



Mercury Photosensitized Polymerization of Acetylene

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are determined from

$$\begin{split} (\tau_3)^{-1} + (\tau_4)^{-1} + (\tau_5)^{-1} &= 2k_1 + k_2 + k_3 + 2k_4 + k_5 + k_6, \\ (\tau_3\tau_4)^{-1} + (\tau_3\tau_5)^{-1} + (\tau_4\tau_5)^{-1} \\ &= (2k_1 + k_2 + k_6)(2k_4 + k_3 + k_5) + 2k_1k_2 + 2k_4k_5 - k_2k_5, \\ (\tau_3\tau_4\tau_5)^{-1} &= 2k_1k_2(k_3 + 2k_4) + 2k_4k_5(2k_1 + k_6). \end{split}$$

The corresponding polarizabilities for a polycrystalline where sample are:

 $\alpha_1 = (\mu^2/3\mathbf{k}T)(3k_1/2k_6)$

$$\times \left(\frac{\tau_2^{-1} - k_6}{\tau_2^{-1} - \tau_1^{-1}}\right) q^{-1} \left[1 + \frac{k_2 + k_6 - \tau_1^{-1}}{k_5}\right],$$

 $\alpha_2 = (\mu^2/3\mathbf{k}T)(3k_1/2k_6)$

$$\times \Big(\frac{k_6 - \tau_1^{-1}}{\tau_2^{-1} - \tau_1^{-1}}\Big)q^{-1} \Big[1 + \frac{k_2 + k_6 - \tau_2^{-1}}{k_5}\Big],$$

$$\alpha_{3} = (\mu^{2}/3\mathbf{k}T)\Gamma_{3}\Lambda_{45},$$

$$\alpha_{4} = (\mu^{2}/3\mathbf{k}T)\Gamma_{4}\Lambda_{35},$$

$$\alpha_{5} = (\mu^{2}/3\mathbf{k}T)\Gamma_{5}\Lambda_{34},$$

$$\alpha_{t} = \sum_{B=1}^{5} \alpha_{\beta} = (\mu^{2}/3kT)[1 - (r/q)^{2}],$$

$$q = 1 + 2(k_1/k_6) + 2(k_1k_2/k_5k_6) + (k_1k_2k_3/k_4k_5k_6),$$

$$r = 1 + (k_1/k_6) - (k_1k_2/k_5k_6) - (k_1k_2k_3/k_4k_5k_6),$$

$$\Gamma_{\beta} = 1/2 \bigg[1 - (k_2/k_5) + \frac{(\tau_{\beta}^{-1} - 3k_5 - k_2)(\tau_{\beta}^{-1} - 2k_1 - k_6)}{k_5k_6} \bigg]$$

and

$$\Lambda_{\beta\gamma} = \frac{(\tau_{\beta}^{-1} - \tau_{\gamma}^{-1}) \left[\tau_{\beta}^{-1} \tau_{\gamma}^{-1} (1 - r/q) - k_1 (\tau_{\beta}^{-1} + \tau_{\gamma}^{-1}) + k_1 (k_6 + 2k_1 - 2k_2) \right]}{\tau_3^{-2} (\tau_5^{-1} - \tau_4^{-1}) + \tau_4^{-2} (\tau_3^{-1} - \tau_5^{-1}) + \tau_5^{-2} (\tau_4^{-1} - \tau_3^{-1})}$$

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Mercury Photosensitized Polymerization of Acetylene

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An investigation has been made of the mercury $({}^{3}P_{1})$ photosensitized polymerization of acetylene. Benzene was found in the reaction products in addition to polymer and hydrogen. Effect of acetylene pressure and light intensity on the rate, effect of pressure on the formation of hydrogen and benzene, and effect of temperature on the rate of benzene formation were studied. The fraction of acetylene reacting to form benzene was constant at 0.29 in the range of the acetylene pressure studied. The quantum yield of the over-all reaction was 4.8 including the yield of benzene and 4.3 excluding it. The reaction mechanism is discussed.

INTRODUCTION

NUMBER of investigations have been made on the mercury photosensitized polymerization of acetylene.¹⁻⁵ However, no qualitative, much less quantitative, analysis of the products except for hydrogen has been performed.

Melville⁴ proposed the following reaction for the primary step

$$Hg^*+C_2H_2=Hg+C_2H_2^*.$$

On the other hand, LeRoy and Steacie⁵ suggest the existence of a free radical process of the type

$$Hg^*+C_2H_2=C_2H+Hg+H.$$

The present paper is devoted to an investigation of

the products and of the mechanism for the primary process of the polymerization of acetylene.

EXPERIMENTAL

The arrangement of the apparatus is shown in Fig. 1. A drop of mercury is contained in a cell R surrounded with an air thermostat for enough time to saturate acetylene gas before irradiation by a rare-gas-filled mercury vapor lamp L. Although mercury vapor may be consumed by acetylene,^{4,5} the drop of mercury will supply a constant pressure of mercury vapor. This was confirmed as follows. Irradiation and keeping in the dark were repeated alternately at intervals of 30 min. A curve of pressure decrease vs time showed no evidence of an increase in rate due to the variation of mercury vapor by the diffusion during the dark period.

Pressure change of acetylene was measured by a mercury manometer M and a traveling microscope with an accuracy of 0.002 mm and by a McLeod gauge. Light intensity entering the cell was measured by a

¹ J. R. Bates and H. S. Taylor, J. Am. Chem. Soc. 49, 2438

<sup>(1927).
&</sup>lt;sup>2</sup> J. C. Jungers and H. S. Taylor, J. Chem. Phys. 3, 338 (1935).
³ E. K. Rideal, Proc. Roy. Soc. (London) A146, 266 (1934).
⁴ H. W. Melville, Trans. Faraday Soc. 32, 258 (1935).
⁵ D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. 12, 117 (1944).



FIG. 1. Apparatus.

uranyl oxalate actinometer, and was varied by inserting a screen of copper wire between the cell and the lamp. Analysis of the products was performed with a mass spectrometer and with a spectrograph. Experimental temperature was always 30°C unless stated otherwise.

RESULTS

(a) Products of the Reaction

The presence of hydrogen in the irradiated acetylene gas was identified by the mass spectrometer, while LeRoy did it by another method.⁵ The quantity of hydrogen produced was measured by the McLeod gauge, taking the noncondensable gas in a liquid nitrogen trap as hydrogen after the irradiation of acetylene.

Spectrum of the irradiated acetylene indicated only the presence of benzene, which was determined quantitatively by a microphotometer. Moreover, there was



FIG. 2. Pressure decrease vs time for various light intensities (quanta/hr). A, 1.76×10^{17} ; B, 6.84×10^{17} ; C, 19.8×10^{17} ; D, 63.4×10^{17} .

no evidence of spectral lines 2808, 2720, and 2687 A belonging to an unknown intermediate which has always appeared in the spectra of the products (in the gaseous state) of photopolymerization of acetylene^{6,7} and which disappeared immediately when the products were again irradiated with a mercury vapor lamp.⁷

(b) Effect of Acetylene Pressure on the **Rate of Polymerization**

As shown in Fig. 2, the pressure decrease varies linearly with time for lower intensities of light, but falls off gradually with time for higher intensities. Therefore the rate of polymerization of acetylene, R_P , expressed by the pressure decrease in mm Hg/min was determined from the slope of the pressure-time curve at time zero.

Figure 3 shows the pressure dependence of the rate R_P in mm Hg/min at 30°C. In agreement with Melville and with LeRoy and Steacie the rate increased pro-



FIG. 3. Rate of pressure decrease vs acetylene pressure.

portionally with the pressure, and then flattened off at higher pressures. The latter fact has not been noted by previous investigators.

(c) Effect of Light Intensity on the **Rate of Polymerization**

The rate R_P is directly proportional to the light intensity as shown in Fig. 4, which is consistent with the results of Melville and of LeRoy and Steacie.

(d) Effect of Acetylene Pressure on the Formation of Hydrogen

The mean rate of formation of hydrogen in 20 min plotted against pressure is shown in Fig. 5. The rate increases rapidly with pressure at lower pressures to a maximum at about 5 mm and then decreases gradually.

⁶ B. L. Dunicz, J. Am. Chem. Soc. 63, 2461 (1941). ⁷ Z. Kuri and S. Shida, Bull. Chem. Soc. Japan 25, 116 (1952).

(e) Effect of Acetylene Pressure on the Formation of Benzene

The mean rate of formation of benzene in 20 min is plotted against pressure as shown in Fig. 6. It may be seen immediately that Fig. 6 is analogous to Fig. 3. Although the rate of formation of benzene is not the value at time zero, the discrepancy may not be so large.

(f) Effect of Temperature on the Rate of Benzene Formation

The logarithm of the pressure of benzene formed was plotted against 1/T in the range of $14-30^{\circ}$ C. The apparent activation energy calculated from the slope is 9 kcal/M, which is, however, not so reliable because of the small temperature range.



FIG. 4. Rate of pressure decrease vs light intensity.

(g) Quantum Yield

The quantum yield of the over-all reaction in the region of constant rate was found to be 4.8, including the yield of benzene, and 4.3 excluding it. These values are comparable with the value of 4.5 obtained by LeRoy and Steacie.⁵

DISCUSSION

The observed hydrogen must be formed by either of the following schemes:

$$\begin{cases} Hg^{*}+C_{2}H_{2}=Hg+C_{2}H_{2}^{*}\\ C_{2}H_{2}^{*}=C_{2}H+H \end{cases}$$
(I)

$$Hg^{*}+C_{2}H_{2}=C_{2}H+H+Hg.$$
 (II)

Scheme (I) means that the excited mercury atom produces excited acetylene, which splits into a hydro-



FIG. 5. Rate of formation of hydrogen vs acetylene pressure.

gen atom and a radical in its life time, while scheme (II) indicates normal acetylene separates a hydrogen atom in an effective collision with an excited mercury atom. Scheme (II) cannot explain the decrease of hydrogen evolution at higher pressures. On the contrary deactivation of excited acetylene molecules by the normal molecules in scheme (I) increases at higher pressures, the effect of which is to diminish the rate of hydrogen evolution. Hence to account for hydrogen evolution scheme (I) is the probable primary step.

For the formation of hydrogen molecules, the following reactions will occur according to LeRoy and Steacie⁸

$$\begin{cases} a \quad H+C_2H_2=C_2H_3 \\ b \quad C_2H_3+H=C_2H_2+H_2 \end{cases}$$
(III)

$$H+C_{2}H_{2}=C_{2}H+H_{2}.$$
 (IV)

Since reaction (III)b occurs only with high hydrogen atom concentrations,⁸ it may be neglected because of the light intensity and mercury vapor pressures employed and the quantity of hydrogen evolved. Therefore hydrogen must be formed by reaction (IV).

It is evident that benzene will be formed from the successive addition of acetylene to excited acetylene.

Finally, the over-all reaction mechanism of the mercury photosensitized polymerization of acetylene



FIG. 6. Rate of formation of benzene vs acetylene pressure.

⁸ D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. 12, 369 (1944).

may be given as follows

$$Hg + h\nu = Hg^*$$
(1)

$$Hg^* = Hg + h\nu \tag{2}$$

$$Hg^{*}+C_{2}H_{2}=Hg+C_{2}H_{2}^{*}$$
 (3)

$$C_2H_2^*+C_2H_2=(C_2H_2)_2$$
 (4)

$$(C_2H_2)_2 + C_2H_2 = C_6H_6 \text{ (benzene)}$$
 (5)

$$C_2H_2^* = C_2H + H \tag{6}$$

$$C_2H + nC_2H_2 = polymer$$
 (7)

$$\mathbf{H} + \mathbf{C}_2 \mathbf{H}_2 = \mathbf{C}_2 \mathbf{H} + \mathbf{H}_2 \tag{8}$$

$$H + C_2 H_2 = C_2 H_3$$
 (9)

$$C_2H_3 + nC_2H_2 = \text{polymer.}$$
(10)

The rate of polymerization R_P is then

$$R_{P} = \varphi_{4}k_{4} [C_{2}H_{2}^{*}] [C_{2}H_{2}] + \varphi_{7}'k_{7} [C_{2}H] [C_{2}H_{2}] + \varphi_{9}'k_{9} [H] [C_{2}H_{2}], \quad (11)$$

where φ_4 , which is the chain length up to benzene, was taken as constant,⁹ and φ_7' and φ_9' , which are those up to higher polymers, were assumed to be proportional to the pressure, that is $\varphi_7' = \varphi_7 [C_2H_2]$, and $\varphi_9' = \varphi_9 [C_2H_2]$. By steady-state method we obtain

$$R_{P} = K \frac{I_{abs} [C_{2}H_{2}]^{2}}{(k_{2} + k_{3} [C_{2}H_{2}])(k_{6} + k_{4} [C_{2}H_{2}])}, \quad (12)$$

where

$$K = \left\{ \varphi_4 k_4 + \varphi_7 \left(1 + \frac{k_8}{k_8 + k_9} \right) k_6 + \varphi_{10} \frac{k_6 k_9}{k_8 + k_9} \right\} k_3.$$



⁹ L. F. Dorfman and F. J. Shipko, J. Am. Chem. Soc. 20, 4723 (1955).

This equation shows qualitatively the pressure dependence of R_P in Fig. 3 and quantitatively the effect of light intensity in Fig. 4.

Equation (12) leads to

$$\begin{bmatrix} C_2 H_2 \end{bmatrix}^2 / R_P = \{k_3 k_4 \begin{bmatrix} C_2 H_2 \end{bmatrix}^2 + (k_2 k_4 + k_3 k_6) \begin{bmatrix} C_2 H_2 \end{bmatrix} + k_2 k_6 \} / K I_{abs}$$
(13)

which shows $[C_2H_2]^2/R_P$ is a function of the second power of the pressure. The results are in good agreement with the prediction since it was found that k_2k_6 was almost negligibly small. Then $[C_2H_2]/R_P$ must vary linearly with pressure which is observed as shown in Fig. 7.

The rate of formation of benzene R_B on the basis of the above mechanism is

$$R_B = k_5 [(C_2H_2)_2] [C_2H_2].$$

By the steady-state method, we have

$$R_{B} = L \frac{I_{abs} [C_{2}H_{2}]^{2}}{(k_{2} + k_{3} [C_{2}H_{2}])(k_{6} + k_{4} [C_{2}H_{2}])}, \qquad (14)$$

where $L=k_3k_4$. This equation is of the same form as Eq. (12) and so indicates $[C_2H_2]/R_B$ should also vary linearly with pressure. The experimental result^{*} is in good agreement with this prediction as shown in Fig. 8.

The fraction of acetylene reacting to form benzene is given by

$$3R_B/(R_P+R_B)=3k_3k_4/(K+k_3k_4)=$$
constant, (15)

the comparison of which with the experimental results is shown in Table I. It is seen the fraction is remarkably constant at 0.29, which is comparable with the corresponding ratio of 0.21 in the radiation polymerization of acetylene,^{9,10} but slightly larger.



¹⁰ C. Rosenblum, J. Phys. Chem. 53, 474 (1948).

$PC_{2}H_{2} (mm)$	R _P (mm/min)	$R_B \ (mm/min)$	$3R_B/(R_P+R_B)$
5	0.056	0.0063	0.30
10	0.085	0.0091	0.29
15	0.090	0.0098	0.30
20	0.098	0.0105	0.29
30	0.099	0.0108	0.29
40	0.100	0.0108	0.30
50	0.103	0.0112	0.29
60	0.105	0.0112	0.29
70	0.105	0.0112	0.29
80	0.105	0.0115	0.29
90	0.105	0.0115	0.29

TABLE I. The fraction of acetylene reacting to form benzene. (Interpolated values of R_P and R_B .)

The rate of formation of hydrogen molecules $R_{\rm H_2}$ from reaction (8) is

$$R_{\mathrm{H}_2} = k_8 [\mathrm{H}] [\mathrm{C}_2 \mathrm{H}_2].$$

The steady-state equations lead to

$$R_{\rm H_2} = M \frac{I_{\rm abs} [C_2 H_2]}{(k_2 + k_3 [C_2 H_2])(k_6 + k_4 [C_2 H_2])}, \quad (16)$$

where $M = k_3 k_6 k_8 / (k_8 + k_9)$. Equation (16) is analogous to Eqs. (12) and (14), which suggests that I_{abs}/R_{H_2} is proportional to the pressure at constant light intensity, in agreement with observation as shown in Fig. 9.

CONCLUSION

We suggest from the above discussion the following diagram for the mercury photosensitized polymerization of acetylene.





FIG. 9. I abs/RH2 vs acetylene pressure.

This scheme for benzene formation from C₂H₂* is analogous to that for the photopolymerization of acetylene. The formation of benzene in both cases appears to suggest that similar reactions are occurring. If to form benzene, the starting electronic state of the acetylene molecule be the same, the spectrum of the unknown intermediate, characterized by the lines 2687, 2720, and 2808 A, produced in the photopolymerization of acetylene might appear also in the case of the mercury photosensitized polymerization; nevertheless it does not. It seems probable that the mercury photosensitized polymerization of acetylene proceeds through the triplet state, while the photopolymerization of acetylene proceeds through the singlet state. The results of radiation polymerization of acetylene^{9,10} resemble considerably the mercury photosensitized reaction. However, future work is needed to decide all the points in question.