[Contribution from Massachusetts Institute of Technology]

Reaction of Olefins with Solid Cuprous Halides

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That olefins react with cuprous salts in solution has long been known. Berthelot[3] observed that ethylene was absorbed by hydrochloric acid solutions of cuprous chloride. Manchot and Brandt[4] found that ethylene at atmospheric pressure was absorbed by such a solution to the extent of one mole for each mole of cuprous chloride, forming a metastable compound which is empirically $CuCl \cdot C_2H_4$. Ethylene is also known to react with ammoniacal cuprous solutions, several patents[5] having been granted for the recovery of ethylene by absorption in ammoniacal solution.

One case of the reaction of an olefin with a solid cuprous halide has been reported by Tropsch and Mattox.[6] They found propylene did not react. Ethylene was selectively recovered from mixtures of ethylene and ethane and of ethylene and propylene, but in a great deal less than stoichiometric proportion. Chavastelon[7] obtained a similar acetylene compound, $Cu_2Cl_2 \cdot C_2H_2$, and reports equilibrium pressures substantially lower than those for ethylene.

The work reported in this paper summarizes the results obtained employing other systems of olefins and solid cuprous salts.

Experimental

Procedure.—The high variation of the equilibrium pressure of the addition compounds with temperature made it desirable to separate the experimental work into two parts, high pressure and low pressure.

In the high pressure work an accurately known quantity of a powdered cuprous salt was mixed with small mesh pumice and introduced into a steel autoclave. The reactor was then charged with ethylene at about 60 atmospheres pressure for twelve hours at 0°, after which the ethylene was bled from the reactor until the pressure fell just below the vapor pressure of liquid ethylene at 0°. The remaining ethylene was then removed at constant temperature by releasing successive portions of known volume. Sufficient time was allowed between the successive proportions of the gas to obtain pressure equilibrium. These equilibrium pressures were plotted *versus* the volume of the gas withdrawn and the curve gave a plateau at the dissociation pressure of the addition com-

pound; the volume of gas corresponding to the length of the plateau represented the amount of olefin combined with the cuprous salt.

The procedure for measuring the equilibrium dissociation pressure as a function of temperature was identical with that outlined above except that the extraction of gas was discontinued when the constant pressure period was reached. The temperature was then increased in steps, and the corresponding equilibrium pressures were recorded.

The low pressure apparatus was constructed of glass, but the operation was similar to that outlined for the high pressure work.

The operation for the study of mixtures consisted of treating the cuprous salt at constant temperature and pressure with a known gas mixture. Analyses and volume measurements were made of both the unabsorbed portion of the gas and of the gas obtained on decomposing the addition compound.

Pressure measurements were, in general, more accurate than temperature measurements for both the low and high pressure apparatus. Pressure measurements at a given temperature checked to within 3 mm. for the low pressure apparatus, and to within 20 mm. for the high pressure apparatus. Temperatures, however, were read with a calibrated thermometer and are subject to an estimated maximum error of 1 °C.

Results

The results show that such reactions are not limited to ethylene and solid cuprous chloride. Propylene combines mole for mole with solid cuprous chloride yielding a highly dissociative compound which may be written empirically as $CuCl \cdot (C_3H_6)$. Isobutylene forms a similar compound which probably is $CuCl \cdot i\text{-}C_4H_8$, although in this case complete saturation of the cuprous chloride was not obtained, presumably due to the fact that equilibrium was not reached. In one experiment 0.62 mole of isobutylene reacted per mole of solid cuprous chloride in contact with liquid isobutylene at −50°. The molal ratios measured are given in the following table.

Table I

Olefin	Mole olefin	Mole CuCl	Mole olefin/mole CuCl
Ethylene	0.186	0.202	0.921
Ethylene	.1468	.150	.979
Ethylene	.1424	.150	.950
Propylene	.01162	.01237	.941
Propylene	.01161	.01237	.940
Propylene	.143	.150	.954
Isobutylene	.0318	.0514	.620
Ethylene	.1328	.1393 (CuBr)	.953

(1) Present address: Standard Oil Co. of La., Baton Rouge, La.
(2) Present address: Ingersoll-Rand Co., New York, N. Y.
(3) Berthelot, *Ann. chim. phys.*, **23**, 32 (1901).
(4) Manchot and Brandt, *Ann.*, **370**, 286 (1909).
(5) French Patent 797,490; British Patent 393,317; U. S. Patent 1,977,659.
(6) Tropsch and Mattox, This Journal, **57**, 1102 (1935).
(7) Chavastelon, *Compt. rend.*, **126**, 1810 (1898).

TABLE II

CuCl·C₂H₄		CuCl·C₃H₆		CuCl·i-C₄H₈		CuBr·C₂H₄	
Temp., °C.	Pressure atm. abs.	Temp., °C.	Pressure atm. abs.	Temp., °C.	Pressure atm. abs.	Temp., °C.	Pressure atm. abs.
−42.0	0.0645	−47.0	0.0342	−55.5	0.0165	0.0	17.5
−37.0	.0986	−41	.0710	−46.0	.0394	5.0	23.2
−34.0	.129	−36.0	.0947	−39.5	.0763	10.0	30.7
−28.0	.209	−33.5	.128	−35.5	.121	15.0	42.3
−26.5	.262	−31.1	.168	−33.5	.147	17.0	49.1
−21.0	.382	−25.5	.258	−30.0	.204		
−17.0	.497	−23.0	.392	−26.5	.300		
−14.0	.636	−18.0	.538	−24.5	.352		
− 8.5	.956	−12.0	.960	−18.0	.600		
− 8.0	1.06	− 8.5	1.21	−15.5	.668		
− 7.0	1.15	− 5.5	1.52	−13.0	.761		
0.0	1.95	− 4.5	1.73	−12.3	.795ᵃ		
12.5	4.25	− 3.0	2.06	− 6.5	.989ᵃ		
24.0	8.06			− 4.5	1.15ᵃ		
35.5	15.9			4.8	1.54ᵃ		
44.0	23.8			6.6	1.62ᵃ		
61.0	52.5						

ᵃ Vapor pressures of liquid isobutylene.

The equilibrium data obtained are given in Table II and Fig. 1. The data obtained for the cuprous chloride–ethylene compound agree well with those of Tropsch and Mattox.[6]

At low temperatures where all three olefins (ethylene, propylene and isobutylene) react with cuprous chloride, the equilibrium pressure curves are almost identical. The propylene and isobutylene curves are practically coincident and the ethylene curve shows only a slight deviation from these two, indicating that the reaction is characteristic of the unsaturated structure and is not markedly influenced by molecular weight. At higher temperatures, molecular weight plays a much more important part in the behavior of the olefins toward solid cuprous chloride than does the unsaturated structure in the molecule. Ethylene has been found to combine with solid cuprous bromide mole for mole, according to the formula CuBr·C₂H₄, indicating that the reaction is not limited to the chloride. The bromide has been found to have different properties from the chloride, but these may be described and explained on the same basis as the chloride.

A consideration of Fig. 1 shows that a gaseous olefin cannot react with the solid cuprous salts at temperatures higher than correspond to the intersection of the dissociation pressure curve with that of the vapor pressure curve of the olefin in question. These maximum reaction temperatures are approximately 20° for propylene with cuprous chloride and −18° for isobutylene with cuprous chloride. Tropsch and Mattox observed that no propylene was absorbed by

cuprous chloride at 23° and 11 atmospheres absolute. This point is very close to the maximum reaction temperature under which condition reaction of the gas would be difficult to observe. Had they operated at a lower temperature reaction no doubt would have been detected.
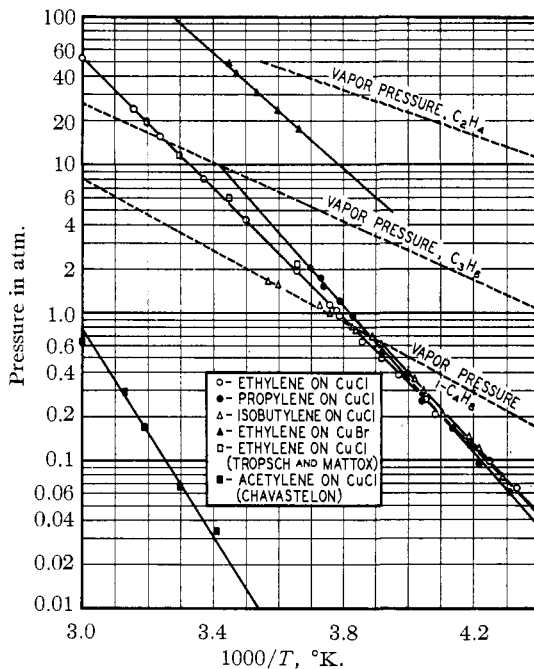

Fig. 1.—Dissociation pressures.

The slopes of the lines of Fig. 1 together with P–V–T data permit the calculation of the heat of reaction at various temperatures. These calculated values of the heat of reaction varied from 10,000 to 11,000 cal. per gram mole at low tem-

peratures down to approximately 7000 cal. per gram mole at the highest temperatures employed.

Under suitable conditions olefins may be recovered from gaseous or liquid mixtures by the use of solid cuprous halides. Consider a gaseous mixture of ethylene and ethane over solid cuprous chloride. Using the Lewis and Randall fugacity rule,[8] the addition equilibrium relation for the mixture can be expressed as

$$yf = f_s$$

where y is the mole fraction of ethylene in the gas phase, f the fugacity of ethylene at the total pressure and temperature of the mixture and f_s the fugacity of ethylene in the equilibrium with the solid complex at the total pressure and temperature. If the difference in volume between the cuprous chloride and the addition compound be neglected, f_s is independent of pressure. Using these assumptions the recovery of ethylene from a given mixture under definite conditions of pressure and temperature may be computed from this equation using the fugacity data given by Lewis and Kay.[9]

Tropsch and Mattox[6] passed a mixture of 60% ethylene and 35% propylene over an excess of cuprous chloride at a pressure of 17.7 atmospheres. They found that "of the 13 liters of ethylene passed only four liters was absorbed, 0.35 mole for each mole of cuprous chloride." Assuming a temperature of 25° the equilibrium value of the recovery calculated as outlined is 4 liters. This calculation is based on an assumed temperature since the authors failed to report the temperature of their observation. These investigators observed that practically no reaction was obtained in the case of a 61% ethylene–35% ethane mixture at 39 atmospheres. The temperature is not reported. Assuming a temperature of approximately 25°, reaction should have proceeded. This is borne out by the success of the present work when dealing with a mixture of ethylene and ethane containing 48% ethylene.

(8) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923.

(9) Lewis and Kay, *Oil Gas J.*, March 29 (1934).

Ethylene was recovered from this mixture to the extent of 0.515 mole per mole of cuprous chloride and concentrated to a purity of 98%. This reaction was carried out at 20° and 50 atmospheres absolute pressure. After the reaction had ceased, the ethylene mixture bled from the reactor in successive portions yielded analyses which checked values that were computed by the fugacity method. In similar fashion, ethylene was also recovered from a mixture of hydrogen and ethylene containing 42% ethylene at a temperature of 20°. Here again saturation was not reached, 0.693 mole of ethylene being combined with each mole of cuprous chloride. In like manner, analysis of the gas bled from the reactor checked the equilibrium values calculated. In this case the purity of the removed ethylene was 97%.

Liquid phase reaction was carried out at atmospheric pressure and temperatures lower than that of the intersection of the vapor pressure curve with the addition-compound curve using a mixture of propane and propylene containing 48% propylene, and employing about 50% excess of cuprous chloride. 86% of the propylene was recovered as compared to a computed maximum recovery of 91% for the conditions of the experiment. The liquid mixture was allowed to remain in contact with the solid for about fifteen minutes and the container was not agitated. The purity of the recovered propylene was 98%.

Summary

Ethylene, propylene and isobutylene are absorbed by solid cuprous chloride and ethylene is absorbed by solid cuprous bromide, indicating that the reaction is characteristic of the olefins and the cuprous halides. Except for isobutylene, approximately one mole of olefin is absorbed for one mole of cuprous halide. Olefins have been absorbed from several mixtures and concentrated by the use of these salts and a method for calculating the theoretical maximum recovery is outlined.