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# The Mercury Photosensitized Polymerization of Cyclopropane\*

H. E. GUNNING\*\* AND E. W. R. STEACIE (Received May 19, 1948)

An investigation has been made of the polymerization of cyclopropane with mercury  $({}^{8}P_{1})$  atoms in a static system over the pressure range from 1-400 mm at 30°C. The only important product of the reaction is a liquid polymer with the formula  $(C_3H_6)_n$ , where n is probably about 6. Small amounts of other products, of low molecular weight, are present at initial pressures below 10 mm. Data are presented which show that propylene is formed only at low initial pressures, suggesting its origin from the collision of trimethylene biradicals with the wall.

The over-all rate of consumption of cyclopropane becomes independent of initial pressures above 40 mm. The quantum yield of cyclopropane disappearance in the complete quenching region is 0.136.

A mechanism is proposed for the polymerization involving the initial formation of an energy-rich trimethylene biradical

#### INTRODUCTION

<sup>•</sup>HE polymerization of cyclopropane, sensitized by  $Hg(^{3}P_{1})$  atoms was first observed by Harris, Ashdown, and Armstrong<sup>1</sup> during the course of an investigation of the Raman spectrum of cyclopropane. These authors found that the rate of pressure decrease was independent of the initial pressure of the cyclopropane over the range from 0.5 to 4 atmospheres. Furthermore, they found that "the product was a viscous colorless oil having a boiling point of nearly 300°C at 760 mm, and showing continuous absorption in the ultraviolet below 2500A." They concluded that the polymer must have the formula  $(CH_2)_n$ .

The present investigation was undertaken in

by the reaction

$$C + Hg(^{3}P_{1}) \rightarrow R_{1}^{*} + Hg(^{1}S_{0}).$$
(1)

The activated radical can then either reform cyclopropane upon collision or form a higher biradical:

$$R_1^* + C \rightarrow 2C, \qquad (2)$$

April, 1949

$$R_1^* + C \rightarrow R_2^*, \text{ etc.}, \tag{3}$$

where C = cyclopropane,  $R_1 = \cdot (CH_2)_3 \cdot$ , and  $R_2 = \cdot (CH_2)_6 \cdot$ . Chain termination will occur when the polymer biradical can no longer furnish sufficient energy to break the C-C bond in cyclopropane. The radical will then stabilize itself by a proton shift. On the basis of the above mechanism, combined with the analytical data, reaction (2) must be at least 43 times faster than reaction (3).

Evidence is also presented for the fact that cyclopropane does not react with the H atoms formed by the collision of  $Hg(^{3}P_{1})$  atoms with hydrogen.

order to elucidate the mechanism of the polymeriza tion, and to gather further information on the properties of the trimethylene biradical.

#### **EXPERIMENTAL**

Two separate series of static runs were made at 30°C. Descriptions of the apparatus used in each series follow:

## Static Runs, "K" Series

In this series of runs a cylindrical, fused quartz cell was employed which was 10 cm in length with windows 5 cm in diameter. The cell was immersed in a metal thermostat provided with a fused quartz window. The distilled water in the bath, which was changed before each run, was maintained at  $30.00\pm0.01$  °C, by means of a thermionic relay circuit, similar to the device described by Serfass.<sup>2</sup> The cell had a volume of 250 cc, while the volume of the entire cell system was 1052 cc. Pressure changes in the system were followed by means of a

<sup>2</sup> E. J. Serfass, Ind. Eng. Chem. Anal. Ed. 13, 262 (1941).

<sup>\*</sup> Joint contribution from the Department of Chemistry, University of Rochester, Rochester, New York, and the Division of Chemistry, National Research Laboratories, Ottawa, Canada. The portion of this work which was done at the University of Rochester was supported by Contract N6onr-241, Task I, with the Office of Naval Research, United States Navy.

<sup>\*\*</sup> Department of Chemistry, Illinois Institute of Tech-

nology, Chicago, Illinois. <sup>1</sup> L. Harris, A. A. Ashdown, and R. T. Armstrong, J. Am. Chem. Soc. 58, 682 (1936).

Run no.	<i>P</i> <sup>0</sup> (mm)	$(-\Delta P/\Delta t)$ ×10 <sup>2</sup> mm/min.		$ \begin{array}{c} [d(\mathrm{H}_2)/dt] \\ \times 10^6 \\ \mathrm{moles/min.} \end{array} $
132K	1.79	0.69	0.032	0.013
133K	4.20	1.12	0.035	0.018
131 <i>K</i>	7.14	1.31	0.019	0.017
130K	$10.8_{5}$	1.52	0.019	0.018
129K	19.95	1.91	0.014	0.020
124K	33.01	2.31	0.008	0.019
125K	39.89	2.33	0.009	0.019
126K	49.85	2.44	0.005	0.022
127K	57.73	2.46	0.009	0.022
128K	72.44	2.44	0.006	0.019

TABLE I. Volume of system = 1050 cc.

multirange McLeod gauge. A description of the mercury resonance lamp used and other experimental details will be found in an earlier publication.3

The mass spectrometric analyses on the products of the "K" runs which were condensible in liquid air were obtained through arrangement with the National Bureau of Standards. The sampling technique employed, as well as the method used in the analyses for hydrogen and methane, have been previously described.4

## Static Runs, "P" Series

In this series of runs the cylindrical, fused quartz cell was 8 cm in length with windows 5 cm in diameter. The volume of the cell was 165 cc. Pressure measurements were made with a Pearson differential manometer, similar to the instrument described by LeRoy.<sup>5</sup> The manometer was carefully calibrated throughout its entire length by filling with mercury and weighing successive portions, using a one-meter cathetometer to measure the displacements in the meniscus of the mercury. The manometer was separately thermostatted to 0.1°C, to avoid changes in pressure due to fluctuations in room temperature. With this manometer it was found possible to measure changes in pressure to

0.01 mm of mercury up to absolute pressures of 500 mm.

The cell was immersed in a metal water bath at  $30.00 \pm 0.01$  °C, exactly as in the "K" runs. The cell and the manometer made up about 80 percent of the volume of the system. The remainder of the cell system was constructed from heavy-walled capillary tubing to minimize temperature effects. The total volume of the system was dependent upon the setting of the manometer. However, all pressure rates reported in this paper have been corrected to a volume of 280 cc.

In the "P" series of runs, cyclopropane and propylene were determined by selective catalytic hydrogenation over nickel catalysts, after the method of Corner and Pease.<sup>6</sup> Attempts were also made to detect propylene using a Perkin-Elmer infra-red spectrometer.

The source used in this series was a Hanovia SC-2537 mercury resonance lamp, wound in the form of a five-coil helix, the coils being about 5 cm in diameter. The lamp was operated from a "neon sign" type transformer, delivering an initial voltage of 3000 volts at 30 milliamperes from the secondary.

The cyclopropane used throughout the entire investigation was the U.S.P. grade supplied by the Ohio Chemical and Manufacturing Company, Cleveland, Ohio. The gas was further purified by several trap-to-trap distillations. The middle fractions from these distillations were stored in twoliter bulbs provided with all-mercury valves of the design suggested by Warrick and Fugassi.<sup>7</sup> Mass spectrometric analyses of duplicate samples of the cyclopropane showed it to be 99.8 percent cyclopropane and 0.2 percent propane.

Before making a run the cell was allowed to stand for two hours in a hot chromic acid solution. It was then thoroughly rinsed with distilled water, and "flamed out" at a bright red heat in a current

		TABLE II.						
Run no.	₽₀ (mm)	-d/dt (cyclopropane)	d/dt (ethane) The rates	d/dt (propylene) are in moles per m	d/dt (propane) iinute×10⁵.	d/dt (methyl cyclo- pentane)	d/dt (methyl hexenes)	d/dt (dimethyl hexanes )
133 <i>K</i> 131 <i>K</i> 130 <i>K</i> 129 <i>K</i> 124 <i>K</i> 125 <i>K</i> 126 <i>K</i> 128 <i>K</i>	$\begin{array}{r} 4.20\\ 7.14\\ 10.8_5\\ 19.9_5\\ 33.0_1\\ 39.8_9\\ 49.8_5\\ 72.4_4\end{array}$	0.85 0.87 0.88 1.06 1.34 1.33 1.37 1.38	0.006 0,006	0.10 0.02 0.01	0.03 0.04 0.04 0.02	0.007 0.004	0.02 0.04	0.007 0.006

<sup>8</sup> H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. 12, 484 (1944).
<sup>4</sup> H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. 14, 544 (1946).
<sup>5</sup> D. J. LeRoy, Ind. Eng. Chem. Anal. Ed. 17, 652 (1945).
<sup>6</sup> E. S. Corner and R. N. Pease, Ind. Eng. Chem. Anal. Ed. 17, 564 (1945).
<sup>7</sup> E. Warrick and P. Fugassi, Ind. Eng. Chem. Anal. Ed. 15, 13 (1943).

of air, to remove any polymer remaining on the cell from previous runs. One cc of distilled mercury was then added to the cell, after which the cell was attached to the system and evacuated to a "sticking" vacuum, as measured on the McLeod gauge. The desired amount of cyclopropane was then frozen in the cell system by placing liquid nitrogen around a small bulb in the system. After another evacuation to remove any non-condensible gas from the cyclopropane, the cyclopropane was allowed to vaporize and remain for 12 hours in the system before making a run, in order that the mercury might attain its vapor pressure at 30°C.

#### RESULTS

#### Results with "K" Series

Cyclopropane showed a similar behavior to propylene,8 isobutene,7 1-butene,9 2-butene,9 and isoprene<sup>8</sup> in that the pressure decreases linearly with time even in the initial stages of the reaction. Droplets of a clear, colorless polymer could be seen forming on the window throughout the course of a run. A study of Table I will show that the rate of pressure decrease becomes independent of the initial pressure above about 30 mm pressure. This is in agreement with the results of Harris, Ashdown, and Armstrong<sup>1</sup> Also from Table I it is apparent that the rates of formation of both methane and hydrogen become independent of pressure in the complete quenching region. The increase in the rate of methane formation at low pressures would suggest wall reactions between methyl radicals and H atoms. Of course, both methane and hydrogen are very minor products in the reaction.

In Table II the results of the mass spectrometric analyses of the "K" runs are tabulated.

The polymer is apparently the only important product above an initial pressure of 20 mm. This polymer must therefore have the formula  $(CH_2)_n$ . Its vapor pressure is  $10^{-4}$  mm at  $30^{\circ}$ C. It is interesting to note that propylene becomes a significant product at low pressures, which would suggest that the propylene might be formed in collisions of trimethylene biradicals with the wall.

#### Results with "P" Series

With the Pearson differential manometer, it was found possible to measure accurate pressure rates up to much higher initial pressures than with the McLeod gauge. Table III shows a typical run, using the manometer. It will be observed that there is a slight pressure rise at the beginning of the run. After about five minutes the pressure begins to

TABLE III. Run no. 163P,  $P_0 = 39.5$  mm.

Time (min.)	-Δ <i>P</i> (mm)
0	0.00
1	-0.01
2	0.06
3	0.14
4	0.21
5	0.28
10	0.76
15	1.25
20	1.70
25	2.18
30	2.65
35	3.11
40	3.57
45	4.03
50	4.50
55	4.96
60	5.43
•	
•	Lamp off
•	,
60.3	5 54
63	5 54
00	0.01

decrease linearly with time. However, at the end of the run, the pressure falls rapidly as soon as the lamp is turned off. The linear portion of the pressure-time curve extrapolates back to 0.18 mm at zero time, while the drop in pressure after turning off the lamp=0.21 mm. The same effect is observed with isobutene.<sup>10</sup> This displacement of the pressure-time curve disappears below initial pressures of 20 mm and becomes independent of initial pressure at 0.2 mm in the complete quenching region. It could conceivably be due either to desorption of gas molecules from the wall, or to the heat of reaction or to a combination of both. More data will shortly be published on this effect.<sup>10</sup>

The rate data are summarized in Table IV. The cyclopropane consumed was calculated from the pressure changes, corrections being applied for the non-condensible gas formed during the run. This method of calculation is valid, since the mass spectrometric analyses of the "K" runs (Table II) show that polymer is the only significant product of the reaction at initial pressures greater than 10 mm. The rate of consumption of cyclopropane is remarkably constant in the complete quenching

TABLE IV. Volume of system = 280 cc.

Run no.	<i>P</i> <sub>0</sub> (mm)	$-\Delta P/\Delta t$ mm/min. $\times 10^{2}$	$\begin{array}{c} d/dt \\ (CH_4+H_2) \\ moles/min. \\ \times 10^6 \end{array}$	$\begin{array}{c} -d/dt \\ (\text{cyclo } C_3H_6) \\ \text{moles/min.} \\ \times 10^6 \end{array}$	φ cyclo C3H6
158P	17.2	7.8	0.070	1.08	0.10
157P	27.0	8.4	0.049	1.19	0.11
163P	39.5	8.7	0.038	1.25	0.12
155P	50.3	9.9	0.029	1.44	0.136
162P	156.8	9.9	0.027	1.44	0.136
156P	219.0	9.8	0.025	1.43	0.135
159P	415.2	9.9	0.027	1.44	0.136

<sup>10</sup> G. A. Allen and H. E. Gunning, J. Chem. Phys. 16, 1146 (1948).

<sup>&</sup>lt;sup>8</sup> H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. 14, 57 (1946). <sup>9</sup> H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. 14,

<sup>&</sup>lt;sup>9</sup> H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. 14, 581 (1946).

region, suggesting that the rate of reaction is determined entirely by the initial quenching process.

In view of the fact that propylene would seem to be a likely product of the reaction, attempts were made to detect propylene in the products by infrared absorption and by catalytic hydrogenation.<sup>6</sup>

In the infra-red method of analysis, a Perkin-Elmer spectrometer was used in conjunction with a 15-cm absorption cell. Preliminary tracings showed that propylene absorbed quite strongly at 10.85 m $\mu$ , while the cyclopropane absorption at



FIG. 1. Pressure vs. time for a mixture of 50-mm cyclopropane and 3-mm propylene.

this wave-length was very weak. In order to obtain quantitative data, a series of calibration tracings were made over a range of pressures for both cyclopropane and propylene. Five one-hour runs were then made over the pressure range from 50 to 400 mm. The products of each run were frozen into the infra-red absorption cell and tracings made with the gas. The results, corrected for cyclopropane absorption, showed no propylene to be present. It was estimated that a minimum of 500 cc-mm of propylene could be detected by this method, or about one percent by volume.

Attempts were also made to detect propylene in the products by catalytic hydrogenation over a kieselguhr-supported nickel catalyst, which had been poisoned by mercury.<sup>6</sup> These results were also negative. The sensitivity of this method is about the same as the infra-red technique used.

#### The Effect of Added Propylene

In Fig. 1 the pressure-time curve is shown for a run on a mixture of 50 mm of cyclopropane and 3 mm of propylene. The portion AB of the curve has a slope of 0.068 mm/min., while the CD portion has a slope of 0.099 mm/min. It is apparent that propylene has a strong inhibiting effect on the rate and that it is rapidly consumed, since the CD portion of the curve corresponds to the uninhibited rate. In Table V and Fig. 2 the initial slopes of added propylene. Maximum inhibition appears to

occur at about two percent by volume of added propylene. These results seem to offer a fairly tangible proof that propylene is not a significant product in the cyclopropane polymerization, except perhaps at low pressures, as indicated in Table II. The fact that the rate of pressure decrease becomes independent of propylene concentration in mixtures richer than two percent by volume in propylene, as seen in Fig. 2 ,would suggest that at these concentrations propylene is doing the major portion of the quenching. It follows that the quenching cross section of propylene for  $Hg(^{3}P_{1})$  atoms must be at least 50 times greater than cyclopropane. Now these values have never been determined directly. However, Steacie and LeRoy<sup>11</sup> found that the quenching cross section of propylene for  $Cd({}^{3}P_{1})$  atoms was some forty times greater than cyclopropane, and it is probable that approximately the same ratio of cross sections would be obtained for these substances with respect to  $Hg(^{3}P_{1})$  atoms.

## Hydrogenation of Cyclopropane\*\*\*

Several runs were made with mixtures containing 90 percent by volume of hydrogen and 10 percent by volume of cyclopropane. The total pressure in these runs was 450 mm. Under these conditions practically all the quenching would be done by hydrogen. After a five-hour irradiation, the pressure fell by only 0.30 mm as measured on the differential manometer. The condensible gas at the end of the run was shown to be pure cyclopropane by the fact that it did not hydrogenate over the mercurypoisoned nickel catalyst, and was completely hydrogenated over the unpoisoned nickel catalyst.<sup>6</sup> Therefore, it is apparent that cyclopropane does not react appreciably with the H atoms generated in mercury photosensitization.

#### The Quantum Yield of the Reaction

In the "K" series of runs the light intensity was determined by filling the cell with ethylene at an initial pressure of 13 mm, and determining the initial rate of formation of hydrogen, by oxidation over copper oxide at 250°C. The average of eight runs gave  $d(H_2)/dt = 2.5 \pm 0.2 \times 10^{-6}$  mole/minute. While LeRoy and Steacie<sup>12</sup> have reported that the quantum yield for the ethylene reaction at 13

to us. <sup>12</sup> D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. 9, 829 (1941).

<sup>&</sup>lt;sup>11</sup> E. W. R. Steacie and D. J. LeRoy, J. Chem. Phys. 11, 164 (1943).
\*\*\* Professor H. S. Taylor has informed us that Dr. R. E.

<sup>\*\*\*</sup> Professor H. S. Taylor has informed us that Dr. R. E. Powell, in some preliminary work at Princeton University, found that the mercury photosensitized hydrogenation of cyclopropane was slower than that of propylene by a factor of at least 100 to 150. We would like to acknowledge our indebtedness to Professor Taylor and Dr. Powell for their kindness in making this unpublished information available to us.

TABLE V. Effect of added propylene. Pressure of cyclopropane = 50 mm.

Run no.	Percent by vol. added C3H6	Initial rate mm/min.
155P	0	0.099
164 <i>P</i>	0.2	0.094
165P	0.5	0.088
166 <i>P</i>	1.75	0.068
160P	3.5	0.067
161 <i>P</i>	5.8	0.067

mm is 0.37, recent work at the University of Rochester<sup>13</sup> suggests that the quantum yield of hydrogen formation under these conditions is 0.25, and on this basis  $I_{ab} = 1.0 \times 10^{-5}$  Einstein per minute in the "K" series of runs. Combining this information with the data in Table II, we obtain 0.14 as the quantum yield of cyclopropane disappearance in the complete quenching region.

On the "P" series of runs, the light intensity was determined by using uranyl oxalate solutions,<sup>14</sup> which gave  $I_{ab} = 1.06 \times 10^{-5}$  Einstein per minute. The over-all quantum yield is recorded in the last column of Table IV as 0.136, in excellent agreement with the "K" runs, considering that two different sources were used.

#### DISCUSSION

Before attempting to devise a mechanism for the polymerization of cyclopropane, sensitized by  $Hg(^{3}P_{1})$  atoms, it might be wise to summarize the essential features of the reaction. These are:

(a) The pressure decreases linearly with time, even in the initial stages of the reaction.

(b) The rate of pressure decrease and the rate of cyclopropane consumption become independent of the initial pressure, in the complete quenching region, i.e., above approximately 40 mm.

(c) A colorless liquid polymer, which has the formula  $(CH_2)_n$ , appears to be the only significant product of the reaction in the complete quenching region.

(d) There are a large number of low molecular weight products at initial pressures below 10 mm. Propylene seems to become a significant product in this low pressure region.

(e) Small amounts of added propylene have a marked inhibiting effect upon the rate of pressure decrease, suggesting that propylene is not a product of the reaction in the complete quenching region.

(f) Runs with 9:1 mixtures of hydrogen to cyclopropane showed that cyclopropane does not react appreciably with the H atoms formed by the quenching of  $Hg(^{3}P_{1})$  atoms with hydrogen molecules.

(g) The quantum yield of cyclopropane disappearance is 0.136 in the complete quenching region.

The reaction of cyclopropane with  $Hg(^{3}P_{1})$  atoms is in remarkable contrast with its thermal behavior, since, as Corner and Pease<sup>15</sup> and others have shown, propylene is the main product of the thermal reaction.

In our discussion of the mechanism we will use the following abbreviations: C = cyclopropane,  $R_1 = \cdot CH_2 - CH_2 - CH_2 \cdot$ ,  $R_2 = \cdot CH_2 - CH_2$ 

Now since cyclopropane does not react with H atoms and, furthermore, since the polymer is the only significant product in the complete quenching region, we postulate that the initial quenching act must involve a C-C bond split with the formation of an activated trimethylene biradical.

$$C + Hg(^{3}P_{1}) \rightarrow R_{1}^{*} + Hg(^{1}S_{0}).$$
(1)

The C-C bond strength in cyclopropane is not known accurately. However, recent work of R. A. Ogg<sup>15</sup> would suggest that the C-C bond strength may be as low as 50 kcal. and, consequently, there may be as much as 62 kcal. per mole of excess energy in the trimethylene biradicals formed in quenching  $Hg(^{3}P_{1})$  atoms. These activated radicals could therefore bring about further decomposition of cyclopropane by the reaction

$$R_1^* + C \rightarrow R_2^*. \tag{2}$$

The low quantum yield of the reaction could then be explained by assuming that cyclopropane can also reform by

$$R_1^* + C \rightarrow 2C. \tag{3}$$

Reaction (2) should be exothermic since the net effect is the rupture of the C-C bond is cyclopropane and the formation of the C-C bond in the hexamethylene biradical. The C-C bond



FIG. 2. The effects of added propylene on the rates.

strength in the linear biradical would probably be about 90 kcal. per mole, with the result that reaction

<sup>15</sup> E. S. Corner and R. N. Pease, J. Am. Chem. Soc. 67, 2067 (1945).

<sup>16</sup> R. A. Ógg, private communication.

 <sup>&</sup>lt;sup>13</sup> G. A. Allen and H. E. Gunning, J. Chem. Phys. 16, 634 (1948).
 <sup>14</sup> G. S. Forbes and L. J. Heidt, J. Am. Chem. Soc. 56, 2363 (1934).

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(2) could be exothermic to as much as 40 kcal., if we adopt the conclusions of Ogg as to the strength of the C-C bond in cyclopropane. Of course, the number of vibrational degrees of freedom over which this excess energy can disseminate itself has also increased during this reaction. Nevertheless, it seems plausible to assume that the energy necessary to propagate the polymer chain can be adequately supplied by a mechanism of the type suggested above.

The polymer which was obtained in this investigation can therefore be explained by the sequence

$$R_{2}^{*}+C \rightarrow R_{3}^{*} \qquad (4)$$

$$\vdots$$

$$R^{*}_{(n-1)}+C \rightarrow M_{n}, \qquad (5)$$

where  $M_n$  represents the polymer molecule. Chain termination will occur when the number of vibrational degrees of freedom has increased to such an extent that the energy available upon collision is no longer sufficient to break the C-C bond in cyclopropane. When the polymer radical has reached this degree of complexity, it could stabilize itself by a proton shift with the formation of an alkene. It is also possible that cyclization might occur during the shifting of the proton.

The presence of propylene at low pressure points strongly to its formation from a collision of a trimethylene biradical with the wall. The work of Bawn and Hunter<sup>17</sup> on the reaction of trimethylene bromide with sodium vapor tends to substantiate our results. They found that the isomerization of the trimethylene biradical to propylene seemed to occur mainly at the wall, while the formation of cyclopropane from the biradical occurred in the gas phase.

If we assume that the low quantum yield arises from reaction (3), it would seem plausible to assume that the reaction

$$R_2 + C \rightarrow M_2 + C \tag{6}$$

might occur also, since Bawn and Milsted<sup>18</sup> found that 1,6-dibromohexane reacted with sodium vapor with the formation chiefly of cyclohexane, with some hexene. However, this reaction is precluded in our case since  $C_6$  compounds are present only at very low pressures, suggesting that they are formed either by the recombination of monoradicals or the isomerization of biradicals at the walls.

The sequence of n+1 steps summarized in reactions (1) to (5) are consistent with our findings

in the complete quenching region. Thus, on the assumption of steady-state concentrations for the radicals, we obtain the relation:

$$-dC/dt = n \cdot I_{ab} \cdot k_2/(k_2 + k_3) = d(M_n)/dt$$

where -dC/dt = rate of disappearance of cyclopropane,  $I_{ab}$  = rate of absorption of resonance radiation,  $d(M_n)/dt$  = rate of formation of polymer, and n = number of units of C<sub>3</sub>H<sub>6</sub> in the polymer. From Table IV,  $\varphi_C = [-dC/dt] \cdot / I_{ab} = 0.136$  in the complete quenching region, and, therefore,

$$k_3/k_2 = (7.3)(n) - 1.$$

The rate of disappearance of cyclopropane on the basis of this mechanism will be independent of pressure in the complete quenching region, if the polymer chain length, n, is also independent of pressure.

Harris, Ashdown, and Armstrong<sup>1</sup> reported that the polymer had a boiling point of 300°C, and this is consistent with our observation that the polymer has a vapor pressure of  $10^{-4}$  mm at 30°C. These data could be roughly identified with an octadecene, i.e., C<sub>18</sub>H<sub>36</sub>, and this would correspond to chain termination by a proton shift at n=6. At any rate it seems plausible from the foregoing remarks that n=6 would be a minimum value, and we can therefore conclude that  $k_3/k_2$  has a minimum value of 43. In other words, the cyclopropane-reforming step (3) must be at least 43 times faster than the radicalforming step (2).

The small amounts of hydrogen, methane, ethane, and propane formed at low pressures, as shown in Tables I and II, could be adequately accounted for if we assume that the reaction

$$\operatorname{cyclo} C_3H_6 + \operatorname{Hg}(^{3}P_1) \rightarrow C_3H_5 + \operatorname{H} + \operatorname{Hg}(^{1}S_0) \quad (7)$$

occurs to a slight extent. It is relevant to note that similar products are found in the mercury-photosensitized reactions of propylene,<sup>19</sup> and these products will ultimately arise in propylene from the interaction of allyl radical with H atoms, followed by hydrogenation and atomic cracking reactions.

It is, of course, possible to construct an activated molecule mechanism which could be made to fit our experimental findings. This is especially true in view of the fact that we have no direct evidence for the existence of the trimethylene biradical. The sequence

$$C + Hg(^{3}P_{1}) \rightarrow C^{*} + Hg(^{1}S_{0}), \qquad (8)$$

$$C^* + C \rightarrow 2C, \tag{9}$$

$$C^*+C \rightarrow R_2$$
, etc. (10)

would yield rate expressions similar to those obtained from the mechanism postulated above, pro-

<sup>&</sup>lt;sup>17</sup> C. E. H. Bawn and R. F. Hunter, Trans. Faraday Soc. **34**, 608 (1938). <sup>18</sup> C. E. H. Bawn and J. Milsted, Trans. Faraday Soc. **35**,

<sup>889 (1939).</sup> 

<sup>&</sup>lt;sup>19</sup> H. E. Gunning and E. W. R. Steacie, J. Chem. Phys., in press.

vided that the activated cyclopropane molecule had a very long life. It is pertinent to note here that Phibbs, Darwent, and Steacie<sup>20</sup> found it necessary to postulate an activated molecule followed by ring opening in the mercury photosensitized decomposition of ethylene oxide, which is structurally somewhat similar to cyclopropane. In the present state of our knowledge, no definite choice can be made between the two mechanisms.

#### CONCLUSIONS

The reaction of cyclopropane with  $Hg(^{3}P_{1})$  atoms is in remarkable contrast to its thermal behavior, where isomerization to propylene seems to be the principal reaction occurring during the decomposition.<sup>15</sup> Furthermore, the cyclopropane reaction is unique among all the mercury photosensitized reactions of the hydrocarbons which have been investigated to date.<sup>21</sup> While it is not possible at the

<sup>20</sup> M. K. Phibbs, B. de B. Darwent, and E. W. R. Steacie, J. Chem. Phys. **16**, 39 (1948). <sup>21</sup> For discussions of the mercury photosensitized reactions of the hydrocarbons, see: E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New

present time to decide whether the collision of an  $Hg(^{3}P_{1})$  atom with a cyclopropane molecule results in the formation of activated molecule or a trimethylene biradical, it seems fairly certain that the polymer chain is propagated by the successive formation of higher and higher biradicals.

Further work is now under way on the cyclopropane reaction in the laboratories of one of us (H.E.G.), together with investigations of the mercury photosensitized decompositions of the higher cyclic paraffins and olefins.

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York, 1946); Keith J. Laidler, J. Chem. Phys. 15, 712 (1947); E. W. R. Steacie, Research, in press.

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# The General Solution of the Secular Equation of Second Degree, with Application to the Class $A_1$ Vibrations of the Symmetrical Triatomic Molecule

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Various solutions of the secular equation of second degree, giving the force constants, normal coordinates, and potential energy distributions in terms of the fundamental vibration frequencies and molecular constants, have been found and their significance discussed. General formulas are obtained for certain critical solutions and illustrative numerical results given for a series of eight symmetrical triatomic molecules, with curves covering all possible solutions in three typical cases. The solution in which the ratios of the contributions to the potential energy from the two square terms in the valenceforce potential energy expression are mutually reciprocal in the two normal modes is shown to be universally applicable; that in which the normal coordinate for the vibration of higher frequency is identical with the corresponding valence-force symmetry coordinate is also quite satisfactory. Both always give real results. Alternative solutions are suggested for use when the difference in frequency of the two modes is small.

#### I. THE SECULAR EQUATION

F the motion of a displaced system specified by two coordinates  $\Delta_1$  and  $\Delta_2$  is simple harmonic, the potential energy, V, contains only quadratic terms and has the following general form

$$2V = d_{11}\Delta_1^2 + d_{22}\Delta_2^2 + (d_{12} + d_{21})\Delta_1\Delta_2, \qquad (1)$$

where the  $d_{ij}$ 's are the force constants,  $(d_{12}=d_{21})$ . It is assumed in this paper that  $\Delta_1$  and  $\Delta_2$  are valencetype coordinates of the required symmetry class. It is usually convenient to express them in terms of further coordinates  $z_1$  to  $z_N$ , as follows

$$\Delta_i = \sum_{k=1}^N a_{ik} z_k, \tag{2}$$

where the coefficients  $a_{ik}$  are determined by the geometry of the system. The secular equation giving the normal vibration frequencies of the system described by the force field (1) can then be written<sup>1</sup>

$$\begin{vmatrix} A_{11}d_{11} + A_{12}d_{12} - \lambda & A_{21}d_{11} + A_{22}d_{12} \\ A_{11}d_{21} + A_{12}d_{22} & A_{21}d_{21} + A_{22}d_{22} - \lambda \end{vmatrix} = 0, \quad (3)$$

<sup>1</sup> E. Bright Wilson, Jr., J. Chem. Phys. 7, 1047 (1939).