The Photopolymerization of Acetylene. On the Formation of Cycloöctatetraene

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Introduction

Ultraviolet light of wave lengths shorter than 2537 Å. induces polymerization of gaseous acetylene. A considerable number of investigations have been made on this reaction, concerning the reaction rate(3), (7), (8) and the reaction mechanism(4), (5), (9), (10) as well as the reaction products.(1), (2), (4), (6), (10)

The photopolymerization of acetylene is generally assumed to be propagated by a chain mechanism. Polymer is formed by the successive addition of acetylene molecules to the activated ones. The dimer of the chain polymerization is considered to be vinylacetylene by W. Kemula and S. Mrazek,(4) while recently B. L. Dunicz(10), (11) assumes that the dimer consists of cyclobutadiene, which so far has not been found to exist. Dunicz makes this assumption from the following facts; the reaction of mixtures of acetylene and vinylacetylene proceeds in a different way from that of acetylene only, and the cyclobutadiene structure has the considerable stability in its triplet state according to the theory of Wheland.(12)

From the cyclobutadiene theory of Dunicz, assuming the following reaction,

$$2C_4H_4(\text{Cyclobutadiene}) \rightarrow C_8H_8(\text{Cycloöctatetraene})$$

we expected cycloöctatetraene to form in the process of the photochemical change of acetylene. We investigated it in detail.

Experiments and Results

(1) Photochemical Properties and Analysis of Cycloöctatetraene (abbr. C. O. T.)

Photochemical Change of C. O. T.—It is not known whether C. O. T. changes photochemically or not, under the ultraviolet light. We tested it and found that C. O. T. in the gaseous state made the photochemical change in the irradiation of ultraviolet light. Spectra of irradiated C. O. T. show two new absorption bands, one of which is characteristic for benzene and the other one is of unknown substances. But the irradiation of one minute or

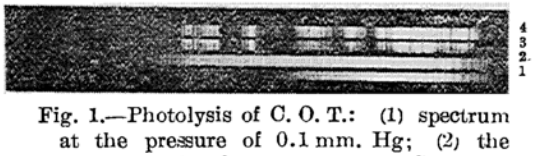

Fig. 1.—Photolysis of C. O. T.: (1) spectrum at the pressure of 0.1 mm. Hg; (2) the same at the lower pressure. (Spectrum of benzene is seen.); (3) and (4) iron spectrum.

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(1) D. Berthelot and H. Gaudechon, *Compt. rend.*, **150**, 1169 (1910).

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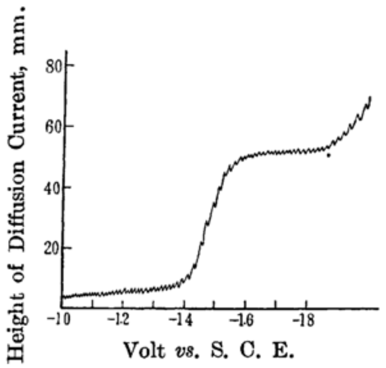

Fig. 2.—Polarogram of 4.6×10^{-4} *M* solution of C. O. T.: the diffusion current is $4.8\,\mu$A and the half wave potential is −1.49 volts *vs.* S. C. E. The sensitivity is 1.2×10^{-7} ampere per mm.

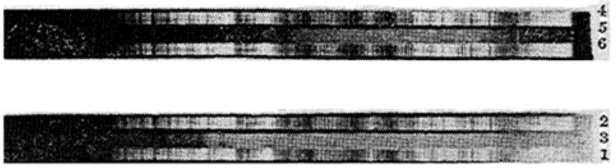

Fig. 3.—Spectra of the products: (5) photopolymerization products at 1.5 mm. Hg; (2) the same products at 0.5 mm. Hg; (1) (3) (4) and (6) iron spectra.

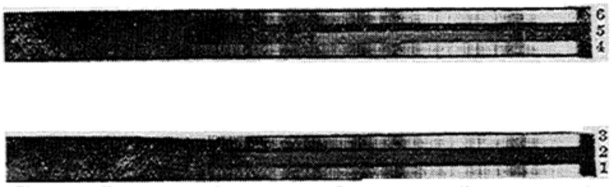

Fig. 4.—Spectra of benzene and styrene: (5) styrene at 0.2 mm. Hg; (2) benzene at 0.1 mm. Hg. (1) (3) (4) and (6) iron spectra.

two does not change the character of absorption spectra of C. O. T. So, in order to get C. O. T., acetylene should be passed in a few seconds under the ultraviolet light, avoiding the photolysis of C. O. T. It is to be found in Fig. 1.

Polarography of C. O. T.—The best way for the quantitative analysis of C. O. T. is the polarographic method.(13) We adopted Elofson's receipt as follows: Ethanol solution of C. O. T. 1 cc., 0.1 *M* solution of tetramethylammonium bromide 1 cc., sodium sulfite solution 0.1 cc.

The half wave potential was −1.49 volt *vs.* S. C. E. at *p*H=7. The diffusion current was linear against the concentration of C. O. T. from 1×10^{-5} to 2×10^{-3} *M* solution. At the sensitivity of $2.4\times10^{-3}\,\mu$A/mm. of the galvanometer, one mm. displacement of the diffusion current corresponds to 2.79×10^{15} molecules of C. O. T. in the cell solution mentioned above. Fig. 2 shows one of the polarograms of C. O. T.

(2) Irradiation of Acetylene in a Continuous Flow

(a) Products of the Reaction.—In order to obtain a larger fraction of the lower polymers, especially smaller than C_8H_8, formed during the reaction, products of irradiation were quickly removed out of the reaction tube to be frozen into the trap cooled by the dry ice at the end of the tube. After passing the dry ice trap, unchanged acetylene was frozen out into another trap cooled by the liquid air.

After the experiment, the thin yellow film was visible at the wall right in front of the light source mercury lamp and a light yellow volatile liquid stayed in the dry ice trap.

Fig. 3 gives the absorption spectra of the products at the pressures of 0.5 and 1.5 mm. Hg respectively. Spectra of pure benzene and pure styrene are given in Fig. 4. Besides benzene, we see a small amount of styrene in the spectral lines characterized by 2877, 2800, and 2780 Å. 2808, 2720, and 2687 Å. lines belong to the unknown substance which is called "c" group and is expected to correspond to acetylene-1-cyclobutene-1 by Dunicz.

C. O. T. was analysed by polarographic method dissolving the products in the cell solution of Elofson's receipt. We found a small but definite quantity of C. O. T., as was expected.

(b) The Rate of Formation of C. O. T. under the Varied Light Intensity.—Acetylene was made to flow continuously through the reaction tube irradiated with the mercury lamp at the space velocity of 2 cm./sec. and at the pressure of 175 mm. Hg for 180 minutes in each experiment. The total gas volume which flowed was 1.45×10^5 cc. and the passing time under mercury light was 5 sec. Light intensity of mercury lamp was varied by the electric current intensity from 3 to 10.4 amp. and was proportional to the current intensity. The weaker light intensity was obtained by the net screening.

The result is shown in Fig. 5. The amount of C. O. T. in 180 minutes, *H*, expressed in mm. of diffusion current of the polarograph at the sensitivity mentioned, is plotted against the abscissa *i*, the current intensity of mercury lamp. The maximum point was obtained at *i*=3.5 amp. Under the higher intensity of light, the amount of C. O. T. had decreased unexpectedly.

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(13) R. M. Elofson, *Anal. Chem.*, **21**, 917 (1949).

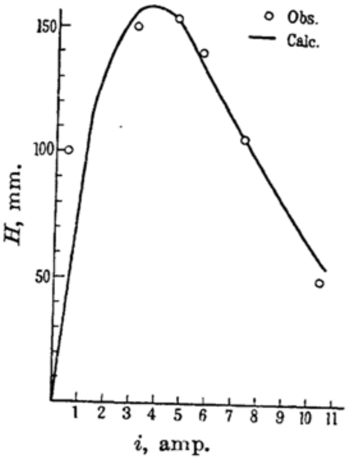


Fig. 5.—Rate of formation of C. O. T. *vs.* intensity of light.

A small percent of air added, quite obstructed the formation of C. O. T. perhaps by the oxydation. The use of a glass filter which is transparent 50% at 2600 Å., decreased the amount of C. O. T. but this was natural.

(c) The Rate of Formation of C. O. T. under the Varied Pressure of Acetylene. —Acetylene gas was made to flow in just the same way as in (2)-b, but the pressure was varied while the light intensity was maintained constant at 4.6 amp. Fig. 6 shows the results.

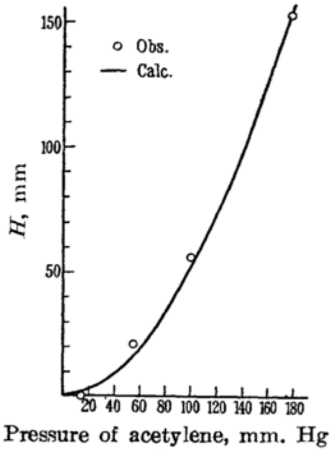


Fig. 6.—Rate of formation of C. O. T. *vs.* acetylene pressure.

The higher the pressure, the greater the rate of formation of C. O. T. However it is not linear to the pressure of acetylene but rather of somewhat higher exponents.

Experimental Details

Acetylene gas was purified by the normal method. The whole arrangement for the experiment is shown in Fig. 7. Purified acetylene is led through A into the liquid air freezing trap B, where the solidified acetylene is rid of the non-condensable gas through L and is fractionated into the reservoir C. From the reservoir, pure acetylene goes through a quartz reaction tube irradiated with mercury lamp E, passing the dry ice cooled trap F into the liquid air trap B. Pressure of acetylene in the tube is read by Bourdon gauge J or mercury manometer K. Reaction products caught in the trap F are evaporated into the reaction tube D, after evacuating the unchanged acetylene. The spectrographic system consists of a hydrogen lamp G, the reaction tube equipped with quartz windows on both ends, and a spectrograph H. An iron spark was used for the standard spectrum.

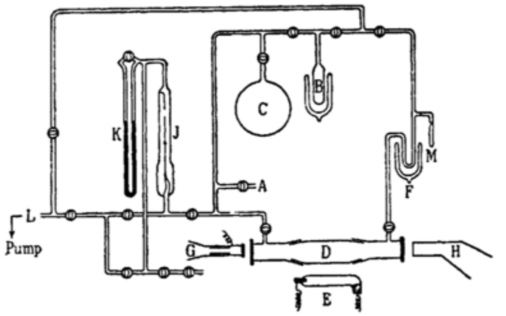


Fig. 7.

For the analysis of C. O. T., products in the trap F were directly distilled into a tiny ampoule M using the dry ice bath, and then the ampoule was cut at the top. Its contents were dissolved in ethanol-tetramethylammonium bromide solution which was submitted to polarographic analysis.

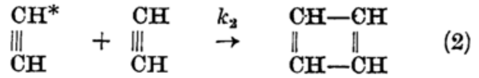
After each experiment, the reaction tube was heated in the air until the sediment on the wall had been removed.

Discussions of the Experimental Results

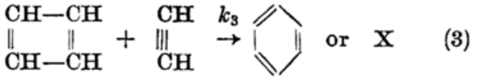
Now we have been able to find C. O. T. as one of the reaction products. Although straight chain dimers such as vinylacetylene can be an intermediate product, we can well expect on the basis of molecular structure that the steric factors for the formation of C. O. T. from such dimers are much smaller than that for the recombination of two cyclobutadiene molecules.

Assuming cyclobutadiene as dimeric intermediate, we propose the following reaction steps for the photopolymerization of acetylene, at least under the conditions employed.

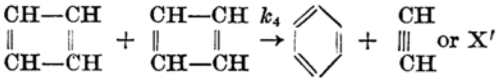
$$\begin{array}{c}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array} + h\nu \xrightarrow{k_1} \begin{array}{c}\mathrm{CH}^*\\ |||\\ \mathrm{CH}\end{array} \qquad (1)$$



$$CH^{*}{\equiv}CH + CH{\equiv}CH \xrightarrow{k_2} \begin{matrix} CH-CH \\ \| \quad \| \\ CH-CH \end{matrix} \quad (2)$$



(3)



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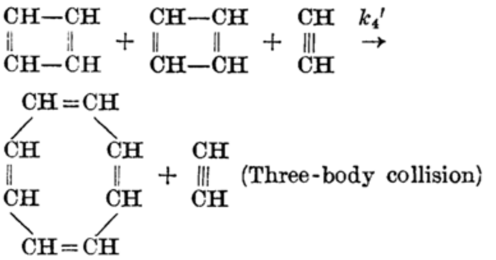

(Three-body collision)

(4)′

For simplicity we will use the abbreviation: acetylene A; cyclobutadiene D; benzene B; C. O. T. C; trimers and tetramers of unknown structures X and X′ respectively. Under the condition of rapid flowing, we can ignore steps forming higher polymers than C_8H_8. Then in the stationary state

$$dA^{*}/dt=k_1I_{abs}-k_2A^{*}A=0 \quad (5)$$

$$dD/dt=k_2A^{*}A-k_3DA-k_4D^2=0 \quad (6)$$

$$dB/dt=k_3DA \quad (7)$$

$$2dC/dt=k_4'D^2A. \quad (8)$$

In Eq. (6) we ignored the consumption of D by (4′) compared with that by (3) and (4).

As cyclobutadiene formed is assumed to be in a higher energy (biradical or triplet) state, three-body collision would be necessary to couple one cyclobutadiene molecule with another to form C. O. T., which is a more stable form of C_8H_8. Bimolecular collision, on the contrary, will lead to the formation of either benzene and acetylene or some other substances. Benzene will be mainly formed by (3).

On the Light Intensity Absorbed.—Although we did not measure the absolute value of light intensity, the following considerations may be made on this respect. In Fig. 8, the light of intensity I_0 from the mercury lamp passes through the precipitated film on the wall of the reaction tube, where it diminishes to the intensity I. Then the light, being partially absorbed by acetylene, leaves the vessel with intensity I_t. Thus the light intensity absorbed by acetylene I'_{abs} is $I'_{abs}=I-I_t$. Here we assume that the time-averaged light-absorbing power of the film produced in a definite time of irradiation is proportional to the light intensity I_0, *i. e.*, $I=I_0e^{-I_0\beta}$, where β is a constant. On the other hand, the light intensity which passes through is represented by $I_t=Ie^{-\mathcal{E}Ad}$, where $\mathcal{E}$ denotes the absorption coefficient of acetylene, A the concentration of acetylene, d the thickness of acetylene layer. So, $I'_{abs}=I-Ie^{-\mathcal{E}Ad} \doteqdot dI\mathcal{E}A$. Then the mean value of light absorbed per cm.[3] across the layer is given by $I_{abs}=I'_{abs}/d=I\mathcal{E}A=I_0\mathcal{E}Ae^{-I_0\beta}$. The light intensity of the mercury lamp was found to be proportional to the current intensity i at constant voltage, *i. e.*, $I_0=iq$, where q is a constant. Therefore

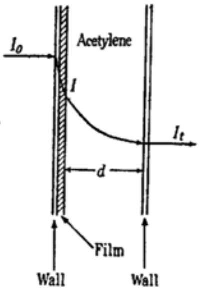

Fig. 8.—Mechanism of light absorption.

$$I_{abs}=\mathcal{E}Aqie^{-iq\beta}=QAie^{-i\alpha}, \quad (9)$$

where α and Q are constants.

Rate Equation of C. O. T. Formation.—From eqs. (5) and (6) we obtain as the stationary dimer concentration

$$D=[-k_3A\pm(k_3^2A^2+4k_1k_4I_{abs})^{1/2}]/2k_4. \quad (10)$$

Here the negative sign must be omitted. The rate constant k_4' is that for the three-body collision reaction and its collision factor is assumed to be 1/1000 of that for the binary collision of k_4 at the acetylene pressure A of 1 atm. Then

$$dC/dt=1/2\,k'_4D^2A=1/2000\,k_4D^2A, \quad (11)$$

where A is to be expressed in atm. unit and the same, zero or very small, activation energy is assumed for k'_4 and k_4. Inserting eq. (10) into eq. (11), we obtain

$$dC/dt=k_3^2/4k_4\times10^3\cdot A^3[1-\{1+(2k_1A/k^2_3A^2/4k_4)I_{abs}\}^{1/2}] +k_1A/2\times10^3\cdot I_{abs}. \quad (12)$$

If the amount of C. O. T. produced is represented by H in terms of the height of polarographic diffusion current, then

$$\mathrm{d}C/\mathrm{d}t=Hn/Vt \text{ molecules, cc.}^{-1}\text{ sec.,}^{-1}$$

where V is the total gas volume passed at the pressure under the experimental conditions, 1.45×10^5 cc., t the pass-time under irradiation, n sensitivity of polarograph for C. O. T. 2.79×10^{15} molecules mm.$^{-1}$ Using the values of constants given here, it follows

$$\mathrm{d}C/\mathrm{d}t=3.84\times10^9H=n_0H. \qquad (13)$$

From Eqs. (9), (12) and (13) we obtain finally

$$H=k_3{}^2A^3/4k_4n_0\times10^3[1-\{1+(2k_1Q/2n_0\\ \times10^3A^2/k^2{}_3A^3/4k_4n_0\times10^3)ie^{-\iota\alpha}\}^{1/2}]\\ +k_1QA^2/2n_0\times10^3\cdot ie^{-\iota\alpha}. \qquad (14)$$

Effect of Light Intensity.—The $H-i$ curve shown in Fig. 5 indicates the apparent effect of the light intensity on the rate of formation of C. O. T. Its true effect may be elucidated by using Eq. (14) as follows. At constant acetylene pressure A_0, putting

$$k^2{}_3A^3{}_0/4k_4n_0\times10^3=a \qquad (15)$$

and $$k_1QA^2{}_0/2n_0\times10^3=K, \qquad (16)$$

we get

$$H=a[1-(1+2K/a\cdot ie^{-\iota\alpha})^{1/2}]+Kie^{-\iota\alpha}. (17)$$

From $\mathrm{d}H/\mathrm{d}i=0$, $i=1/\alpha$ or ∞ follows. Comparing this result with the experimental curve in Fig. 6, we obtain $\alpha=1/3.5$. When this value of α is inserted into Eqs. (15) and (16), the constants a and K can be determined from two equations with different values of i; that is, $a=4$ and $K=151$. As seen in the figure, the theoretical curve obtained from Eq. (17) using these values of a and K is in good agreement with the observed values.

If the steric factors, the collision numbers and the activation energy for the reactions (3) and (4) are denoted by P, Z and E respectively, Eq. (15) can be rewritten in the form

$$a=k^2{}_3A^3{}_0/4k_4n_0\times10^3=P^2{}_3Z^2{}_3e^{-2E_3/RT}/\\ 4P_4Z_4e^{-E_4/RT}n_0\times10^3\cdot A^3{}_0. \qquad (18)$$

Assuming(14) that $P_3=P_4=10^{-2}$ and that E_4 for the activation energy of the reaction between the two biradical (triplet) molecules is equal to zero, and using the values $n_0=3.84\times10^9$ molecules cc.$^{-1}$ sec^{-1}. mm.$^{-1}$, $A_0=175/760$ atm., $Z_3=Z_4=8.6\times10^{28}$ and $T=303$°K., we obtain $E=7.8$ Kcal./mol, which is not unreasonable for the activation energy of a propagation process in polymerization reaction.

Combination of Eq. (10) with Eqs. (15) and (16) leads to the expression

$$D=-k_3A/2k_4+k_3A/2k_4\cdot(1+2K/a\cdot ie^{-\iota\alpha})^{1/2}. \qquad (19)$$

When $i=4.6$ amp., using the numerical values obtained above, we obtain

$$D=1.85\times10^{-3}\text{ mm. Hg.}$$

Effect of Acetylene Pressure.—When the acetylene pressure was varied, even if the light intensity of mercury lamp remaining constant, the light intensity absorbed by acetylene was also varied. The light absorbing power of the colored film on the wall might therefore, possibly be changed with the pressure. However, this effect seemed to be relatively small and neglected, because the coloring of the film was observed to depend on the irradiating, not absorbed, intensity of light. Then, if we gather the constants in Eq. (14) as follows,

$$k^2{}_3/4k_4n_0\times10^3=m \text{ and } k_1Q/2n_0\times10^3=n,$$

Eq. (9) becomes

$$H=mA^3[1-(1+2n/mA\cdot ie^{-\iota\alpha})^{1/2}]+nA^2ie^{-\iota\alpha}. \qquad (20)$$

The numerical values of m and n in the present experimental conditions are

$$m=a/A^3{}_0=3.28\times10^2 \text{ and } n=K/A^2{}_0=2.85\times10^3.$$

Eq. (20) gives the relation between the amount of C. O. T. produced and the pressure of acetylene A. The calculated values from this equation of H at $i=4.6$ amp. are plotted against A in Fig. 7 and compared with the observed values. The agreement is satisfactory.

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(14) *cf.* M. G. Evance and M. Szwarc, *Trans. Faraday Soc.*, **45**, 940 (1949).