only on the total rate of hydrolysis but also on the relative amount hydrolyzing by the different paths. Furthermore, they emphasized the fact that the agreement which they obtained between their experimental data in sulfuric acid solutions and the calculated results was due to their arbitrary selection of a *p*H value for these solutions. Later, unpublished work in this Laboratory by Dr. P. T. Youle has shown that acetate and formate ions also have specific effects on lactone hydrolysis, the acid ester possibly being formed as an intermediate. We, therefore, wish to restrict consideration to the hydrolysis in water and in potassium hydroxide solution in spite of the concordant results which we obtained in the sulfuric acid solutions.

Summary

β-Butyrolactone was hydrolyzed in heavy oxygen water to form β-hydroxybutyric acid. The potassium salt of the acid was decomposed by heating to form water and potassium crotonate. The water from the decomposition was then analyzed for isotopic oxygen content.

The results are in complete agreement with the mechanism of hydrolysis advanced by Olson and Miller, and are contradictory to the carbonium ion mechanism proposed by Rørdam.

BERKELEY, CALIFORNIA RECEIVED JUNE 2, 1941

[CONTRIBUTION FROM PHYSICAL CHEMISTRY DEPARTMENT AT THE JAN KAZIMIERZ UNIVERSITY IN LWÓW, POLAND]

The Mechanism of the Photochemical Change of Acetylene*

BY BOLESLAW LUDWIK DUNICZ

I. Introduction

Ultraviolet light of wave lengths smaller than 2350 Å. produces polymerization in gaseous acetylene. A considerable number of authors have investigated this reaction as well as the similar reaction which is sensitized by mercury vapor.[1-10]

In these investigations a number of facts have been established which may be summarized briefly. At room temperature the main product of the reaction is a yellow powder precipitated from the gas phase, which is of unknown structure and closely resembles cuprene. The reaction rate increases strongly with the temperature; above 270° the character of the reaction undergoes a change and a second solid is formed, a hard coating of dark yellow color, partly soluble in ether, not insoluble like cuprene. This second solid resembles the product of the purely thermal polymerization of acetylene.

The photochemical reaction proceeds proportional to the pressure of acetylene, at least at small pressures where the absorption is proportional to the pressure. At higher pressures the rate becomes constant, being dependent only on the intensity of the effective light, but during the process it is decreased gradually because of the light absorption by the reaction product precipitated from the gas phase onto the walls of the reaction vessel. Besides the solid product, a small amount of benzene is formed; its bands can be found in the absorption spectrum of the gas phase. Some of the additional bands found in the spectrum were attributed to naphthalene hydrocarbons. The absence of hydrogen and methane in the gas phase was confirmed by several authors, which result proves that acetylene is not decomposed, in this reaction, into hydrogen and carbon.

The reaction is generally assumed to proceed by a chain mechanism. Bates and Taylor[3] suggested, for the unsensitized reaction as well as for the mercury sensitized reaction, that the polymer is formed by the successive addition of acetylene molecules to one which has been activated. The chain length of the reaction had been found to vary with the temperature, from $n = 10$ at 20° to $n = 100$ at 250°, and it was found to depend neither on the light intensity nor on the pressure of acetylene.[10] There is little certain knowledge, however, about the

---

* Original versions of this manuscript received May 2 and November 29, 1940.

(1) A. Thénard, *Compt. rend.*, **78**, 219 (1874).

(2) D. Berthelot and H. Gaudechon, *ibid.*, **150**, 1169 (1910).

(3) J. R. Bates and H. S. Taylor, THIS JOURNAL, **49**, 2438 (1927).

(4) H. Reinicke, *Z. angew. Chem.*, **41**, 1144 (1928).

(5) S. Kato, *Bull. Inst. Phys. Chem. Research* (Tokyo), **16**, 343 (1931).

(6) S. C. Lind and R. Livingston, THIS JOURNAL, **54**, 94 (1932).

(7) W. Kemula and S. Mrazek, *Z. physik. Chem.*, **B23**, 358 (1933).

(8) S. C. Lind and R. Livingston, THIS JOURNAL, **56**, 1550 (1934).

(9) S. C. Lind and C. H. Schiflett, *J. Phys. Chem.*, **38**, 377 (1934).

(10) H. W. Melville, *Trans. Faraday Soc.*, **32**, 258 (1936).

TABLE I

ABSORPTION SPECTRUM OF VINYLACETYLENE. PART I

Vinylacetylene at pressures of 0.04 to 40 mm.; thickness of gas layers, 120 cm.

Absorption maxima Å.	cm.$^{-1}$	Pressures, mm. 0.04	0.11	0.33	1	3	5	11	40
2256	44326	5 e							
2263	44189	2 d				Continuous absorption			
2273	43995	3 e	5 e						
2306	43365	2 e	3 e	6 e					
2322	43066		2 b	4 d					
2342	42698	1 b	3 b	3 b	6 d				
2352	42517			1 b	5 b				
2363	42319				2 b				
2373	42141	1 e	3 e	3 e	6 e				
2381	41999		3 b	3 b	5 b				
2392	41806				2 b	6 b	6 d		
2404	41597		2 b	2 b	5 d	6 e	6 e		
2411	41476				2 b	4 b	6 b		
2421	41305				2 b	3 b	3 b		
2426	41220				2 d	3 d	3 e		
2433	41101				2 a	2 b	3 b	5 b	
2447	40866				2 b	2 d	4 d	6 d	
2468	40519				1 a	1 d	2 e	3 e	
2483	40274						1 b	2 d	5 d
2492	40128						1 b	2 b	4 b
(m) 2507	39888								3 f
2533	39479								2 a
2549	39231								2 a
(m) 2553	39170								2 f

Explanation to abbreviations in Tables I and II:

1, scarcely perceptible	a, very narrow	(m) the middle
2, very weak	b, narrow	(s) the strongest (relative)
3, weak	c, rather narrow	(w) the weakest (relative)
4, rather strong	d, rather broad	~ approximately
5, strong	e, broad	
6, very strong	f, very broad	

specific steps of this chain mechanism. Kemula and Mrazek[7] believed the first step to consist in the formation of vinylacetylene; this assumption was founded on the absorption spectrum of the gaseous phase of the reaction products. This spectrum shows, apart from the band structure already mentioned, a continuous absorption which has to be attributed to an intermediate product, since its intensity depends only on the initial pressure of acetylene and not on the time of irradiation: for 53 mm. initial pressure the long wave length limit was found to be at 2410 Å., and for 389 mm. at 2565 Å. On the basis of the data of Lind and Livingston[11] on the continuous absorption of vinylacetylene, Kemula and Mrazek assumed the identity of their intermediate product with vinylacetylene.

II. Experiments and Results

In order to prove or disprove the formation of vinylacetylene as a first step in the reaction, and to acquire in general a deeper insight into the mechanism of the photochemical polymerization of acetylene, various lines of investigation were carried out.

1. **Absorption Spectrum of Vinylacetylene.**—Lind and Livingston[11] investigated the regions of absorption of vinylacetylene in the ultraviolet, but a more detailed knowledge of the absorption spectrum was necessary for this investigation. Absorption spectra at various pressures were taken. The results, in general agreement with the findings of these authors, are given in Fig. 1 and in Tables I and II, for pressures between 0.04 and 40 mm. and for 600 mm., respectively. The dispersion was too small to make any definite statements about the structure of the bands, but the general aspect of the spectrum is in agreement with the assumption of an easily polarized molecule: the sharp bands in the long wave length region of the ultraviolet are followed by

---

(11) S. C. Lind and R. Livingston, THIS JOURNAL, **55**, 1038 (1933).

TABLE II

ABSORPTION SPECTRUM OF VINYLACETYLENE. PART II

Vinylacetylene at 600 mm. pressure. Thickness of gas layer, 120 cm.

Band groups			Bands			
Group	Absorption	Broadness of the group, cm.$^{-1}$	Absorption maxima Å.	Absorption maxima cm.$^{-1}$	Absorption	Broadness
0			to 2580	38760	Continuous	
			2584	38700	5	a
			2601	38447	3	b
			2614	38255	3	d
1	4, diffuse	939	~2653	37693	4	f
			~2670	37453	4	e
2	5, diffuse	832	~2750	36364		
3	(s) diffuse	1201	~2820	35461		
4	5	1067	2882	34698	2	e
			2886	34650	2	a
			2893	34566	2	a
			2898	34506	(s)	b
			2904	34435	3	b
			2925	34188	2	b
5	4	1057	2976	33602	(s)	b
			2983	33523	5	a
			3005	33278	1	a
			3024	33069	2	a
			3033	32971	1	a
6	3	1196	3060	32680	(s)	b
			3068	32594	5	a
			3080	32467	3	a
			3087	32394	2	a
			~3091	32352	1	a
			~3111	32144	1	e
			3128	31970	2	b
			~3141	31837	5	b
			~3155	31696	1	a
7	2	828	3168	31566	2	b
			3174	31506	2	b
			3190	31348	1	c
			3204	31211	1	c
			3217	31085	1	c
8	(w)		3250	30769	(s)	b
			3263	30647	5	b
			~3275	30534	3	b
			~3294	30358	3	b
			~3305	30257	2	b

diffuse bands in the short wave length region, which finally border on a continuous spectrum.

2. Irradiation of Enclosed Volumes of Gases

(a) Irradiation of an Enclosed Volume of Acetylene.—The absorption spectrum of irradiated acetylene was then investigated under strongly variegated conditions. The initial pressure of acetylene was varied in one set of experiments, in another set the acetylene was diluted with nitrogen, the light source was varied in still another series, and finally acetylene was irradiated in solidified form. The products in the gaseous phase, in all these cases, appeared to be essentially the same. Benzene was found to be the only gaseous product which increased steadily during the reaction, since the intensity of its bands depended on the time of irradiation. All the other components of the gaseous phase proved to be intermediate products in equilibrium concentration, since the intensity of the other bands depended only on the initial pressure of acetylene and the effective intensity of the irradiation. On the basis of structure resemblance, location and sharpness these other bands can be divided into three groups with maxima as listed: group "a," bands, 2286, 2384 Å.; group "b," 2414, 2432, 2513 Å.; group "c," 2689, 2718, 2814 Å.

Each of these groups seems to represent a different substance, since variations of conditions alter their intensity independently, and it is probable that "a" represents a higher polymer while "b" and "c" belong to the lower more volatile polymers. In any case, none of these substances could be identified with vinylacetylene, according to the spectral evidence. Before considering this result, however, a few other facts have to be mentioned concerning these various series of experiments.

The pressure of acetylene was varied over a wide range—from 341 to 5.5 mm. Bands belonging to benzene were found in all cases and, in agreement with the reported findings of Kato,[5] the bands situated at 2528, 2539, 2589, 2595 and 2600 Å. were particularly strong. Of the other bands, two of them, situated at 2286 and 2384 Å., were especially evident at the lowest initial pressure of 5.5 mm. At higher pressures the other bands already mentioned made their additional appearance. With regard to the course of the reaction, observations of previous authors were confirmed. The yellow precipitate was formed as well in the gas phase where it produced a Tyndall effect, as at the wall where its absorption cut out part of the effective radiation; accordingly the reaction proceeded fastest in the beginning.

Dilution with an excess of nitrogen (91%) did not change the course of the reaction as can be seen by comparing Fig. 3 with Fig. 2. Fig. 4 shows that the results of irradiation by a lead spark coincide with the result of the earlier irradiation by a quartz mercury lamp, at least qualitatively. The formation of cuprene was likewise observed. This should be mentioned in view of Kato's[5] assumption that these two light sources produced entirely different reactions.

(b) Irradiation of an Enclosed Volume of Vinylacetylene, Alone and in Mixture with Acetylene.—The absence of vinylacetylene bands in the spectrum of irradiated acetylene, found in the previous paragraph, does not quite conclu-

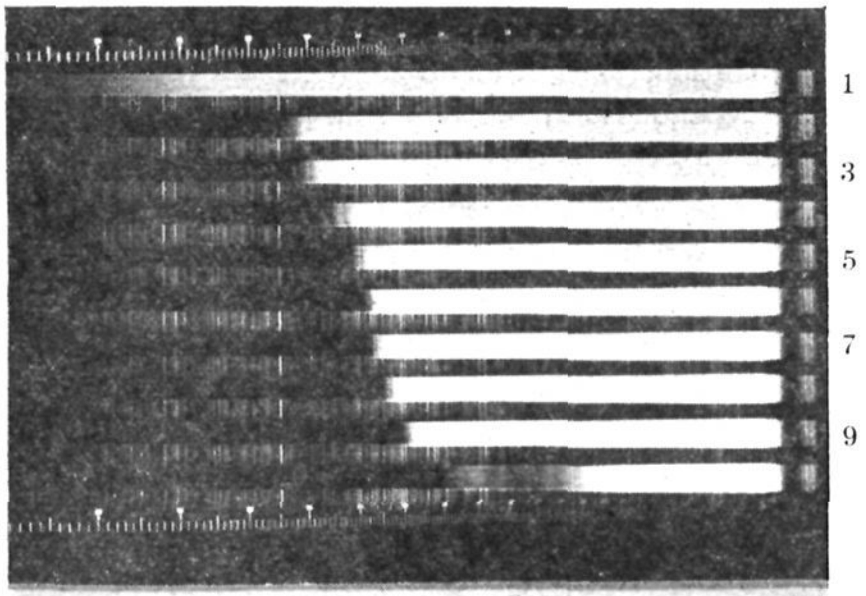


Fig. 1.—1, Vacuum; 2-10, vinylacetylene (p = 0.04, 0.11, 0.33, 1, 3, 5, 11, 40 and 600 mm., respectively).* Beneath each absorption spectrum is shown the tungsten spark spectrum.

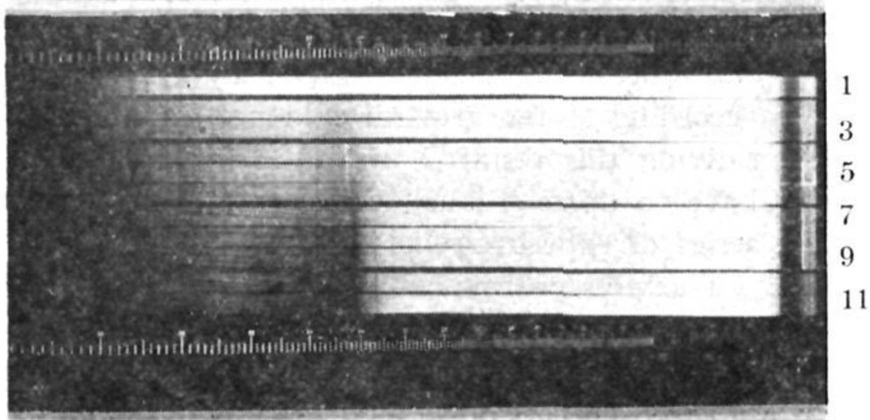


Fig. 2.—1, Acetylene (p = 5.5 mm.); 2-9, acetylene after 20 sec., 1, 2, 5, 10, 20, 60, and 120 min., respectively, of total illumination at 3 cm. distance from the reaction tube; 10 shows state 9 after 12 hours; 11 shows acetylene after further (330 min.) illumination through a new spot of the reaction tube.**

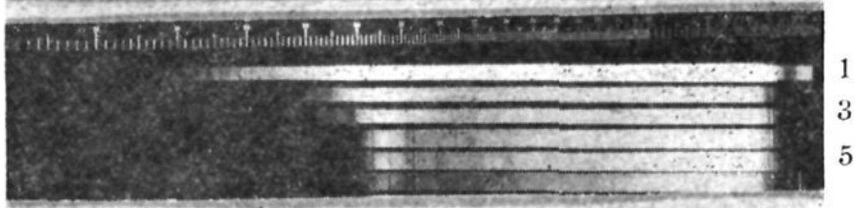


Fig. 3.—1, Acetylene (p = 40 mm.) ten-fold diluted with nitrogen; 2-6, acetylene after 1, 6, 21, 51 and 81 min., respectively, of total illumination at 1 cm. distance from the reaction tube.***

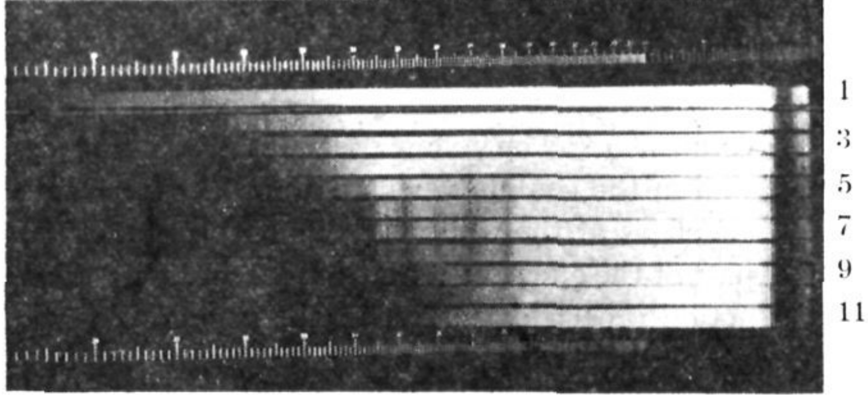


Fig. 4.—1, Vacuum; 2, acetylene at p = 99 mm.; 3-10, acetylene after 10, 20 sec., 1, 3, 10, 30, 60, 105 min., respectively, of total illumination with lead spark at 1 cm. distance from the reaction tube; 11, state 10 after an interval of several hours.***

* Exposure time for each spectrum, 2 min.; spectrograph slit, 0.025 mm. wide.

** Exposure time for each spectrum, 1 min.; spectrograph slit, 0.05 mm. wide.

*** Exposure time for each spectrum, 3 min.; spectrograph slit, 0.025 mm. wide.

sively prove that vinylacetylene plays no part in the course of the reaction. If the disappearing reaction of vinylacetylene proceeds very quickly, the stationary concentration might be so low that the bands escape observation. It seemed essential, therefore, to investigate the reaction of vinylacetylene under irradiation.

The absorption of vinylacetylene in the ultraviolet is about 10^5 to 10^6 times as strong as the absorption of acetylene—already at 2537 Å. all the radiation was absorbed in the tube, at a pressure of 345 mm. At shorter wave lengths, the radiation at that pressure was completely absorbed in the gas layers next to the light entrance. Consequently there was no Tyndall effect in the gas phase, the polymer being precipitated at the walls near the entrance of radiation. Because of this precipitate absorbing effective radiation

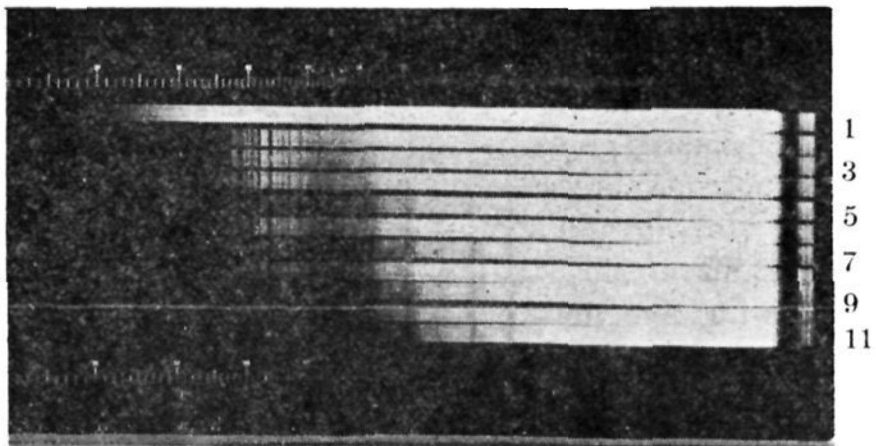


Fig. 5.—1, Vacuum; 2 and 3, acetylene at p = 307 and 200 mm., respectively; 4, 6, 8, and 10, acetylene at p = 200 mm., after 5, 25, 85 and 265 min., respectively, of illumination in solid state; 5, 7, 9 and 11, same as 4, 6, 8 and 10, except for p = 307 mm.*

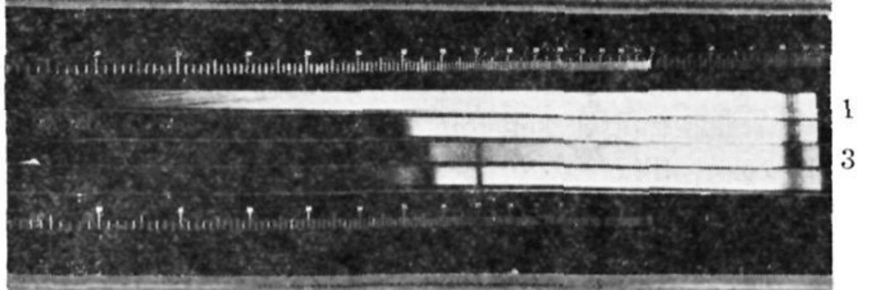


Fig. 6.—1, Vacuum; 2, vinylacetylene (p = 39 mm.) with acetylene (p = 216 mm.); 3, same mixture after several tens of minutes of illumination at 3 cm. distance from the reaction tube; 4, products of the catalytic polymerization of acetylene ($p \sim 1.5$ mm.).*

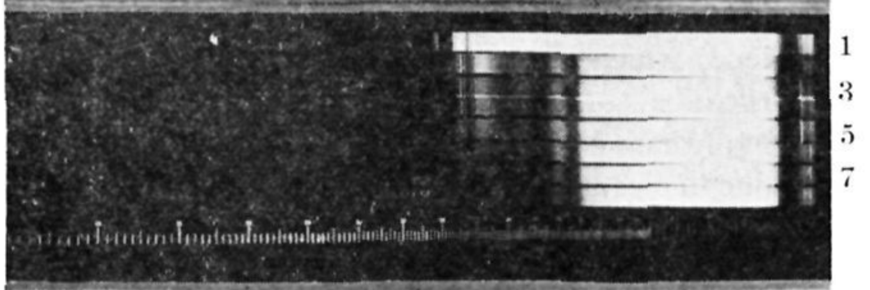


Fig. 7.—1, Vinylacetylene (p = 100 mm.) with benzene (p = 12 mm.); 2–8, the mixture after 20 sec., 1, 2, 5, 10, 20 and 60 min., respectively, of total illumination at 3 cm. distance from the reaction tube.*

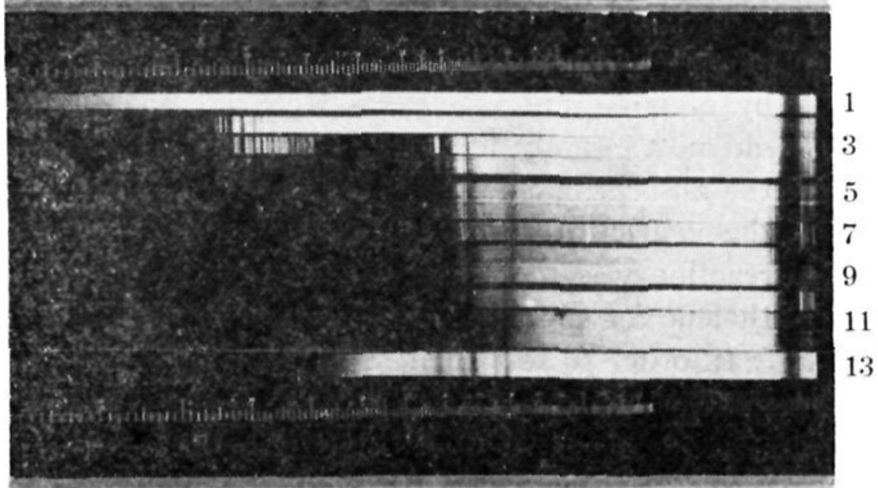


Fig. 8.—1, Vacuum; 2, acetylene (p = 250 mm.) with benzene (p = 22 mm.); 4–12, the mixture after 20 sec., 1, 2, 5, 10, 20, 60, 120 and 300 min., respectively, of total illumination at 2 cm. distance from the reaction tube; 13, naphthalene vapor.*

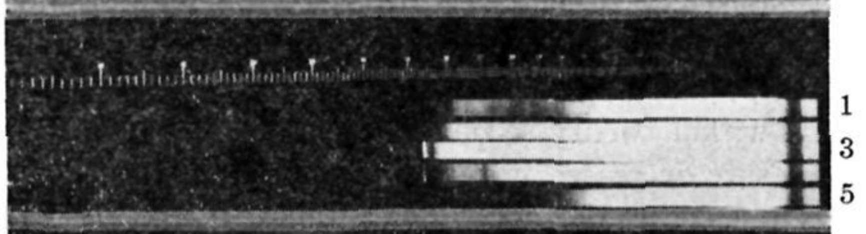


Fig. 9.—1–3, Vinylacetylene (p = 605, 392 and 176 mm., respectively); 4 and 5, vinylacetylene (p = 176 and 602 mm., respectively) after passing in fifteen minutes through the illuminated reaction tube (vinylacetylene was kept in the bottle Z_5 at an initial pressure $\sim$330 mm.). The plate was not sensitized.*

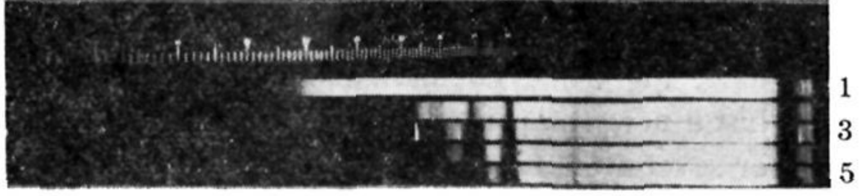


Fig. 10.—Explanation given in the text. The plate was not sensitized.*

the over-all pressure change was small; ten hours of irradiation brought only a decrease of 5 mm. The absorption limit remained unchanged during the irradiation, but some very faint new bands were observed; the strongest of these are at 3215 and 3169 Å. None of the bands of the "c" group which would be observable in this experiment, appeared.

* Exposure time for each spectrum, 2 min.; spectrograph slit, 0.025 mm. wide.

Irradiation of a mixture was then tried, containing one part of vinylacetylene to 5.5 parts of acetylene. The results were completely different from the results of irradiation of either of the components alone, only the pressure change was of the same order as with vinylacetylene. The change in the absorption spectrum occurred in the very first minutes, longer irradiation brought no further change. This indicated that the new absorption bands belonged to intermediate products and that none of the final products was in a gaseous state. Benzene bands were, indeed, conspicuously absent; the formation of a benzene molecule from the addition of acetylene to vinylacetylene obviously does not occur. Two very distinct new bands at 2550 and 2690 Å., were found to be able to vary independently in intensity, thus indicating that they belonged to different products. Another band, so indistinct as to be questionable, appeared at 2513 Å. This last band coincides with one of the bands of group "b" in irradiated acetylene—the only connection between the two spectra. A close resemblance was found, however, with the spectra given by the volatile products of the polymerization of acetylene proceeding under the catalytic influence of Cu_2Cl_2, in which some quite similar bands have been observed as can be seen in Fig. 6. Since the bands under comparison appear in the catalytic vinylacetylene evaporated into another tube, they belong to the most volatile products, which means the lowest polymers. In the catalytic polymerization of acetylene Klebanski and his collaborators[12] found the aliphatic trimers divinylacetylene and acetylenedivinyl to be among the most abundant products, second only to the dimer, vinylacetylene. It seems reasonable to ascribe the two bands at 2550 and 2696 Å. to these two aliphatic trimers. The former band is more intense and could be ascribed to divinylacetylene, which prevails in quantity over the other trimer, if it were certain that their molecular extinction is equal.

So far the main results of this series of experiments can be summarized as follows: under the influence of ultraviolet radiation a mixture of vinylacetylene and acetylene gives products of polymerization. Benzene is not among the final products, and the main volatile products presumably from the intermediate reactions are the aliphatic trimers, divinylacetylene and acetylenedivinyl. There is no evidence for the presence of the intermediate products found in the photochemical polymerization of acetylene, at least not in appreciable quantities.

(c) **Irradiation of an Enclosed Volume of Benzene, in Mixtures with Vinylacetylene and with Acetylene.**—The method of irradiating gas mixtures was then used in order to investigate the possible presence of naphthalene as another product of polymerization. The presence of naphthalene among the products of the photochemical polymerization of acetylene had been a point of dissension among previous investigators. The absorption spectrum of irradiated acetylene shows two absorption bands, at 2689 and 2718 Å. (placed in group "c" in this present investigation and assigned to a trimer of acetylene) which Kemula and Mrazek[7] identified with the bands of 2690 and 2720 Å. characterizing some naphthalenic hydrocarbon. They supposed that one molecule of vinylacetylene joined with one molecule of benzene in forming this hydrocarbon which then decomposed photochemically into naphthalene and hydrogen. Evidence for this photochemical decomposition had been given by Kemula and Dunicz.[13] Kemula and Mrazek did not actually find any naphthalene bands in the absorption spectrum, but they assumed that the concentration of benzene produced by the reaction was too low to furnish sufficient naphthalene for spectral observation.

In order to test their supposed mechanism for the production of naphthalene, benzene vapor of an appreciable concentration (p = 12 mm.) was mixed with vinylacetylene (p = 100 mm.) for irradiation. A rapid photochemical reaction set in, changing the absorption spectrum completely within twenty seconds; in seven hours the pressure decreased from 112 to 105 mm., and a sediment was formed at the walls. There was no evidence, however, for the presence of naphthalene; Fig. 7 does not show any naphthalene bands, but a new absorption spectrum, belonging to one or several unknown products, which might be of styrene structure: the nearer ultraviolet shows strong absorption with very broad diffuse bands, their maxima are at about 2804 and 2911 Å.; there is in addition a group of stronger bands at 3044, 3058 and 3070 Å.

---

[12] A. L. Klebański, L. G. Zürich and I. M. Dolgopolski, *Bull. Acad. Sci. U. R. S. S.*, 189 (1935).

[13] W. Kemula and B. L. Dunicz, *Z. physik. Chem.*, **A181**, 389 (1938).

Although no evidence was found for the formation of naphthalene from vinylacetylene and benzene, irradiated acetylene was found to produce naphthalene, if a sufficient amount of benzene was present; 22 mm. of benzene in 250 mm. of acetylene gave the bands of 2784, 2750 and 2710 Å. which are characteristic for the naphthalene spectrum. They are to be seen in Fig. 8, which also shows clearly the distinct band at 2814 Å., known already from the spectrum of irradiated acetylene; in the course of the reaction this band appeared first of all. A weak band at 2877 Å. might point to traces of styrene but this is not quite certain since it was impossible to find other bands characteristic of styrene. Neither was it possible to investigate whether styrene is an intermediate product, by using the indirect method of irradiating acetylene with styrene; for the absorption of styrene is so strong in the region of the expected naphthalene bands that they would be obscured even if most of the styrene were removed by the reaction.

One additional fact seems worth mentioning. The formation of naphthalene from acetylene and benzene was not accompanied by any decrease in pressure. This could be explained by the assumption of Kemula and Mrazek that a naphthalene hydrocarbon is formed at first which subsequently gives naphthalene and hydrogen.

3. Irradiation of Flowing Gases at very Low Pressure

(a) **Irradiation of Acetylene in a Continuous Flow.**—The results of the experiments reported under 2 (b) of this paper seemed to indicate that vinylacetylene is not formed as a preliminary step in the photopolymerization of acetylene. This, however, does not exclude the possibility of the formation of vinylacetylene during the reaction. Under the prevailing conditions no indication of the presence of vinylacetylene had been found; it seemed advisable to change these conditions by decreasing the possibility, for the first product, of further immediate reaction with acetylene.

With this aim in mind a constant flow of acetylene at very low pressure was sent through the reaction tube by passing the gas slowly through a tap into the tube from one side and freezing it out with liquid air on the other side. The melting point of acetylene lies at $-81.8°$, and consequently its vapor pressure is practically negligible, so that the pressure in the reaction tube could be kept very low. Under these conditions, there was not enough sediment at the walls of the reaction vessel to be visible, but more acetylene was undergoing polymerization in a given time than by the static method previously used.

The absorption spectrum after irradiation showed all the bands obtained in the previous experiments and some very weak bands in addition: at 2392, 2404, 2411, 2421 and 2426 Å. A comparison with Table I shows that they are characteristic of vinylacetylene at pressures between 1 and 5 mm.

(b) **Irradiation of Vinylacetylene in a Continuous Flow.**—Vinylacetylene irradiated during its flow through the reaction tube reacted so quickly that the yellow sediment in the tube was easily visible. This is quite understandable in view of its very strong and extended absorption in the ultraviolet. Cooled with liquid air after irradiation it showed a yellowish color and left a resinous yellow residue after evaporation.

The intermediate products received by this method proved to be completely different. In Fig. 9 the absorption spectrum of the products formed was taken after the passage of the gas through the reaction tube, the duration of the flow being fifteen minutes. The spectrum shows an extension of the continuous spectrum to longer wave lengths and only one new band, rather diffuse, at 2705 Å. Repeated transmission of the gas through the reaction tube produced neither more new bands nor the intensification of the band at 2705 Å.

4. Irradiation of Gases in Intermittent Flow.—In order to obtain a larger fraction of the lower polymers formed during the reaction, especially the trimers, the flow method was slightly changed, so that the products of irradiation were less quickly removed. While the gases were entering the reaction tube in a continuous flow they were not frozen out immediately at the other end of the tube; instead, the connection between reaction tube and the freezing trap was opened for short times only at regular intervals. The passage, in this way, of the whole amount of gas through the reaction tube, took only a few minutes.

(a) **Acetylene Irradiated in Intermittent Flow.**—With acetylene, more gas was undergoing polymerization in a given time by this method than by either of the methods previously employed;

this time the yellow sediment at the walls was quite visible. A yellow volatile liquid stayed in the freezing tube, after evaporation of unchanged acetylene at room temperature.

Figure 10 gives a comparison between the spectrum of acetylene at 583 mm. and the spectrum of products contained in the acetylene after passage through the reaction tube. It shows, beside the groups "b" and "c" known from the previous experiments, a series of new weak bands; the most distinct of them are at 2786, 2797, 2932 and 3082 Å. As the figure shows, the spectrum was not changed by repeated irradiation, but only intensified.

The intermediate products found under these conditions underwent a slow reaction in the dark: for during several hours of standing the gas pressure in the apparatus decreased, and group "c" in the absorption spectrum was weakened.

(b) Irradiation of Vinylacetylene in Intermittent Flow did not give any different results from the continuous flow at very low pressure. This is not surprising; for considering the different volatilities of the dimers of acetylene and vinylacetylene, higher polymers of vinylacetylene could not be expected to be found in the gaseous phase, not even trimers.

III. Experimental Details

1. Preparation of Substances.—A specially purified technical acetylene was used, prepared by The Gas Accumulator Company in Katowice. For further purification from traces of acetone and from oxygen it was thoroughly washed with a dilute potassium hydroxide solution in water, with 10% chromous acid and finally with an alkaline pyrogallol solution. Fractionation was then applied repeatedly by alternately sublimating and precipitating the gas at liquid air temperature, with the first and the last fraction always discarded.

The vinylacetylene used was prepared from acetylene according to a prescription given by Klebanski, Zürich and Dolgopolski.[12] At the rate of 1 liter per minute acetylene was passed through a spiral in a washing flask of 250 cc. which was heated to 80° and contained as a catalyst a solution of 80 g. of Cu_2Cl_2, 46 g. of ammonium chloride and 2.6 cc. of hydrochloric acid of sp. gr. 1.19 in 80 cc. of water. The gases then passed through 30% sulfuric acid at 0° and a column with calcium chloride and were precipitated at −77°. The mixture contained, besides the small yield of vinylacetylene, mostly water, acetylene and some higher polymers. Repeated distillation gave pure vinylacetylene with a boiling point (at 740 mm. pressure) at 4.8°.

2. Experimental Arrangement. (a) Absorption Spectra.—A quartz tube of 120 cm. length and 3 cm. external diameter with quartz windows on both ends, contained the gases for absorption measurements. In Fig. 11 it is indicated by Z_1. The light source LH_2 was a hydrogen discharge tube of the Bay and Steiner type (2800 v., 0.3 amp.). The spectrograph S was the Hilger model E 370, and a tungsten spark was used to obtain the standard spectrum. The accuracy amounted to ±1 Å. in the short wave length region and to ±3 Å. in the long wave length region of the ultraviolet. The photographic plates were "Alfa" U. R. Ortho-Antihalo plates, sensitized with vaseline for the short wave length region. The radiation of the hydrogen lamp was sufficiently strong to produce a sediment of polymer on the window through which this light entered the tube. To prevent this, absorption spectra measurements were made with short exposures. In many cases the gas was circulated through the tube during the exposure.

(b) Irradiation Experiments.—The apparatus schematically pictured in Fig. 11 was made of glass, with the exception of the quartz tube Z_1 which was used as the reaction vessel V in these experiments. The whole apparatus, without the vessels Z_4 and Z_5, had a volume of about 1.1 liters. The gases, entering through the line with the stopcocks 1, 2 and 3, could be evacuated through stopcock 4, leading to a Toepler pump, and 6, leading to a two-step Leybold apiezon oil vacuum pump. Mercury vapor from the Toepler pump was absorbed by thin gold leaves protecting stopcock 4. The Lybold magnetic pump p. m. was able to transport the gases with a velocity of 280 liters per hour. Tube Z_3, used for purification, was filled with gold leaves and phosphorus pentoxide; the metallic Bourdon gage M registered pressure changes down to ±1 mm.

With one exception, when a lead spark was used (Fig. 4), the source of irradiation LHg was a quartz mercury lamp (110 v. d. c., 2 amp.) with an arc length of 17 cm., placed in a distance from the tube which varied between 3 and 50 mm. A parabolic mirror E on the other side of the tube increased the intensity of irradiation. The temperature effect of the lamp on the reaction was considered to be negligible, since the temperature at 3 mm. distance from the surface was found to be not more than 70°.

Before each experiment the gases were collected, at liquid air temperature, in the receiver Z_2 and any residual traces of gas were removed by pumping. After each experiment the apparatus was heated and air was pumped through, until every trace of sediment had been removed.

For the irradiation of acetylene as a solid the vessel Z_4 in Fig. 11 was used, the profile of which is shown in Fig. 12. Spoon D was filled with liquid air and the lamp was placed just outside the quartz window K (diameter 3 cm.), which was connected to Z_4 by a ground joint, in 9.5 cm. distance of D. The glass cylinder F served to protect the grease of the joint against the ultraviolet radiation.

For the experiments with flowing gases both Z_5 and Z_4 were used. The procedure for the continuous flow experiments was as follows. The gas collected at liquid air temperature in Z_2 was evaporated into the storage vessel (2-liter) Z_5, with stopcocks 14 and 8 open, while the remaining stopcocks prevented the connection of these two vessels with the other parts of the apparatus. Then the pressure was measured in M, A in Z_4 filled with liquid air and the stopcocks opened to allow the flow of the gas through the reaction tube and stopcocks 12 and 10 into Z_4. The flow was regulated by means of stopcock 5, on the basis of the readings of pressure decrease. After all the gas had been

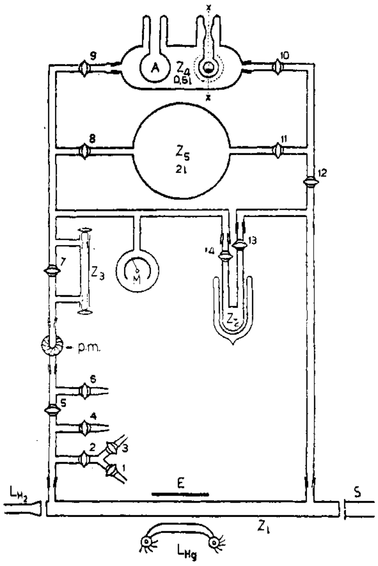


Fig. 11.—Description to be found in the text.

collected in Z_4, it was again removed to Z_2. From there it was either evaporated into the absorption tube Z_1, or the operation was repeated and the gas was again stored in Z_5.

For the experiments with intermittent flow stopcock 10 was kept closed during the flow from Z_5 into Z_1, till M registered a pressure decrease in Z_5 of either 5 or 10 mm. (depending on the experiment). Then 10 was open just long enough to freeze the content of Z_1 in Z_4 (A being filled with liquid air) and closed again, until the gas pressure in Z_5 had decreased for another 5 or 10 mm.

IV. Discussion of Results

According to the experimental results of this investigation, it seems highly improbable that the formation of vinylacetylene could be a step in the photochemical polymerization of acetylene. Vinyl acetylene has been shown to produce, on irradiation with acetylene, chain trimers which are absent if acetylene alone is irradiated, whereas benzene, produced by this latter reaction, is not produced in the chain which is started in the vinylacetylene–acetylene mixture. In looking for the compound which represents the first step in the polymerization of acetylene, the following experimental evidence has to be considered: this compound and acetylene react with formation of higher polymers; at a low acetylene pressure, however, when the chances for this reaction are not so overwhelming, it partly is transformed into vinylacetylene. We shall tentatively assume, therefore, that the first step in the photochemical polymerization of acetylene is an unstable isomer of vinylacetylene.

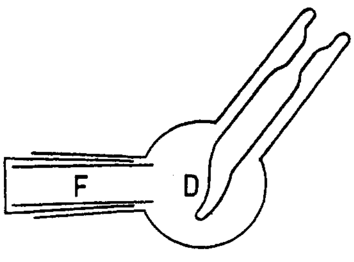


Fig. 12.—Profile of vessel Z_4 (Fig. 11) along *xx* plane. Description to be found in the text.

For stereochemical reasons only one structure could be given to an isomer of vinylacetylene: the structure of cyclobutadiene. Its formation in this reaction was not suggested in any previous investigation, for the very good reason that cyclobutadiene so far has not been found to exist in any detectable quantity. Moreover, it is generally assumed[14] that the tension in a tetracarbon ring of this kind would be strong enough to prevent its existence, and Penney[15] has shown that quantum mechanical considerations support this view. But this applies only to the ground state of the molecule. Wheland,[16] using the molecular orbital treatment, derived a high degree of stability for a cyclobutadiene in a state of electric asymmetry. It is very probable that enough surplus energy for such an activated state of cyclobutadiene would be available, since there would be the considerable heat of formation of cyclobutadiene, in addition to the energy of the photochemically activated acetylene molecule. The formation of a cyclic compound with tensions in the ring, rather than the formation of an aliphatic chain, should be expected for two acetylene molecules under the influence of a great activation energy, in keeping with Michel's rule[17a] and the rule of stage reactions.[17b] An experimental analogy can be found in Bergmann's[18] remark that ultraviolet irradiation shows a characteristic peculiarity of causing dimerization of olefins into cyclobutene compounds.

The formation of cyclobutadiene seems even more plausible when considered in connection with the first step of the photochemical reaction. The energy available from the ultraviolet radiation is sufficient for either of the three following reactions: the breaking up of the CH bond, the polarization of the C–H bond, the polarization of the C≡C bond.

---

(14) E. Hückel, *Z. Elektrochem.*, **43**, 780 (1937).

(15) W. G. Penney, *Proc. Roy. Soc.* (London), **A146**, 223 (1934).

(16) G. W. Wheland, *ibid.*, **A164**, 397 (1938).

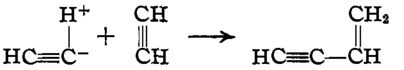
(17) W. Hückel, "Theoretische Grundlagen der organ. Chemie," Leipzig, 1935, (a) p. 267; (b) p. 278.

(18) E. Bergmann, *Trans. Faraday Soc.*, **35**, 1025 (1939).

Lind and Livingston[8] favored the first of these reactions, the splitting off of a hydrogen atom from the acetylene molecule, leaving the radical C_2H for further reaction. The absorption spectrum of acetylene does not indicate a primary dissociation, at wave length longer than 1850 Å., but the authors suggested predissociation or dissociation by collision.

This assumption cannot be ruled out for the shortest wave lengths, but the efficiency of the reaction ought to decrease rapidly toward its long wave length limit and for this there has been no experimental evidence, so far.

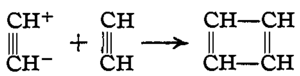
We consider next the formation of a dimer from a molecule with a polarized C–H linkage with a normal acetylene molecule.



$$\mathrm{HC{\equiv}C^{-}(H^{+}) + CH{\equiv}CH \longrightarrow HC{\equiv}C{-}CH{=}CH_2}$$

This would lead to the formation of vinylacetylene, with the release of 32 kcal. per mole. But the experimental evidence has shown that vinylacetylene does not form a step in the chain of polymerization by irradiation. The equation shown above suggests that for the formation of vinylacetylene the induction of electric charges from the CH linkage has to affect the C≡C linkage in the inactivated molecule; this possibly occurs only under the influence of an electric field, which would explain that vinylacetylene plays a decisive part in the catalytic polymerization of acetylene.

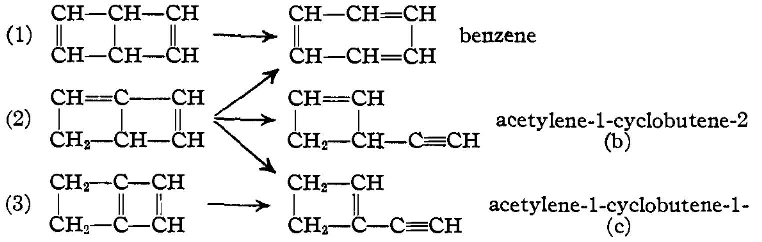
Finally, we consider the dimerization of an acetylene molecule with a polarized C≡C linkage with a normal acetylene molecule.



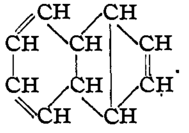
$$\mathrm{CH^{+}{\equiv}CH^{-} + CH{\equiv}CH \longrightarrow cyclo\text{-}(CH{=}CH{-}CH{=}CH)}$$

This dimerization gives cyclobutadiene, and it may well be that the greater concentration of charges in the carbon–carbon linkage facilitates the inductive effect on the inactivated molecule.

Tentatively we may now picture the formation of trimers, by addition of acetylene to active cyclobutadiene, assuming equal linkages between the carbon atoms. We shall get the unstable products (1), (2) and (3) which can change into benzene, acetylene-1-cyclobutene-2 and acetylene-1-cyclobutene-1:



The two trimers of cyclobutene structure are not necessarily unstable, although doubtless reactive. We might consider them to be characterized by the set of bands "b" and "c," respectively, which we had ascribed to non-aliphatic trimers found in the photochemical polymerization of acetylene. In acetylene-1-cyclobutene-1 a triple bond is coupled with a double bond: therefore its absorption can be expected to occur at longer wave lengths than the absorption of its isomer. For this reason it was supposed to be characterized by the bands "c," and acetylene-1-cyclobutene-2 by "b." The formation of some aliphatic acetylene trimers from irradiation of vinylacetylene–acetylene mixtures may be explained as due to formation of side products from the cyclobutadienic isomer in the same way as of vinylacetylene from cyclobutadiene. As support of the mechanism suggested, it has been shown from observation of absorption spectra that of the two possible acetylene–cyclobutenes, acetylene-1-cyclobutene-1 and acetylene-1-cyclobutene-2, the former is definitely absent when a vinylacetylene–acetylene mixture is irradiated. Its absence would necessarily follow from the suggested mechanism, which would permit the formation only of the 1:2 isomer in this reaction.

By the same method of structural equations which was used to demonstrate the formation of benzene, the reaction of an activated acetylene molecule with a benzene molecule can be shown to lead to a cyclobutene structure attached to the benzene ring, which compound forms naphthalene by the addition of another acetylene molecule, followed by separation of a hydrogen molecule from an intermediate dihydronaphthalene, presumably  . It can be shown also that vinylacetylene could not give the same results. Both these statements agree with the experimental findings.

It should be emphasized, however, that this reaction needs an excited acetylene molecule, and that the very small concentration of benzene in irradiated acetylene would nearly exclude the collision of a benzene molecule with an excited acetylene molecule. For all practical purposes, then, the formation of benzene stops the chain of polymerization, but it can reasonably be assumed that the other trimers are reactive enough to continue the chain with inactive acetylene molecules. It seems quite feasible that the addition of two more acetylene molecules follows a cycle which closely resembles the first cycle treated here, that this second cycle is followed by a third one, and so on. In each cycle we should expect the formation of a stable aromatic compound which would stop some of the chains, analogous to the part played by benzene. The average chain length would then be determined by the ratios of probability for the formation of the stable compounds and their active isomers.

Such a mechanism would meet the demands made by Melville[10]: that acetylene should be able either to continue or to stop the chains, since the average chain length is independent of acetylene pressure.

A generalization of this mechanism for the photochemical changes and quantum yields of acetylene can be applied to substituted acetylenes with the following two-fold reaction for methyl- and dimethylacetylene: (a) similar to the behavior of acetylene; (b) formation from acetylene of an intermediate diradical which then reacts with a second molecule of the acetylene giving a deactivated hydroaromatic cyclopentadiene ring.

In the case of deuterium substituted acetylenes, owing to the reduced mobility of the deuterium atom compared to the hydrogen atom, monodeuteroacetylene ought to react with a yield intermediate between that of acetylene and that of methylacetylene undergoing the type (a) reaction, and dideuteroacetylene ought to show greater tendency to termination of reaction chains through formation of aromatic rings.

Present experimental values for quantum yields are within the somewhat wide limits predicted by this theory.

This work was carried out in the Physical Chemistry Department at the Jan Kazimierz University in Lwów, Poland. The author expresses his deepest gratitude to Director of the Department, Professor Dr. Wiktor Kemula for his encouragement in the investigations as well as for his precious advice and remarks.

The author wishes also to thank most deeply Mr. Feliks Wiślicki, President and Founder of the Tomaszów Artificial Silk Factory Foundation, Warsaw, Poland, for the grant awarded to the purpose of studying the problem.

At the same time the author asks the Direction of the Polish branch of the Gas Accumulator Company, Katowice, Poland, to accept his gratitude for the gratuitous delivery of the acetylene for the researches.

The author's special gratitude is due to Dr. Gertrud Kornfeld of the Eastman Kodak Company Research Laboratory, Rochester, N. Y., and to Dr. Sherwood Kimball Haynes of Brown University, Providence, R. I., for their generous help and valuable remarks when preparing the material for publication.

V. Summary

1. Acetylene on irradiation with ultraviolet light below 2350 Å., decreases in pressure and gives as main products of polymerization a yellow powder related to cuprene, and a small amount of benzene. Both these products increase steadily during the reaction. Intermediate products in the gaseous phase were traced by their absorption spectra.

2. In the pressure range between 5.5 and 341 mm. of acetylene the reaction products are essentially the same, nor is the course of the reaction changed in an atmosphere of nitrogen. Acetylene, irradiated in the solid state, reacts in the same way.

3. There is no qualitative difference in the course of the reaction, whether a quartz mercury lamp or a lead spark is used for irradiation. This is contrary to Kato's statement. The intensity given by the two light sources differed too much to allow a quantitative comparison.

4. The dimer which is the first step in the chain of polymerization is not vinylacetylene. This is shown by the absence of the vinylacetylene spectrum from the spectrum of the intermediate products, and further by the reaction course produced in an irradiated mixture of acetylene with vinylacetylene, in which completely different volatile products, identified as two aliphatic acetylene trimers were observed to be formed, benzene being absent.

5. Vinylacetylene can be produced as a side product in the course of the photochemical poly-

merization; this is accomplished by keeping the pressure of acetylene very low during the irradiation. Under these conditions an unstable dimer might change into vinylacetylene before having the opportunity to react further with acetylene.

6. The assumption is made that this dimer is cyclobutadiene, and that the intermediate trimers characterized by their absorption spectra in irradiated acetylene, are acetylenecyclobutenes, very reactive in both isomeric forms. Cyclobutadiene ought to be present in an excited state of electrical asymmetry, since its ground state is completely unstable. In a similar way divinylacetylene and acetylenedivinyl found to be the volatile products in the irradiation of a vinylacetylene–acetylene mixture would be expected to be formed as side products from isomerization of the unstable intermediate vinyl-cyclobutadiene.

7. It is suggested that the further addition of acetylene proceeds in the same pattern, over cyclobutene structures. This suggestion is supported by the following experimental analogy: irradiated acetylene reacts with a sufficient amount of benzene in giving naphthalene, whereas no naphthalene is formed by irradiation of vinylacetylene mixed with benzene; thus acetylene and vinylacetylene differ in the formation of naphthalene in the same way as in the formation of benzene.

8. It is reasonable to assume that in each cycle an inactive aromatic isomer is formed, just as benzene is formed in the first cycle, so that some of the chains do not proceed any further. The average chain length depends on the relative probability of formation of these inactive compounds. This mechanism meets Melville's demand that acetylene ought to be responsible both for continuing and stopping the chain.

UNIVERSITÉ DE POLOGNE
À L'ETRANGER, PARIS
RECEIVED MARCH 24, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Color and Bond Character

BY KENNETH S. PITZER AND JOEL H. HILDEBRAND

A good deal of attention has recently been given to bond character, using as criteria mainly bond energy and bond distance, each of which has been shown to vary with the shift from covalent to ionic bonding.[1] The purpose of this paper is to discuss the use of color as an additional criterion.

Our attention was first drawn to this subject by the interesting behavior of stannic iodide, contrasting strongly with that of stannic chloride. The latter, for example, like most other tetrachlorides, is highly hydrolyzed, and cannot be prepared in the presence of water. The hydrolysis of the iodide, on the other hand, is so easily reversed that we can prepare pure stannic iodide by action of aqueous hydriodic acid upon solid SnO_2 and subsequent evaporation. This can hardly be explained otherwise than by a more covalent bond between iodine and tin. Indeed, if we use Pauling's negativity scale, we find that these elements are so close together as to indicate only about 11% of ionic bonding.

This conclusion is reinforced by the deep orange red color of the compound not only in the solid state and in solution in non-polar solvents, but in aqueous solution as well, if observed either immediately on solution before hydrolysis occurs, or later, if hydrolysis is prevented by using aqueous hydrochloric acid or hydriodic acid. The partition of stannic iodide between CCl_4 and HCl aq. is nearly equal. The color in all these solutions appears to be the same. Now if the iodine and tin did not form a covalent bond, we would expect the solution to be colorless since iodide ion is colorless, as in the alkali iodides, which are unquestionably ionic.

The first suggestion of this nature that we have been able to find was made by Bichowsky[2] in 1918 in a paper dealing with "atom color" and valence in which he remarked that when the color of a compound deviates from the sum of the ion colors "the electrons are no longer acted on by only one nucleus but are acted on by both," and later "compounds of one or more electronically stable atoms with one electronically less stable are likely to have a color which is the sum of the valence colors of its constituent atoms, while

---

(1) For one discussion see L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

(2) F. R. Bichowsky, THIS JOURNAL, **40**, 500 (1918).