33	40.0	43.5	16.7	100.0	1.21
	Feed Gas				
	42.0	41.2	16.3		

It is interesting to note that the absorption of butadiene is nearly quantitative when the solution is 50% saturated. The concentration of butadiene in the exhaust gas at this point is only 2.5%.

The foregoing solution was then heated to 121.5° C., the temperature at which acetic acid begins to distill, and about 25% of the absorbed butadiene was desorbed.

EXAMPLE VII

A procedure similar to that described in Example V was employed to separate octene-1 from octane. Seventy-five mls. of the one molar catalyst solution were placed in a separatory funnel and 10 ml. of various mixtures of 1-octene and octane were added to the solution in several single extraction runs. The concentration of octene-1 is given for each run in Table XI. Two immiscible layers appeared at once; the lower layer was composed of the complex solution and the upper layer was primarily octane. The octane layer was analyzed after each run and the results are given in Table XI.

TABLE XI

Concentration of octene-1 in initial octene-1/octane mixture, volume percent	Concentration of octene-1 in upper layer after one extraction with catalyst solution, volume percent	Percent reduction of octene-1 in upper layer after single extraction run
10	6.6	34
20	4.4	78
30	7.8	74

EXAMPLE VIII

This example describes the absorption of ethylene from a nitrogen-ethylene mixture by the copper complex described in Example I. The procedure employed was as follows: A modification of a Fisher Orsat gas analyzer was used. Ethylene and nitrogen were supplied to the system from a one-liter separatory funnel reservoir by liquid displacement. The displacement liquid for the ethylene reservoir and the gas buret was distilled water acidified with HCl to the acid side of methyl orange indicator. The reaction flask was immersed in an oil bath which had heating means and temperature control for the oil. To the reaction flask were added three grams of copper metal and 5 mls. of the appropriate molar copper complex from a 10 ml. syringe. The reaction flask was then connected to the gas supply system and sealed from the atmosphere. Approximately 200 cc. of nitrogen were added to the reservoir and then evacuated into the hood. The gas buret was filled with nitrogen and then the nitrogen was transferred to a gas expansion bag through the reaction flask and then evacuated through the exhaust port into the hood. Approximately 200 cc. of ethylene were added to the reservoir and then evacuated to the hood. The reservoir was then filled with ethylene to be drawn upon for absorption experiments. The gas manifold and gas buret were then flushed with approximately 100 cc. of ethylene. The transfer of ethylene through the apparatus was the same as in an Orsat analysis. In order to assure the same volume of gas remained in the absorption flask and gas bag as when started, the manometer was balanced and the valves were closed before reading the gas buret. The absorption of ethylene was done on a semi-automatic basis. Exactly 100 cc. of ethylene were added to the reaction flask and gas expansion bag from the gas buret. The complex absorbed the ethylene from the gas expansion bag at its own rate. When the gas expansion bag was nearly collapsed, a measurement of the amount not absorbed was made. This gas was then recharged to the reaction flask and gas bag. A second 100 cc. were then charged to the absorption flask and gas bag. Readings of the amount absorbed were taken at approximately 5-minute intervals. Absorption was considered complete when the rate of absorption was less than 0.1 cc. per minute between 5-minute readings. The unabsorbed ethylene was then exhausted into the hood.

The desorption portion was then started immediately after exhausting the unabsorbed ethylene. The oil bath temperature was increased to a maximum temperature of 126° C. The flow of gas to the gas buret and U-tube was maintained and flow to the gas bag was closed off. The manometer balance was maintained during the desorption of ethylene and the amount of ethylene desorbed was recorded at 5° intervals. The temperature was increased rapidly to approximately 115° C., and an attempt was made to hold the temperature constant between 118 to 120° C. Desorption was considered complete when ethylene was absorbed with a 1° C. drop in temperature. When desorption was complete, the oil bath was cooled to the absorption temperature and the next cycle started.

The continuous absorption experimental work was carried out in equipment in which nitrogen and ethylene were metered through rotameters and then blended. The flow rate to the reaction flask was carefully adjusted. Excess mixture was diverted to a fume hood.

The reaction flask was prepared for each continuous run by adding 3 grams of copper metal and 10 mls. of copper complex solution through a 10 ml. syringe. The reaction flask was then flushed with nitrogen, connected to the feed line and brought to temperature. The nitrogen and ethylene were started to the rotameter at 17 to 18 p.s.i.g. and sent through the micrometer needle valve with a back pressure of 10 p.s.i.g. The flow rate was adjusted to the desired flow of 20 to 25 cc./min., samples of feed were taken for analysis in a Fisher Gas Partitioner, System D. When the analysis indicated a constant composition had been reached, continuous absorption was started. Samples of the absorber exhaust were taken at regular intervals and analyzed. The run was considered to be complete when the concentration of ethylene in the exhaust gas approached that in the feed gas.

A series of experiments conducted to determine the optimum concentration of the complexing agent in acetic acid and optimum absorption temperatures for ethylene are summarized in Table XII. The highest concentration of copper complex in acetic acid prepared and used was a 2-molar solution. A ten-fold dilution with acetic acid was used as the minimum concentration. Temperatures of 25, 50 and 75° C. were chosen as the absorption temperature. The data show the absorption of ethylene by the complex is stoichiometric and that desorption is incomplete in the 2-molar solution while there is nearly complete desorption in the 1-molar solution. Little loss of ethylene was observed in a saturated solution and heating the complex from 25° C. to 75–80° C. However, ethylene was then gradually desorbed up to 100° C. and rapidly desorbed above that temperature. The thermal stability up to 75–80° C. implies that a stoichiometric coordination compound is formed and is stable up to that temperature.

TABLE XII.—ABSORPTION-DESORPTION AT VARIOUS CONCENTRATION AND TEMPERATURES

Complex molarity	Absorption temp., ° C.	Absorption per cc. complex at absorption temp.	Cc. ethylene still absorbed at— 85° C.	105° C.	110° C.
Blank HOAc	75	3.4	3.1	2.2	1.7
HBF_4 in HOAc (1.3 M)	75	1.9	1.4	0.6	0.3
$Cu(OAc)_2$ in HOAc (1.0 M)	75	2.0	1.6	0.2	−0.1
Copper Complex:					
0.2	25	9.2	8.3	6.0	4.9
0.2	50	10.4	8.3	5.9	4.7
0.2	75	8.3	7.8	5.8	4.8
1.0	25	39.8	37.8	31.7	29.0
1.0	50	41.5	37.3	31.1	28.0
1.0	75	42.5	41.6	36.2	32.9
2.0	25	63.4	62.3	56.6	51.8
2.0	50	72.8	70.7	59.6	56.4
2.0	75	66.8	66.1	59.1	55.0

EXAMPLE IX

To demonstrate the superior absorption nature of the copper complex of this invention, experiments using copper acetate, fluoboric acid and silver fluoborate as absorbents were run by the procedure of Example VIII. The results are shown for the copper complex of this invention in Table XII and for the others in Table XVI. Solutions of copper acetate and fluoboric acid absorbed less olefin than the glacial acetic acid in the absence of an absorbent. The absorption of ethylene on the silver fluoborate was not stoichiometric, and the solution appeared to release ethylene linearly with an increase in temperature. This indicates that the thermal decomposition of the silver complex occurs over a wide temperature range. In order to obtain the stoichiometric absorption claimed in British Pat. No. 1,046,416, it would be necessary to use a 12-molar solution of $AgBF_3OH$.

EXAMPLE X

The data in Table XIII demonstrate that no major changes occur in the effectiveness of the copper complex over a period of three cycles. Recycling with absorption temperatures of 75 to 100° C. gives comparable results. The variation of the data is due to the absorption taking place at a temperature where the desorption slope is sharp. A slight variation in temperature in this range can cause a significant change in amount of ethylene absorbed in the complex.

TABLE XIII.—RECYCLE ETHYLENE THRU 1 MOLAR COPPER COMPLEX ABSORPTION TEMPERATURE, 100°C.

Cycle	Absorption cc. complex at absorption temperature	Cc. ethylene still absorbed at— 105° C.	110° C.
1	29.4	28.4	26.6
2	27.0	25.9	23.7
3	23.0	21.4	19.2

EXAMPLE XI

An attempt to absorb nitrogen by the copper complex described in Example I in acetic acid is shown in Table XIV. The data show that the solution is initially saturated with nitrogen in cycle 1. The small amount of nitrogen absorbed and desorbed in cycles 2 and 3 is attributed to physical solubility and not necessarily to chemical absorption.

TABLE XIV.—RECYCLE NITROGEN THRU 1 MOLAR COPPER COMPLEX CONCENTRATED ACETIC ACID AS BLANK ABSORPTION TEMPERATURE, 75° C.

Cycle	Solution	Absorption cc. complex at absorption temperature	Cc. nitrogen. still absorbed at— 85° C.	105° C.	110° C
1	Complex	0	−0.2	−0.7	−0.9
2	do	2.0	1.8	1.2	1.0
3	do	1.6	1.4	0.8	0.6
1	Blank	0	−0.2	−0.7	−1.0
2	do	1.4	1.2	0.6	0.4

EXAMPLE XII

The absorption of propylene over the copper complex of Example I is shown in Table XV.

TABLE XV.—RECYCLE PROPYLENE THRU 1.0 MOLAR COPPER COMPLEX ABSORPTION TEMPERATURE, 75° C.

Cycle	Absorption cc. complex at absorption temperature	Cc. propylene still absorbed at— 85° C.	105° C.	110° C.	118° C.
1	36.8	36.3	32.3	29.3	5.5
2	35.9	34.9	29.9	25.9	5.7
3	33.5	32.2	25.7	22.7	4.6
1 (HOAc blank)	6.6	6.2	4.6	4.3	3.2

It appears that the absorption of propylene is greater than the absorption of ethylene; however, a comparison of the physical solubility of propylene and ethylene in acetic acid shows their differences in chemical absorption by the complex are approximately equal to their differences in physical solubility in acetic acid. A comparison of ethylene absorption in $AgBF_4$ with the fluoborate of the copper complex is shown in Table XVI.

TABLE XVI.—RECYCLE ETHYLENE THRU 1.0 MOLAR $AgBF_4$ ABSORPTION TEMPERATURE, 75° C.

Cycle	Absorption per cc. complex at absorption temperature	85° C.	105° C.	110° C
1	8.7	7.7	2.9	1.4
2	12.2	10.0	4.8	3.5
3	8.2	8.1	0.8	−0.6
4	11.6	9.4	4.2	
HOAc blank	3.4	3.1	2.2	1.7
HBF_4 blank	1.9	1.4	0.6	0.3

EXAMPLE XIII

A one molar copper complex solution was prepared by the procedure of Example I from 50 g. of copper II acetate monohydrate, 49 g. of glacial acetic acid, 43 ml. of perchloric acid dihydrate, 136 ml. of acetic anhydride and 1.6 g. of metallic copper. This complex was similar to the complex of Example VIII in the selective absorption of ethylene from ethylene-nitrogen mixtures by the procedures described in Example VIII.

We claim:

1. The process for separating an olefinic hydrocarbon from mixtures containing same comprising selectively absorbing and desorbing said olefinic hydrocarbon by means of a copper complex resulting from the reaction of (1) copper II fluoborate or copper II perchlorate, (2) a carboxylic acid or anhydride having from 2 to 20 carbon atoms, and (3) a reducing agent selected from the group consisting of metallic copper, metallic nickel and an electric current.

2. The process of claim 1 wherein the olefinic hydrocarbon is a monoolefin having from 2 to 20 carbon atoms or a diolefin having from 4 to 20 carbon atoms.

3. The process of claim 2 wherein the copper complex is prepared at a temperature in the range of about 0° C. to about 230° C.

4. The process of claim 3 wherein the absorption is done at about atmospheric pressure and in the range of about 25–85° C.

5. The process of claim 4 wherein the desorption is done at about atmospheric pressure and in the range of about 100–200° C.

6. The process of claim 5 wherein the olefinic hydrocarbon is ethylene, (1) is copper II fluoborate, (2) is acetic acid, and (3) is metallic copper.

7. The process of claim 5 wherein the olefinic hydrocarbon is propylene, (1) is copper II fluoborate, (2) is acetic acid, and (3) is metallic copper.

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