[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Absorption of Ethylene by Solid Cuprous Chloride

BY HANS TROPSCH AND W. J. MATTOX

Only a few instances of the absorption of ethylene by cuprous chloride have been recorded in the literature. These absorptions were observed at atmospheric pressure and, usually, with aqueous solutions.

Berthelot[1] in 1901 observed that the ethylene absorbed by a hydrochloric acid solution of cuprous chloride agreed with the relationship CuCl, 0.17 C_2H_4. With propene the ratio was CuCl, 0.25 C_3H_6. Manchot and Brandt[2] found that cuprous chloride and ethylene combine forming a dissociative compound in which one mole of ethylene is united with one mole of cuprous chloride; the combination did not occur in the absence of water. Dubois[3] states that olefins are absorbed quantitatively from mixtures with other gases by acid cuprous chloride and ammoniacal cuprous chloride.

A patented process[4] for separating ethylene from its homologs consists in absorbing it in an ammoniacal cuprous solution and recovering it therefrom by heating and (or) reduced pressure.

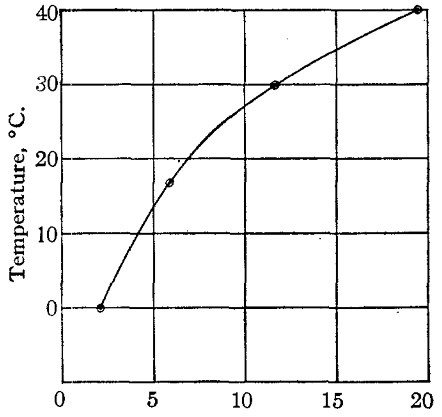

Fig. 1.—Dissociation pressure curve of $CuCl\text{-}C_2H_4$.

Blacet, MacDonald and Leighton[5] have used solid cuprous chloride containing a small amount of potassium hydroxide for the quantitative absorption of acetylene; no ethylene was absorbed by this reagent.

The present work on the absorption of ethylene by solid cuprous chloride was made with regard to the extent of the absorption, the liberation of the ethylene, and the possibility of using this absorbent in concentrating or purifying ethylene contained in gas mixtures.

Quantitative absorption experiments were made by placing approximately 50 g. of cuprous chloride, accurately weighed, in a glass tube inside a small steel bomb of known volume under a pressure of 60 to 62 atmospheres of ethylene until saturated. The pressure was then released and the volume of ethylene liberated measured by displacement over salt water. By allowing for the free space in the bomb, the amount of ethylene absorbed by the cuprous chloride was found to be one mole of ethylene for each mole of cuprous chloride, indicating the formation of the addition compound $CuCl\cdot C_2H_4$. This addition compound decomposed at atmospheric pressure, slowly at 25° but rapidly at temperatures around 100°. After removing the ethylene, a higher activity was observed in subsequent absorptions.

The dissociation pressure of $CuCl\cdot C_2H_4$ was determined at 0° by saturating 50 g. of powdered cuprous chloride at 0°, quickly releasing the excess of ethylene, and observing the pressure when equilibrium was reached. The temperature of the thermostat in which the pressure apparatus was kept was then raised to 16.8, 30.0 and to 40.0° and the pressure, at equilibrium, observed at each of these temperatures. The dissociation pressures observed at these temperatures are given in the following table and graphically in Fig. 1.

Temp., °C.	0	16.8	30.0	40.0
Press., atm. (abs.)	2.14	5.95	11.70	19.49

Temperature and the state of division of the cuprous chloride influenced the rate at which it absorbed ethylene. The rate of absorption at 0°, measured by the time required for the pressure of the ethylene when confined over 50 g. of cuprous chloride to fall from 50 to 20 atmospheres, was 1.4 times the rate at 17°.

The presence of less than 10% of infusorial earth in the cuprous chloride increased the rate of absorption. After removing the absorbed ethylene by releasing the pressure, the cuprous chloride exhibited a higher activity, and the speed of absorption of ethylene was 2.7 times that with the pure cuprous chloride. A small amount of water vapor also slightly increased the rate of absorption.

Ethylene was not absorbed at 60 atmospheres pressure (25°) by a suspension of cuprous chloride in water.

No polymerization of ethylene was observed in the presence of cuprous chloride at pressures of 65 to 80 atmospheres and temperatures of 100 to 200°.

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(1) Berthelot, *Ann. chim. phys.*, **23**, 32–39 (1901).

(2) Manchot and Brandt, *Ann.*, **370**, 286–296 (1909).

(3) Dubois, *Przemysl Chem.*, **14**, 313–318 (1930).

(4) Watts and Imperial Chemical Industries Ltd., British Patent 393,317, June 2, 1933.

(5) Blacet, MacDonald and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **5**, 272 (1933).

No absorption of propene by cuprous chloride was observed after seventy-two hours at 11 atmospheres pressure and 23°.

The absorption of ethylene from a 60% ethylene–35% propene mixture was made by passing 22.3 liters of the mixture at 17.7 atmospheres pressure over 50 g. of cuprous chloride contained in a glass-lined pressure tube at a rate of 0.8 liter per hour. Four and one-half liters of absorbed gas was released from the cuprous chloride which contained no propene and 90% of ethylene. However, of the 13 liters of ethylene passed only 4 liters was absorbed, 0.35 mole for each mole of cuprous chloride.

Following a similar procedure, 0.2 liter of gas, which contained 70% of ethylene, was absorbed from 12.1 liters of a 61% ethylene–35% ethane mixture at 39 atmospheres pressure. In this case only 0.012 mole of ethylene was absorbed for each mole of cuprous chloride.

Summary

1. Ethylene under pressure gives an addition compound with solid cuprous chloride which contains one mole of ethylene for one mole of cuprous chloride, $CuCl \cdot C_2H_4$. The dissociation pressure of this addition compound varies from 2.14 atmospheres at 0° to 19.49 atmospheres at 40°. The addition compound decomposes completely at atmospheric pressure, slowly at 25° but rapidly at 100°.

2. Propene under pressure is not absorbed by solid cuprous chloride.

3. Ethylene in mixtures with ethane and propene was selectively absorbed and concentrated but the absorbed ethylene amounted to only 0.012 and 0.35 mole for each mole of cuprous chloride.

RIVERSIDE, ILL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

Hydroxy Polyketones. I. The Alkylation of Benzoylformoin

BY A. H. BLATT

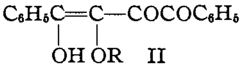
This article presents one part of what is planned as an extensive survey of the chemical behavior of the hydroxytriketone benzoylformoin (I), the benzoin of phenyl glyoxal, and of certain other structurally analogous substances.[1] Our interest in this group of compounds was occasioned in part by their unusual reactivity but, primarily, by the possibility of their existence as enols. For the enols of certain hydroxy polyketones would contain the ene-diol grouping characteristic of ascorbic acid and they should enable us to study, using synthetic material of definite structure and easy availability, the chemical behavior of the ene-diol system.

Benzoylformoin and a number of its analogs were first prepared and investigated by Söderbaum and by Abenius,[2] while the latter studied in detail the chemical behavior of benzoylformoin itself.[3] Abenius showed that benzoylformoin when dissolved in an alcohol and treated with hydrogen chloride formed a monoalkyl derivative and that a second alkyl group could be introduced into this monoalkylation product by means of an alcoholate and alkyl halide. The dialkyl derivatives on solution in sulfuric acid lost one alkyl group to form monoalkyl benzoylformoins isomeric with the monoalkylation products obtained from benzoylformoin itself. By using dialkyl derivatives containing two *different* alkyl groups Abenius showed that the alkyl group introduced by means of alcohol and acid was always the one eliminated by treatment with sulfuric acid. He also found that benzoylformoin and its first monoalkyl derivatives, in contrast to the dialkyl derivatives and the monoalkylation products derived from them, were oxidized by acid oxidants to diphenyl tetraketone. Abenius assigned to the monoalkyl derivatives obtained by the use of alcohol and acid the structure (II), to the dialkyl derivatives the structure (III), and to the second series of monoalkyl derivatives the structure (IV). Benzoylformoin, he considered

$C_6H_5COCHOHCOCOC_6H_5$ I

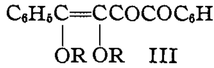
$C_6H_5C(OH){=}C(OH)COCOC_6H_5$ Ia

$C_6H_5COC(OH){=}C(OH)COC_6H_5$ Ib



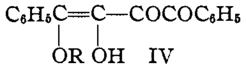
$$\underset{\textstyle OH}{C_6H_5\overset{|}{C}}{=}\underset{\textstyle OR}{\overset{|}{C}}{-}COCOC_6H_5$$

II



$$\underset{\textstyle OR}{C_6H_5\overset{|}{C}}{=}\underset{\textstyle OR}{\overset{|}{C}}COCOC_6H_5$$

III



$$\underset{\textstyle OR}{C_6H_5\overset{|}{C}}{=}\underset{\textstyle OH}{\overset{|}{C}}{-}COCOC_6H_5$$

IV

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[1] We are publishing certain of our results at this time because of the recent appearance of an article on formoins by Karrer and v. Segesser, *Helv. Chim. Acta*, **18**, 273 (1935).

[2] (a) Söderbaum, *Ber.*, **24**, 1381 (1891); (b) Abenius and Söderbaum, *ibid.*, p. 3034; (c) Söderbaum, *ibid.*, **25**, 3459 (1892); (d) Abenius and Söderbaum, *ibid.*, p. 3468.

[3] Abenius, (a) *Bihang Till K. Sv. Vet.-Akad. Handl.*, **20**, 3 (1894); (b) *Ber.*, **27**, 706 (1894).