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The Mercury Photosensitized Polymerization of Acetylene and Acetylene- d_2

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The mercury photosensitized polymerization of acetylene and acetylene- d_2 has been studied. The rate of reaction is 30 percent greater with acetylene than with the deuterio-compound, over the whole pressure range investigated. At low pressures, the rate varies as the acetylene pressures but in the pressure range 0.7–4 cm the initial rate of polymerization is practically independent of the acetylene

pressure and determined by the intensity of absorbed resonance radiation. The quantum yield is approximately 6.5 for acetylene and 5 for acetylene- d_2 lower than the yield for acetylene at the same temperature in the photochemical reaction ($\lambda \sim 2000\text{\AA}$). The results are also compared with corresponding studies of the polymerization process under the influence of α -particles.

WE have applied the technique developed by us in our studies of the mercury photosensitized decomposition of the deutero-ammonias² to a comparison of the polymerization of acetylene and acetylene- d_2 under the influence of excited mercury. Bates and Taylor³ indicated qualitatively that acetylene could be polymerized to solid cuprene under such conditions. The straight photochemical polymerization of acetylene has already been studied by Lind and Livingston⁴ who have determined the influence of pressure and temperature and the quantum yield, this latter being compared with the ion yield in the parallel determinations of polymerization under the influence of α -particles.⁵ One of us (J.C.J.) has already, in collaboration with Lind, compared the rates of polymerization of acetylene and acetylene- d_2 under the influence of α -particles and found that these rates were identical within the error of experiment.⁶ It was of interest to ascertain whether this identity of reaction rates extended to the reactions induced by light.

APPARATUS

The experiments were carried out with the apparatus already described by us in our record of the work on the deuteroammonias.² The quartz reaction-vessel there employed was very suitable also in the present work owing to the

device employed for increasing the sensitivity of the pressure measurements which were made after compression of the reacting gases to a small volume. This permitted us to study accurately small amounts of polymerization at relatively low pressures and thus to avoid the difficulties attendant on photochemical experiments in which opaque deposits of product form on the reaction vessel. As source of resonance radiation we again employed the Hanovia quartz mercury vapor, rare gas discharge tube, Sc-2537, operating at 5000 volts from the 110-volt a.c. lighting circuit through a 30-milliamper transformer. The advantages of this type of tube have already been described.² We used the radiation transmitted through a quartz cell containing 25 percent acetic acid, 1.5 cm in thickness which eliminated the short wavelength light that is photochemically active, but which transmits the resonance radiation. Between each experiment, the quartz reaction vessel was cleaned by heating it in the presence of oxygen.

MATERIALS

The samples of acetylene and acetylene- d_2 were prepared by interaction of the vapors of water and of pure deuterium oxide ($d_{25}^{26} = 1.1079$) with samples of pure calcium carbide. This carbide was placed at our disposal by the Union Carbide and Carbon Research Laboratories, Inc., through the courtesy of Dr. C. E. MacQuigg. The sample which the donor believed to be quite pure was entirely different in outward appearance from commercial products. It was nut-brown in color and was preserved in a moisture-proof can. For the preparations, the inner cores of freshly broken lumps were chosen, introduced into the

¹ C.R.B. Fellow from Louvain University, 1934–35.

² Jungers and Taylor, *J. Chem. Phys.* **2**, 373 (1934).

³ Bates and Taylor, *J. Am. Chem. Soc.* **49**, 2444 (1927).

⁴ Lind and Livingston, *J. Am. Chem. Soc.* **54**, 94 (1932).

⁵ Mund and Koch, *Bull. Soc. Chim. Belg.* **34**, 125, 241 (1925); Lind and Bardwell, *J. Am. Chem. Soc.* **48**, 1556 (1926).

⁶ Lind, Jungers and Shiflett, *Phys. Rev.* **46**, 825 (1934).

preparation vessel, heated and exhausted in vacuum at $400^\circ C$ for 24 hours before reaction with the water vapors. The products were condensed in liquid air and the middle fractions only used for experimental work. We cite the data of Glockler and Davis,⁷ on the Raman spectrum of our acetylene- d_2 preparation as evidence of its distinctive characteristics as compared with acetylene and acetylene- d_1 .

EXPERIMENTAL RESULTS

The rates of polymerization of the two acetylenes, at pressures of 0.1, 0.25, 0.7 and 4 cm, are shown graphically in Fig. 1. The measurements were made at room temperatures (*ca.* $25^\circ C$) with the gases confined over mercury and hence saturated with mercury vapor at that temperature. It is immediately evident that, over the pressure range employed, the rate of acetylene polymerization is always greater than that of the acetylene- d_2 . Computation shows that, at each pressure, the rate, in the case of the light acetylene, is 30 percent greater than that of the heavy acetylene. The curves at the lowest pressure represent approximately 90 percent total reaction. At the higher pressures the change is not followed so far. It is also evident that, at the lower pressures, the initial rate of polymerization is strongly dependent on the pressure, but the data at the higher pressures show that the rate has become practically independent of the acetylene pressure. This pressure dependence is undoubtedly governed by the effectiveness of the acetylenes in taking up the energy of the excited mercury and reveals that there is no essential difference between the two acetylenes in this respect. In the higher pressure range the rates are therefore determined by the concentration of excited mercury

$$\begin{aligned}-d(C_2H_2)/dt &= k[Hg'], \\ -d(C_2D_2)/dt &= k[Hg'].\end{aligned}$$

The available intensity of resonance radiation was ascertained by measurement of the rate of reaction of an electrolytic gas mixture ($2H_2 + O_2$) under identical operating conditions. It was found that the rate of polymerization of acetylene

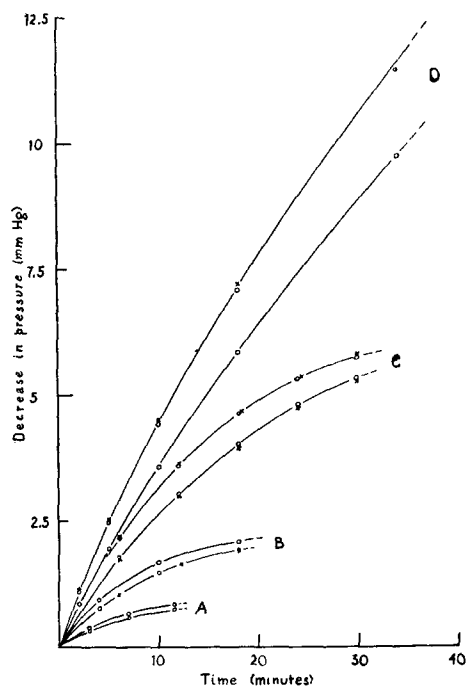


FIG. 1. Velocity of polymerization of acetylene and acetylene- d_2 at (A) 0.11, (B) 0.25, (C) 0.7 and (D) 4 cm initial pressure.

in the high pressure range was approximately 30 percent greater than that of the hydrogen-oxygen reaction under the same conditions of illumination and mercury pressure. Since the quantum yield in this latter reaction is found to be less than $3H_2O_2$ per quantum⁸ or approximately 5 molecules of hydrogen plus oxygen disappearing, we assign a quantum yield of not more than 6.5 to the photosensitized polymerization of acetylene and a 30 percent lower yield, or approximately 5 molecules per quantum for heavy acetylene.

DISCUSSION

The experiments which we have performed serve still further to differentiate the polymerization of the acetylenes under the action of ions

⁸ Marshall, J. Phys. Chem. **30**, 34, 1078, 1634 (1926); J. Am. Chem. Soc. **45**, 4460 (1923). Frankenburger and Klinkhardt, Zeits. f. physik. Chemie **8**, 138 (1930); **15**, 421 (1932).

⁷ Glockler and Davis, Phys. Rev. **46**, 535 (1934).

and of light. Whereas with the former (α -particles), there is no difference in the rates of polymerization with the heavy and light molecules, in the present work the heavy acetylene polymerizes at a markedly slower rate under the same intensity of excited mercury. There is a progression, also, in the yield of the respective processes. Under the influence of β -particles,⁹ 26 molecules of acetylene polymerize per ion pair. With α -particles the rate of disappearance of the two acetylenes is 18–20 molecules per ion pair¹⁰ practically independent of temperature. Lind and Livingston found a value for the photochemical polymerization ($\lambda \sim 2000\text{\AA}$) of 9.5 molecules per quantum at 25°C and values varying from 7 to 11 per quantum in the temperature range of 7–40°C, with the temperature coefficient of 1.25 per 10° increase in temperature responsible for this variation, the absorption coefficient being temperature independent within the limits of accuracy of the measurements. With the smaller quantum of light energy involved in the photosensitized polymerization ($\lambda = 2537\text{\AA}$), the quantum yield falls still further to 6.5 molecules per quantum at 25°C.

All these data point to the conclusion that the polymerization process in the case of the acetylenes rapidly dissipates the energy which is employed to initiate the process. With agents such as α -particles, β -particles and cathode rays the chain mechanism is most pronounced and the velocities of polymerization identical in the case of light and heavy acetylenes. In the case of acetylene radiated by α -particles it is known that the only observable effect of temperature is

slightly negative (2 percent in 100°) and this has been explained on the basis of decreasing capture of molecules by the charged particle with increase in temperature.¹¹ We conclude that the electrostatic attraction of the charged particles produced by the radiation determines the magnitude of the ion yield and serves in place of the activation energy of collision necessary where such attractive forces are absent. With less energetic agents such as light, temperature activation is a markedly contributory factor, the evidence indicating that the heavy acetylene requires greater thermal activation for the chain process. In this respect, there is a possibility that the exchange of energy between excited mercury and acetylene- d_2 is not so efficient as with acetylene. The absence of pressure effect at the higher pressures makes this, however, appear improbable. The effect of temperature as an auxiliary agent cannot be followed into the higher temperature ranges since it is known that in the region of 250°C the product is no longer cuprene, a complex of products, including benzene, being formed.¹² In the thermal polymerization process, which requires an activation energy of the order of 40,000 calories,¹³ cuprene is also not produced but a complex mixture of products. All these polymerization processes as well as those of methyl acetylene and allene¹⁴ appear to involve only short chains, in contrast to the polymerization of styrene and vinyl acetate in which the chain length may reach thousands of molecules per quantum absorbed.¹⁵

¹¹ Mund, Ann. Soc. Sci. Brussels **B54**, 30 (1934).

¹² Kato, Bull. Inst. Phys. Chem. Res. (Tokyo) **10**, 343 (1931); Kemula and Mrazek, Zeits. f. physik. Chemie **B23**, 358 (1933); Livingston and Shiflett, J. Phys. Chem. **38**, 377 (1934).

¹³ Pease, J. Am. Chem. Soc. **51**, 3470 (1929).

¹⁴ Lind and Livingston, J. Am. Chem. Soc. **55**, 1036 (1933).

¹⁵ Taylor and Vernon, J. Am. Chem. Soc. **53**, 2527 (1931).

⁹ Mund and Jungers, Bull. Soc. Chim. Belg. **40**, 158 (1931).

¹⁰ An explanation for this lower yield with α -particles has already been put forward by Mund and Jungers, reference 9. Recombination of ions, due to their greater concentration in the path of the α -particle, may account for the lower value as compared with β -particles.