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ACETYLENE POLYMERS AND THEIR DERIVATIVES. I. THE CONTROLLED POLYMERIZATION OF ACETYLENE

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As early as 1906 the observation was made that if acetylene is passed into a solution of cuprous chloride and sodium or potassium chloride, there is developed a most peculiar odor, very unlike that of acetylene. A number of unsuccessful attempts were made to separate what was thought to be a derivative or compound formed by the action of acetylene on the copper salt mixture, but it was not until 1921 that the idea occurred that only by the use of a more highly concentrated cuprous chloride solution could satisfactory results be hoped for. Recalling that the desired high concentration could be obtained by the use of ammonium chloride or amine salts, the earlier work was repeated, using several liters of solution, in order to obtain measurable amounts of the new compound. It was at first supposed that the derivative might be a gas and appropriate apparatus was constructed for catching it. However, on distilling the product formed by the absorption of acetylene in an aqueous solution of cuprous chloride and ammonium chloride, the receiver was found to contain several cubic centimeters of a highly refractive liquid, with an odor resembling that observed in the earlier work. About four years were spent at Notre Dame in modifying the process so as to obtain the maximum yield in the shortest time.

The du Pont Company had for some time been interested in acetylene reactions and in the possibility of the manufacture of synthetic rubber, because of the well-known limitations of natural rubber and especially because of the lack of an adequate supply in this country. Acetylene had been considered the ideal starting point because of the availability of unlimited quantities of the raw materials, lime and carbon. The work started at Notre Dame was therefore continued at the Jackson Laboratory with the general purpose of broadening our knowledge of acetylene polymers, and in the hope that the highly reactive product of the acetylene reaction above noted might prove a satisfactory starting point for the preparation of synthetic rubber.

Although a satisfactory synthetic rubber was not obtained from this compound, which was found to be divinylacetylene, the work resulted in the preparation of a new drying oil, from which could be made films of great hardness and most unusual chemical stability, which are not softened by any known solvents. Furthermore, the ground was prepared

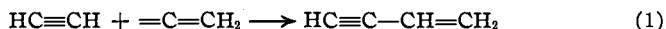
for the development of a number of interesting fields of research, the various phases of which will be made the subject of future papers. In this paper will be described the polymerization of acetylene and the properties of the compounds obtained.

Theoretical

The polymerization of acetylene in contact with suitable aqueous cuprous chloride solutions is undoubtedly more complex than the scope of our definite knowledge. Intermediate addition products of cuprous chloride with acetylene and vinylacetylene, as well as divinylacetylene, have been isolated, but their instability has hampered all efforts to purify them for exact analysis. Our knowledge of the progressive reactions taking place in the catalyst is definite with respect to the end products, and the speculations with regard to the intermediates have proved a valuable working basis for the development of plant processes.

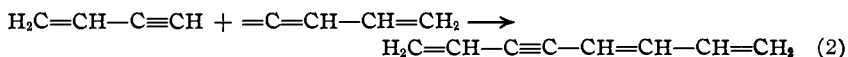
A saturated solution of ammonium and cuprous chlorides will absorb acetylene with the formation of a heterogeneous crystalline mass of dissolved and precipitated addition products of C_2H_2 and Cu_2Cl_2 . Whether these partially soluble salts also contain ammonium chloride, as might be deduced from the work of Chavastelon,¹ is questionable. From the results of the present work, it would appear more probable that one or two molecules of acetylene enter the cuprous ammonium chloride complex with a displacement of the ammonium chloride. If the $C_2H_2-Cu_2Cl_2$ product is heated soon after formation, acetylene is almost completely regenerated, but if it be allowed to stand for a period of 120 hours or longer, no acetylene is found in the distillation product, but, instead, polymers of acetylene with molecular weights corresponding to C_6H_6 and C_8H_8 . The primary addition product undergoes a progressive reaction resulting first in the formation of C_4H_4 , which then combines either with itself or with another C_2H_2 to form C_8H_8 and C_6H_6 , respectively. This is verified, for the catalyst solution will similarly absorb vinylacetylene (C_4H_4) and in due course convert it completely to C_8H_8 . This reaction is limited to acetylenic compounds containing ($-C\equiv C-H$), therefore C_8H_8 and C_6H_6 are the ultimate products of complete reaction, for these contain no acetylenic hydrogen and can react no further with acetylene.

The mechanics of this may well be pictured as the formation of a complex cuprous salt which is in equilibrium with normal acetylene and activated acetylene, possibly $=C=CH_2$. Upon aging, the activated C_2H_2 slowly reacts with acetylene with which it is associated in the complex molecule, to produce vinylacetylene



¹ Chavastelon, *Compt. rend.*, **124**, 1364 (1897); **126**, 1810 (1898); **130**, 1634, 1764 (1900); **131**, 48 (1900); **132**, 1489 (1901).

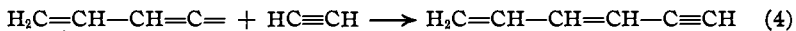
Vinylacetylene, as formed, is capable of similar absorption by cuprous chloride to form an addition product analogous to that of acetylene, and likewise it is apparently in a state of equilibrium with normal, absorbed and activated C_4H_4 , the activated molecules being present to a much smaller degree than in the case of C_2H_2 . It therefore may undergo a similar reaction with another molecule of vinylacetylene, but at a slower rate



The latter product, which will be referred to as "tetramer," is substantially the only product obtained from vinylacetylene when it is reacted in the catalyst in the absence of acetylene. In the presence of acetylene, C_4H_4 and C_2H_2 may react to produce divinylacetylene



To this extent, the reaction mechanism is substantiated by the products both with regard to quantity and constitution. The mechanism should also permit the reaction of active vinylacetylene with acetylene to form an isomeric C_6H_6 which might subsequently react to form $C_{12}H_{12}$ as an end product.



This reaction has not been established, though the existence of such a product in small quantities has been evidenced by the appearance of tests for acetylenic hydrogen in samples of divinylacetylene which have been rectified to remove vinylacetylene. The small quantity of this material which can be present precludes the existence of more than a trace of $C_{12}H_{12}$. The activation of C_4H_4 as determined by reaction (2) is very much slower than the activation of C_2H_2 , hence (4) is very slow as compared to (3), if it takes place at all.

Acetylene Polymers

Vinylacetylene.—Vinylacetylene is a colorless liquid with the sharp but sweet odor associated with synthetic butadiene; its density is given by the equation

$$d_0^t = 0.7095 - 0.00114t$$

for temperatures between -3 and -80° , at $t = +1.5^\circ$, d_0 0.705. Table I gives the vapor pressures of pure vinylacetylene.

The structure of vinylacetylene, $HC\equiv C-CH=CH_2$, has been proved by catalytic hydrogenation to *n*-butane with the absorption of six atoms of hydrogen, and by hydration of the triple bond in the presence of $HgSO_4$ and H_2SO_4 to 1-butene-3-one, $CH_2=CH-CO-CH_3$. It forms the usual white silver salt and a yellow salt typical of acetylenic hydrogen when treated with ammoniacal solutions of the suitable reagents; it forms a

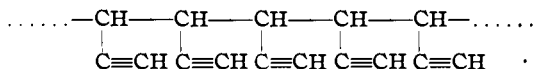
TABLE I

VAPOR PRESSURES OF VINYLACETYLENE

Temp., °C.	Vapor pressure, mm.	Temp., °C.	Vapor pressure, mm.
-47	48.8	0	621
-35	107	+ 5	757
-28	160	+12	952
-21	237	+17.6	1166
-15	320	+22.4	1380
-10	401	+40	2400 (\approx 100)
- 5	499	+60	4100 (Calculated)

crystalline hydrate of uncertain composition, probably $C_4H_4 \cdot 2H_2O$, at temperatures below -10° in the presence of moisture.

Under pressure, with or without the usual polymerization catalysts such as benzoyl peroxide, sodium perborate, etc., vinylacetylene is readily polymerized by heat to form viscous drying oils and finally hard resinous solids. The polymers of C_4H_4 contain acetylenic hydrogen and it is believed they possess the structure



Divinylacetylene (DVA).—Divinylacetylene is a colorless liquid, rapidly becoming straw-colored upon exposure to light, which possesses an unusual alliaceous odor. Table II gives the vapor pressures of divinylacetylene at various temperatures.

TABLE II

VAPOR PRESSURES OF DIVINYLCETYLENE

Temp., °C.	Vapor pressure, mm.	Temp., °C.	Vapor pressure, mm.
-20	7	70	500 ^a
0	21	80	695 ^a
+10	64	83.5	760
30	103	90	980 ^a
50	240		

^a Figures for temperatures above 50° , other than at the boiling point, are subject to slight possible error due to polymerization.

The density and refractive index are d_4^{20} 0.7851; n_D^{20} 1.504 \pm 0.002 (both of which are very sensitive to polymerization).

Divinylacetylene may be hydrogenated to *n*-hexane by the addition of exactly eight atoms of hydrogen, and brominated by the addition of six atoms of bromine forming a mixture of the geometrically isomeric 1,2,3,4,5,6-hexabromo-3-hexenes, m. p. 81 and 114° . Further direct bromination results in substitution as well as addition. Divinylacetylene rapidly absorbs oxygen from the air, forming a highly explosive peroxide (or ozonide) which has been found to detonate spontaneously with violence

upon standing. When pure, divinylacetylene thermally decomposes at 105–110°, but if heated at temperatures below this point in an inert atmosphere, it may be polymerized first to a viscous liquid and finally to a hard brittle resin which is insoluble in all known solvents.²

The intermediate liquid products are synthetic drying oils³ possessing high stability, but drying by oxidation and polymerization to films of good quality which display chemical resistance to an unusual degree.

No solvent or combination of solvents is capable of even softening the films, while acids, alkalis and reagents other than vigorous oxidizing agents have no effect upon this unique resin. In the pure form, divinylacetylene may be stabilized for storage by the addition of antioxidants. Hydroquinone, catechol, dibutylamine, phenyl- α -naphthylamine, etc., are examples taken from a considerable list of compounds capable of preventing the formation of explosive oxidation products in the liquid.

Tetramer.—The so-called "tetramer" of acetylene is believed to be 1,5,7-octatriene-3-ine. This structure is chosen because of the fact that the material will absorb ten atoms of hydrogen to form *n*-octane, and in view of the theoretical considerations already presented. The tetramer is a colorless liquid resembling divinylacetylene chemically; it possesses an apparent boiling point of 156° with violent decomposition, and boils with polymerization at 40° (20 mm.), 50° (30 mm.), and 82° (100 mm.); other characteristic physical properties are d_{20} 0.830, n_D^{20} 1.576.

Experimental

Laboratory Preparation of Monovinylacetylene.—Although the preparation of monovinylacetylene proved to be more difficult than that of divinylacetylene, we have been able to modify the reaction so as to obtain substantial amounts of the monovinyl derivative. Since the details of this modification are complex, while the principle is rather obvious, it appears preferable to treat this problem in a separate paper. Small quantities of monovinylacetylene may be obtained by careful fractionation of the low boiling portions from crude divinylacetylene, but laboratory quantities are perhaps best prepared by the method of Willstätter and Wirth.⁴

Laboratory Preparation of Divinylacetylene.—The following procedure provides a satisfactory method of preparing laboratory quantities of divinylacetylene with good yields.⁵ Introduce into a 2-liter round-bottomed flask 1000 g. of cuprous chloride, 390 g. of ammonium chloride, 100 g. of precipitated copper powder, 30 g. of hydrochloric acid (37%) and 425 g. of water. This mixture of dissolved and undissolved salts should be tightly stoppered to prevent access of air and aged on a steam-bath for twenty-four hours, or until all of the copper is in the cuprous state as indicated by the disappearance of the green cupric salt color.

When reduced, the catalyst is cooled to room temperature and charged with acetylene by sweeping the flask and shaking the catalyst under a slight pressure of acetylene

² J. A. Nieuwland, U. S. Patent 1,812,541, June 30, 1931.

³ A. M. Collins, U. S. Patent 1,812,544 and 1,812,849, June 30, 1931.

⁴ Willstätter and Wirth, *Ber.*, **46**, 535 (1913).

⁵ J. A. Nieuwland, U. S. Patent 1,811,959, June 30, 1931.

gas until absorption practically ceases. Acetylene for this purpose should be washed with water, sulfuric acid and sodium hydrosulfite solution (or pyrogallol) to remove acetone, oxygen and other impurities. If the absorption slows down, it may be speeded by sweeping again with acetylene to displace inert gas. During the absorption the catalyst may warm up, which may be allowed to progress up to 40–50° without harm. The catalyst will become light yellow in color as insoluble addition compounds of acetylene, cuprous chloride and ammonium chloride are formed. Over one hundred grams of C_2H_2 will be taken up.

Allow this charged catalyst mixture to age at room temperature for five to seven days. At the end of this period, acetylene polymers are distilled off by heating the catalyst in an oil-bath to 100–110° (inside temperature) until nothing but water comes over. The temperature of the bath should not exceed 180°. The distillate will separate into two layers; the lower aqueous layer should be separated and returned to the catalyst mixture, which may then be recharged with acetylene and used again (catalyst color after distillation is red-brown). The oil layer, which is a mixture of divinylacetylene, a tetramer of acetylene, C_8H_8 , and small amounts of chlorine-containing by-products should be dried over sodium sulfate and distilled in vacuo using a water-bath. Divinylacetylene should be distilled off at about 200 mm. and if it is then desired to bring over the tetramer, the pressure should be dropped to at least 20 mm. The temperature of the flask will have to be nearly 100°, for the boiling point of the tetramer will be elevated by the associated polymers.

The yield based on acetylene absorbed is: divinylacetylene, 70–80%; tetramer, 10%; loss, 10–20%.

Divinylacetylene is extremely dangerous to handle. The viscosity of the freshly prepared material rises rapidly on standing at room temperature, resulting in a gel and finally a hard resin. *These products can neither be distilled nor handled without explosions varying in degree from rapid decompositions to violent detonations.* The safest place for the hydrocarbon is in the catalyst mixture and this method of storage is recommended with distillation just prior to use.

Summary

A low temperature catalytic polymerization of acetylene has been described, producing vinylacetylene, divinylacetylene and a tetramer thought to be 1,5,7-octatriene-3-ine. A mechanism for this polymerization in the presence of aqueous cuprous chloride has been suggested and laboratory procedures have been briefly described. This paper describes the initial work in a successful search for synthetic rubber starting from acetylene.

WILMINGTON, DELAWARE