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## The Mercury Photosensitized Polymerization and Hydrogenation of Butadiene\*

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 (Received November 3, 1944)

An investigation has been made of the mercury ( $^3P_1$ ) photosensitized polymerization and hydrogenation of butadiene. The main products of the reaction of butadiene with mercury ( $^3P_1$ ) atoms are hydrogen, an acetylenic compound in the  $C_4$  fraction, dimer, and polymer. In the presence of excess hydrogen, the products are mainly butane, butene, and octanes. The variation of the rate of the polymerization reaction with time, and with the pressure of butadiene, suggests the following mechanism:  $C_4H_6 + Hg(^3P_1) \rightarrow C_4H_6^* + Hg(^1S_0)$ , followed by  $C_4H_6^* + C_4H_6 \rightarrow 2C_4H_6$ , or  $C_4H_6^* + C_4H_6 \rightarrow (C_4H_6)_2$  or  $C_4H_6^* \rightarrow C_4H_4 + H_2$ . Polymerization arises largely by a free radical mechanism  $H_2 + Hg(^3P_1) \rightarrow 2H + Hg(^1S_0)$ ,  $H + C_4H_6 \rightarrow C_4H_7$ ,  $C_4H_7 + C_4H_6 \rightarrow C_8H_{13}$ , etc. The mechanism is shown to be consistent with the value found for the quantum yield.

## INTRODUCTION

ALTHOUGH the mercury [ $^3P_1$ ] photosensitized reactions of many of the lower paraffins and olefins have been studied,<sup>1</sup> no papers have as yet appeared on either the mercury photosensitized polymerization or hydrogenation of butadiene. This conjugated alkadiene is of very considerable interest, and the work described herein was undertaken in the hope that some light might be thrown on the mechanisms involved in its reactions.

## PART I. THE MERCURY PHOTOSENSITIZED POLYMERIZATION OF BUTADIENE

## Static Runs

Both static and single-pass runs were made, the former at 30°C, and the latter at room temperature.

In the earlier part of the work with a static system a quartz annular cell was employed having a volume of 342 cc. The mercury "resonance" lamp used in conjunction with this cell was fashioned in the form of a trap. The trap was constructed entirely of Pyrex glass with the exception of the lower half of the outer tube, which was of quartz and joined to the Pyrex portion by means of a graded seal. The electrodes were sealed to the inlet and outlet tubes by means of uranium glass seals. The lamp was filled with neon at 3-mm pressure, and was operated at about 120 milliamp. from a 6000-volt

sign transformer. The lamp and cell were immersed in a thermostat containing distilled water, and maintained at  $30.0 \pm 0.1^\circ\text{C}$ , the quartz portion of the lamp being placed in the center of the annular cell. The temperature was controlled in the thermostat by means of a thermoregulator of the DeKhotinsky type connected to a knife-blade heater. It was found necessary to run the lamp continuously for at least 48 hours before its light intensity became constant. During this time the intensity fell to about 50 percent of its original value.

In order to facilitate the determination of the quantum yield, and of the effect of light intensity on the rate, the cell system was modified to some extent. A cylindrical fused quartz cell, 10 cm in length, with windows 5 cm in diameter, was substituted for the annular cell. Its volume was 240 cc. The cell was immersed in a metal water bath provided with a fused quartz window. The distilled water in the bath was kept at  $30.00 \pm 0.01^\circ\text{C}$ , by means of a thermoregulating system consisting of a mercury thermoregulator, a knife-blade heater, and a thermionic relay employing a 117L7GT rectifier-beam, power amplifier tube in its circuit as recommended by Serfass.<sup>2</sup> The mercury resonance lamp was made by fusing two Pyrex-to-quartz, 13-mm O.D., graded seals together at the quartz ends, and bending the tube in the form of a U. The electrodes were fused to the Pyrex ends by uranium glass seals. The lamp was filled with neon at a pressure of 3 mm and clamped securely outside

\* Contribution No. 1248 from The National Research Laboratories, Ottawa, Canada.

<sup>1</sup> For references, see: D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.* **10**, 676, 683 (1942).

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

the thermostat about 2 cm from the fused quartz window.

The butadiene used in the experiments was obtained from the Ohio Chemical and Manufacturing Company and was shown by analysis to be 98.5 percent butadiene. It was further purified by several trap-to-trap distillations, and finally stored in a one-liter flask, connected to the manifold of the system. The storage flask was provided with a modified Stock valve, as designed by Warrick and Fugassi.<sup>3</sup> This valve proved to be a very convenient method of introducing definite quantities of gas into the cell system.

The nitric oxide used in the work was prepared by the action of mercury on a 2 percent solution of sodium nitrite in concentrated sulphuric acid.<sup>4</sup> The other oxides of nitrogen present were removed by passing the gas through two long glass spirals, the first immersed in a dry-ice acetone mixture at  $-78.5^\circ\text{C}$ , and the second in petroleum ether at  $-148^\circ\text{C}$ . The nitric oxide was then frozen out in a trap with liquid air, and subjected to several trap-to-trap distillations, the middle fraction being collected and stored in a similar storage flask to the one used for butadiene.

Pressure changes were followed on McLeod gauges covering the range from  $2 \times 10^{-5}$  to 110 mm of mercury.

### Analytical Methods

The analytical methods employed underwent several modifications during the course of the work. Non-condensable gas was drawn off through a "pumped down" liquid air trap, by means of a two-stage diffusion pump, backed by a Toepler pump. The hydrogen in the non-condensable gas was measured either by circulation over copper oxide deposited on glass wool, and maintained at  $300^\circ\text{C}$ , or by transferring the sample to a Blacet-Leighton gas analysis apparatus, if its volume was small.

Isolation of the fractions of various carbon numbers in the products was accomplished by a method of fractional condensation and vaporization, using the Ward apparatus,<sup>5</sup> as modified by

Savelli, Seyfried, and Filbert.<sup>6</sup> Four traps were connected in series, and separated from each other by stopcocks. This trap system was connected at one end to the system through a modified Stock valve,<sup>3</sup> and to the other end were connected a two-stage diffusion pump, an all-mercury Toepler pump, a gas measuring burette, and a copper oxide tube for determining hydrogen. Each trap was provided with internal and external copper-constantan thermocouples. The traps were maintained at the desired temperature either by surrounding them with the appropriate substance at its freezing point, or by the modified Ward method.<sup>6</sup> In this method a copper cylinder wrapped with resistance wire was slipped over the trap, and the ends of the resistance wire attached to binding posts on a control panel. These binding posts were connected to General Radio 200-CM Variac transformers, giving a variable voltage from 0–135 volts. The copper cylinder was then filled with a light gasoline. A glass cylinder, filled with gasoline, and a Dewar flask were then slipped concentrically over the copper cylinder. The Dewar flask was kept filled to the top with liquid air during the analysis. By a careful adjustment of the Variac it was found possible to keep the temperature constant to  $0.5^\circ\text{C}$  over the range from  $-10^\circ\text{C}$  to  $-175^\circ\text{C}$ .

The acetylene compound found in the  $C_4$  fraction was estimated by the method of Ross and Trumbull,<sup>7</sup> as modified by Le Roy and Steacie<sup>8</sup> for their determination of acetylene. Butadiene did not react with the neutral 2.5 percent silver nitrate solution, used to absorb the acetylene compound.

The temperatures used in the traps and the cutting pressures are given in reference 6. The cutting pressures were determined with a McLeod gauge. An atmospheric Toepler pump was attached to the system for transferring fractions for analysis in the Blacet-Leighton apparatus.

### Single-Pass Runs

About a dozen single-pass runs were made in order to study the initial products of the reac-

<sup>3</sup> E. Warrick and P. Fugassi, *Ind. Eng. Chem. Anal. Ed.* **15**, 13 (1943).

<sup>4</sup> A. Klemenc, *Die Behandlung und Reindarstellung von Gasen* (Akad. Verlagsges., m. b. H., Leipzig, 1938), p. 166.

<sup>5</sup> E. C. Ward, *Ind. Eng. Chem. Anal. Ed.* **10**, 169 (1938).

<sup>6</sup> J. J. Savelli, W. D. Seyfried and B. M. Filbert, *Ind. Eng. Chem. Anal. Ed.* **13**, 868 (1941).

<sup>7</sup> W. H. Ross and H. L. Turnbull, *J. Am. Chem. Soc.* **41**, 1180 (1919).

<sup>8</sup> D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.* **9**, 829 (1941).

tion without the complications arising from secondary reactions. The system consisted of a large trap connected to a quartz annular cell through a fine capillary. The cell contained a drop of mercury, and was attached to the system with ground glass joints in order to facilitate removal for cleaning. The lamp used was a Hanovia Sc 2537, of the double-U type. It was inserted through the annulus. The cell was connected in turn to the analytical unit described above.

In these runs the butadiene was first frozen out with liquid air in the large trap, after which, the system was pumped down to a pressure of  $10^{-5}$  mm of mercury, in order to remove any traces of air or other permanent gases that might have been present. The temperature of the trap was then raised to  $-78.5^{\circ}\text{C}$ , by immersing it in dry-ice acetone. Butadiene has a vapor pressure of 11.2 mm of mercury at this temperature. The system was then left for six hours in order that the vapor pressure of the mercury might attain its equilibrium value. To start the run the lamp was turned on and the valve connecting the cell

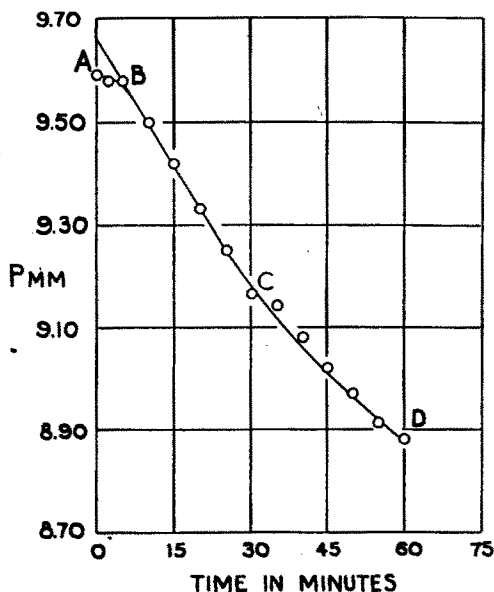


FIG. 1. Pressure vs. time for a typical static run.

to the analytical unit was opened. The butadiene flowed in turn through the cell, then through a trap at  $-85^{\circ}\text{C}$ , and finally was condensed in a liquid air trap. The dimer formed in the reaction was frozen out in the trap at  $-85^{\circ}\text{C}$ . The

acetylene compound condensed with the butadiene in the liquid air trap. The mercury vapor pump on the analytical unit served to pump off the hydrogen formed, which was collected in a gas burette and analyzed by combustion over copper oxide at  $300^{\circ}\text{C}$ .

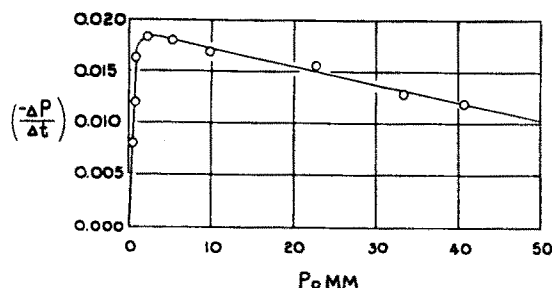


FIG. 2. The initial rate vs. the initial pressure for the static runs.

## RESULTS

### Static Runs

#### *The Effect of Pressure on the Rate*

Figure 1 shows a typical one-hour run at an initial pressure of 10 mm of butadiene. As can be seen from the diagram, the curve consists of three portions. There is a period of induction *AB*, during which time the pressure decrease is very small. This is followed by a linear portion *BC*, and the slope of this line is considered as the rate of the over-all reaction. Finally *CD* represents a falling off of the rate, caused, as has been shown, by the accumulation of polymer on the window of the cell. The length of the period of induction *AB* is directly proportional to the initial pressure of butadiene in the system, being about 10 minutes at 10 mm and increasing to about 28 minutes at 30 mm.

Taking, then, the rate of the over-all reaction as the slope of the portion *BC* of the curve, this value is plotted in Fig. 2 against the initial pressure of the butadiene. The fact that the rate of the reaction as defined in this manner reaches a maximum at about 2 mm is undoubtedly caused by the incomplete quenching of the  $\text{Hg}(^3P_1)$  atoms by the butadiene at lower pressures.

That the falling off of the rate in the *CD* portion of the curve in Fig. 1 is caused entirely by the accumulation of a polymer on the window of the cell can be shown by pumping off the

butadiene after a run, and then making another run at the same pressure, without cleaning the cell. The rate is reduced to a value equal to the slope of the *CD* portion of the curve.

The polymer, which was clearly discernible on the window of the cell through which the light entered, was removed between runs with a hot saturated solution of chromic oxide in concentrated sulphuric acid. In certain cases it was found necessary to flame out the cell in order to ensure the complete removal of polymer. This was imperative in the case of the runs made with nitric oxide-butadiene mixtures, suggesting that the character of the polymer was different in this case.

Kublitskii<sup>9</sup> found that the polymer formed upon illuminating butadiene sealed in quartz ampules with light from the mercury arc, absorbed  $\lambda 2537$ , in agreement with our observations. Another interesting characteristic of the polymer is that it seems to exhibit the phenomenon of "dark growth." If the butadiene and products are pumped off at the end of a run, and the cell again filled with butadiene, without removing the cell from the system for cleaning, it was found that the rate for the second run decreased the longer the cell was left before making the second run.

#### *The Effect of Nitric Oxide on the Rate*

Rate-inhibition by nitric oxide is usually taken to be an indication that free radical chains play an important part in a reaction. For this reason the effect of nitric oxide on the rate of the butadiene reaction was studied. Figure 3 shows a typical run with a mixture of 8 vol. percent of nitric oxide in butadiene. There is no period of induction in the reaction, and the falling off of the rate is caused by an accumulation of polymer on the wall. The rate of the reaction in Fig. 3, as measured by the rate of pressure decrease, is about  $2\frac{1}{2}$  times as great as the rate with pure butadiene at the same pressure.

The rate was measured over a concentration range of 0.2 percent to 20 percent of added nitric oxide, and it was found that the rate of this reaction, with a constant partial pressure of butadiene, was directly proportional to the

amount of nitric oxide present. Analysis of the products of the reaction showed that the nitric oxide had been used up in the course of the reaction. All the above facts seem to suggest that we are dealing here with the mercury photo-sensitized reaction of nitric oxide with butadiene, and for our purpose, therefore, these results are irrelevant.

### THE PRODUCTS OF THE REACTION

#### (a) Static Runs

Small amounts of hydrogen and ethane were formed in the reaction, together with a large amount of a dimer and of course the polymer which forms on the window of the cell, through which the light entered.

Analysis of the gas non-condensable in liquid air from several one-hour runs, made at an initial pressure of 25 mm of butadiene, showed 0.06 mole of hydrogen formed for every mole of butadiene decomposed. Two-hour runs at the same initial pressure yielded only 0.01 mole of hydrogen for each mole of butadiene decom-

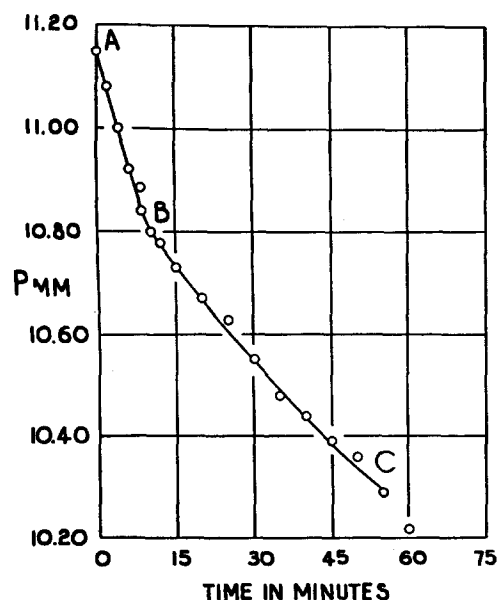


FIG. 3. Pressure vs. time for a static run with 8 vol. percent of nitric oxide and 92 vol. percent of butadiene.

posed, showing that the hydrogen formed initially was being used up in the course of the reaction.

By freezing out the condensable products in liquid air in a small bulb attached to a capillary manometer, and then pumping off the butadiene

<sup>9</sup> K. M. Kublitskii, *Sintet. Kauchuk (U.S.S.R.)*, No. 7/8, 30-32 (1936).

from dry-ice acetone at  $-78.5^{\circ}\text{C}$ , a colorless dimer was isolated. By surrounding the bulb with various freezing mixtures a series of vapor pressure measurements were made after the manner described by Benson.<sup>10</sup> Measurements were made from  $-78.5^{\circ}\text{C}$  to  $50.0^{\circ}\text{C}$ . An extrapolation of the plot,  $\log(\text{vapor pressure})$  vs.  $1/T$  to 760 mm gave a value of  $95^{\circ}\text{C}$  for the normal boiling point of the dimer. Gravimetric micro-analysis gave C = 88.2 percent, H = 11.7 percent. Calculated for  $\text{C}_8\text{H}_{12}$ , C = 88.8 percent, H = 11.2 percent.

The dimer showed a great tendency to polymerize both in vacuum and in air. In both cases a yellow translucent solid is formed, which slowly loses the "double bond" odor of the original dimer. Oxygen does not seem to affect the rate of the polymerization.

About 0.6 mole of dimer were formed for every mole of butadiene decomposed. This was the average of 5 two-hour runs at a pressure of 25 mm.

A small amount of an acetylenic compound was found in the  $\text{C}_4$  fraction by using the method of Ross and Trumbull,<sup>4</sup> as adapted by Le Roy and Steacie.<sup>8</sup> This may be vinyl acetylene.

The amount of the polymer formed decreases markedly with increasing pressure. At an initial pressure of 100 mm there is no falling off of the rate even after two hours illumination. Furthermore, there is no visible evidence of polymer on the window of the cell.

#### (b) Single-Pass Runs

The products from these runs were hydrogen, an acetylenic compound in the  $\text{C}_4$  fraction, a dimer, and a trace of polymer. The mean of four 12-hour runs gave:

Products	Millimoles
Hydrogen	2.0
Acetylenic c.p.d.	0.5 (as $\text{C}_4\text{H}_4$ )
Dimer	0.37 (as $\text{C}_8\text{H}_{12}$ )
Polymer	trace.

#### The Effect of Light Intensity

The effect of light intensity on the rate was determined by inserting a calibrated copper

<sup>10</sup> S. W. Benson, *Ind. Eng. Chem. Anal. Ed.* **14**, 189 (1942).

screen between the lamp and the cell, which reduced the light intensity to 0.32 of its full value. The rate at this intensity was 0.39 of the value obtained by using the full output of the lamp. From this it can be seen that the rate is approximately directly proportional to the light intensity.

#### The Quantum Yield

A rough determination of the quantum yield was made by comparison with the initial pressure rise in the Hg-photosensitized reaction of ethylene.<sup>8</sup> Le Roy and Steacie found that the

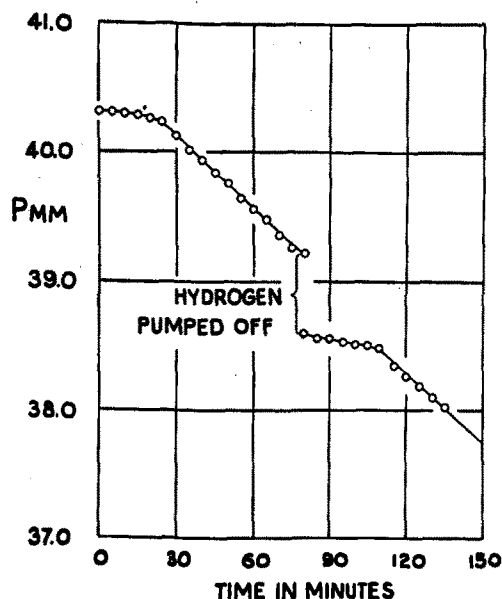


FIG. 4. The effect of pumping off the hydrogen in a static run.

quantum yield of the ethylene reaction was 0.37 at 13-mm pressure of ethylene.<sup>8</sup> The quantum yield of the butadiene reaction calculated on this basis was  $0.8 \pm 0.5$  at 25-mm pressure. According to Gee, as quoted by Bolland and Melville,<sup>11</sup> the quantum yield of the mercury photosensitized reaction of butadiene is in the neighborhood of unity. This is in agreement with our results within the limit of error.

#### The Effect of Hydrogen on the Rate

Two sets of runs were made in order to find out whether any relation existed between the

<sup>11</sup> J. L. Bolland and H. W. Melville, *Proc. Rubber Tech. Conf.*, No. 90, p. 248 (1938).

period of induction and the hydrogen found in the products. Figure 4 shows a typical run in which the hydrogen has been pumped off after the reaction had reached the linear part of the curve. It is obvious from Fig. 4 that a new period of induction is begun when the reaction is resumed after pumping off the hydrogen.

Another series of runs was made in which a small amount of hydrogen was added to the butadiene before starting the run. The period of induction was completely eliminated in these runs. The same effect is produced by stopping the reaction in its period of induction and adding a small amount of hydrogen.

The slope of the linear portion of the curve increased with the percentage of added hydrogen. This is in accordance with the results from the hydrogenation of butadiene with Hg(<sup>3</sup>P<sub>1</sub>) atoms; the rate of this reaction for a 10:1 ratio of hydrogen to butadiene is about ten times as fast as the reaction with pure butadiene.

### Discussion

#### (a) Static Runs

Any mechanism proposed to explain the reactions of butadiene photosensitized by Hg(<sup>3</sup>P<sub>1</sub>) atoms must be consistent with the following facts.

(a) There is a period of induction in the reaction the length of which is directly proportional to the initial pressure of the butadiene.

(b) Small amounts of hydrogen and an acetylenic C<sub>4</sub> compound are found in the products of the reaction. The hydrogen disappears slowly upon prolonged illumination.

(c) If the reaction is stopped, after the linear portion of the pressure-time curve has been reached, and the hydrogen pumped off from liquid air, the period of induction reappears when the reaction is resumed.

(d) Adding a small amount of hydrogen to the butadiene eliminates the period of induction, and the resultant rate increases with increasing amounts of added hydrogen.

(e) The rate as defined above decreases slowly with increasing pressure.

(f) Appreciable amounts of a liquid dimer are formed.

(g) A highly unsaturated polymer is formed

which absorbs λ<sub>2537</sub>. The amount of the polymer formed decreases with increasing pressure.

(h) The quantum yield of the reaction is approximately unity.

By analogy with the results found by Le Roy and Steacie<sup>10</sup> for the mercury photosensitized reactions of ethylene, the formation of an activated molecule seems the most probable primary step:

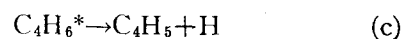


Indeed, the formation of an activated butadiene molecule of relatively long life by the collision of a butadiene molecule with a mercury (<sup>3</sup>P<sub>1</sub>) atom would seem even more likely than with ethylene since butadiene has a larger number of degrees of freedom over which the energy imparted upon collision might distribute itself.

Since the C—H bond strength in the olefins probably is not much different from that in the paraffins, the reactions



and



may occur to some extent, although these reactions do not seem to be of importance as initial steps at room temperature.

The period of induction in the reaction is presumably the result of competition between a pressure-increasing and a pressure-decreasing reaction. By analogy with the ethylene reaction, and in the light of our own findings, these would be:



and



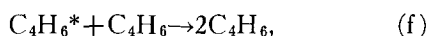
Reaction (d) would explain the small amounts of hydrogen found in the products, and the presence of an acetylenic compound in the C<sub>4</sub> fraction. The acetylenic compound would most probably be vinyl acetylene. The dimer formed by reaction (e) would explain how the liquid dimer is formed which was found in the products. According to Wasserman,<sup>12</sup> the Diels-Alder bimolecular dimerization of butadiene results in the formation of 4-vinylcyclohexene. Vaughan<sup>13</sup> isolated what appeared to be a bicyclooctadiene.

<sup>12</sup> A. Wasserman, J. Chem. Soc., p. 612 (1942).

<sup>13</sup> W. E. Vaughan, J. Am. Chem. Soc. 54, 3863 (1932).

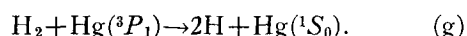
It is probable that the dimer formed in the photosensitized reaction is of a similar nature to these compounds.

Reactions (d) and (e) are probably the only reactions of importance occurring during the period of induction which would have any effect upon the over-all pressure. Increasing pressures would favor reaction (e), and consequently the pressure decrease in the induction period is more apparent at higher pressures. The quantum yield of 0.8, together with the decrease in rate with increasing pressure, strongly suggests that a deactivating reaction also occurs:

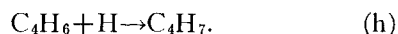


as in the case of the ethylene reaction (8).

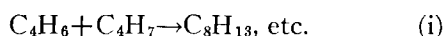
During the period of induction, then, reaction (d) will result in the accumulation of hydrogen in the system. Eventually the hydrogen will reach a high enough concentration to quench the  $\text{Hg}(^3P_1)$  atoms to an appreciable extent:



The hydrogen atoms formed by (g) will then be used up by hydrogenating the butadiene:



By analogy with the ethylene reaction (h) should have an activation energy of 5 kcal. or less. Polymerization would then occur by



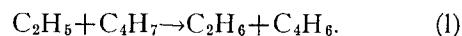
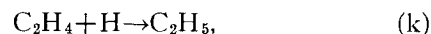
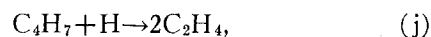
The end of the induction period will occur when the hydrogen has built up to a high enough concentration to quench the  $\text{Hg}(^3P_1)$  atoms to an appreciable extent, by reaction (g). The fact that a very small amount of hydrogen will bring about a large pressure decrease, and result in the formation of considerably more polymer is additional and convincing evidence that at least part of the polymerization occurs by means of a free radical reaction.

The above mechanism is also in accordance with the fact that the length of the induction period increases with increasing pressure. At higher pressure it would take a proportionately longer time for the hydrogen formed by (d) to attain a sufficiently high concentration to be able to quench an appreciable number of the  $\text{Hg}(^3P_1)$  atoms, and thereby initiate polymerization, by (g), (h), and (i).

The runs done on the effect of hydrogen upon the rate also afford a striking confirmation of the above mechanism. The fact that the period of induction can be reproduced by pumping off the hydrogen present, when the reaction has reached a stage where the pressure is varying linearly with the time, shows that the main part of the polymerization must be initiated by H atoms, as in the case with the mercury photosensitized ethylene reaction (8).

Moreover, in the light of the above mechanism, one would expect that at higher pressures the polymerization would be depressed in favor of the dimerization. This would result in a smaller yield of polymer at higher pressures, a larger yield of dimer, and a decrease in rate. All this is in complete agreement with our findings. The quantum yield will always be small since deactivation by (f) will always remove a large proportion of activated molecules.

The small amount of ethane identified in the products may have been formed by some sequence such as



#### (b) Single-Pass Runs

In the single-pass runs the rate of flow of butadiene through the cell was so adjusted that the reaction remained essentially in its period of induction throughout the course of the run. Under these conditions the main reactions would be (a), (d), (e), and (f). The hydrogen formed by (d) would never reach a high enough concentration in the cell to quench the  $\text{Hg}(^3P_1)$  atoms to any appreciable extent. Therefore one would expect that the ratio

moles of dimer formed/moles of hydrogen formed would be small in the single-pass runs, and large in the static runs, where the hydrogen is being continuously used up by (g). Our analyses are in accord with this conclusion;

	Moles dimer formed/ Moles hydrogen formed
Static runs (1 hour)	10
Single-pass runs	0.2.



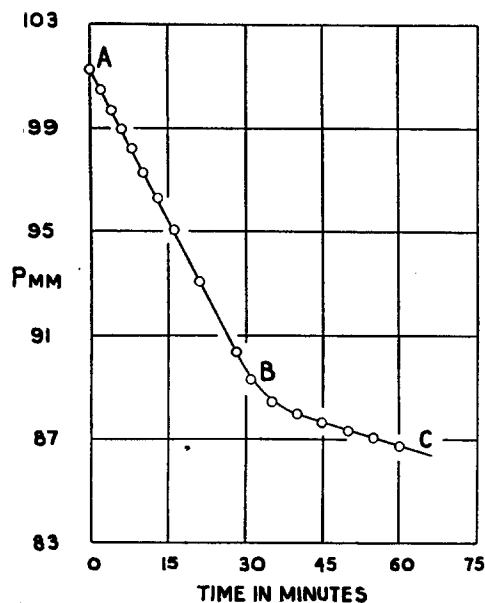
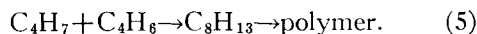
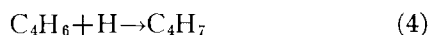
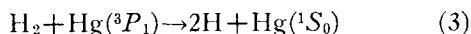
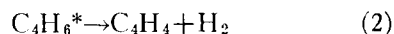


FIG. 5. Pressure vs. time for a static run with 15 vol. percent of butadiene and 85 vol. percent of hydrogen

The trace of polymer formed in the single-pass runs suggests that, under these conditions, polymerization may have been initiated to some extent by  $C_4H_5$  radicals resulting from reactions (b) and (c).

## PART II. THE MERCURY-PHOTOSENSITIZED HYDROGENATION OF BUTADIENE

The work previously described on the polymerization of butadiene, sensitized by  $Hg(^3P_1)$  atoms, strongly suggested that the polymerization of butadiene was initiated by hydrogen atoms in the following manner:



The work described herein on the mercury ( $^3P_1$ ) photosensitized hydrogenation of butadiene was undertaken in order to gain additional information on the polymerization reaction.

### Experimental

The experiments were carried out, at  $30^\circ C$ , in a static system similar to the one employed above.

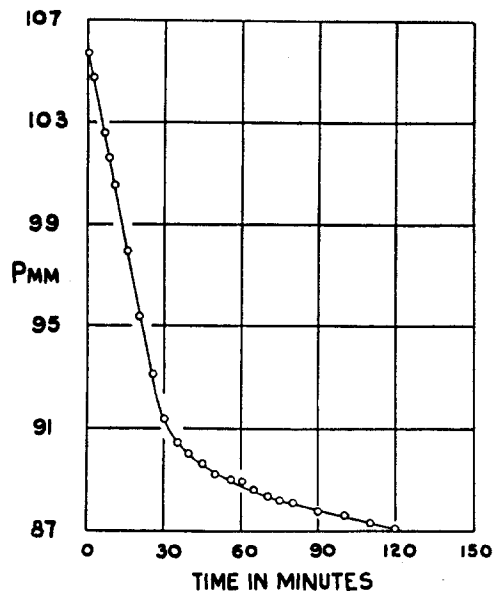


FIG. 6. Pressure vs. time for a static run with 9 vol. percent of butadiene and 91 vol. percent of hydrogen.

The hydrogen used in the runs was prepared by passing hydrogen from a cylinder through two liquid-air traps, and then through a combustion tube containing platinized asbestos at  $500^\circ C$ . It was stored in a two-liter flask provided with a modified Stock valve.<sup>3</sup>

The mixtures of butadiene and hydrogen were made up by first introducing the butadiene into the cell system and measuring its pressure on a large McLeod gauge. The hydrogen was then admitted after the butadiene had been frozen out in liquid air. The partial pressure of hydrogen in the mixture was taken as the difference between the total pressure and the pressure of the butadiene.

### THE EFFECT OF TOTAL PRESSURE AND HYDROGEN CONCENTRATION ON THE OVER-ALL RATE

Figures 5 and 6 show two runs, the first made with a fivefold, and the second with a tenfold, excess of hydrogen. There is no period of induction, and the initial rate is about ten times as great as the rate obtained when no hydrogen has been added. The falling off of the rate in the BC portion of the curve in Fig. 5 was shown to be caused by the accumulation of a polymer on the window of the cell through which the light entered. This was done by adding more butadiene

at the end of the run and then re-illuminating the mixture. The resulting rate corresponded to a continuation of the *BC* portion of the curve.

The falling off of the rate in Fig. 6 was caused not by an accumulation of polymer on the window, but by a complete conversion of the butadiene present to saturated products. Upon adding butadiene at the end of this run, a rate was obtained which was only slightly less than the initial rate. An analysis of the products of this run is given below. Only a few patches of polymer were found on the window of the cell.

The effect of hydrogen concentration on the rate is shown in Fig. 7. The initial rate is here plotted against mm of added hydrogen, the partial pressure of the butadiene being maintained constant at 10 mm. The relation is roughly linear for mixtures containing less than 80 vol. percent of hydrogen. At higher concentrations the rate falls off as would be expected.

Increasing the total pressure at constant composition did not perceptibly affect the rate up to a total pressure of 300 mm. However, the amount of polymer formed was markedly affected—so much so that at 300 mm the accumulation of polymer was sufficient to render the window opaque to  $\lambda 2537$ , and stop the reaction, when only 5 percent of the butadiene had reacted.

### The Products of the Reaction

The products of the reaction were separated into fractions of the same carbon number by the analytical technique previously described. The  $C_4$  fraction was analyzed by passing the gas over maleic anhydride at  $100^\circ\text{C}$ , to constant volume, and then determining the butene in the residue by bromination, using the method of Uhlig and Levin, in the microadaptation of Benson.<sup>10</sup>

The products of the runs made with mixtures containing more than 90 mole-percent of hydrogen consisted mainly of butane with smaller amounts of methane, ethane, and octanes, together with a small amount of polymer. Analysis of the run shown in Fig. 5 gave 10 percent methane, 1 percent ethane, a trace of propane, 70 percent butane, 5 percent butene, 10 percent octanes, and a small amount of polymer.

Qualitative analyses were carried out on the products of the runs from mixtures containing less than 90 percent hydrogen, and these showed

that the products were preponderately butene and butane, and polymer.

### Discussion

The quenching cross section for hydrogen is  $8.6 \times 10^{-16} \text{ cm}^2$ , while that for butadiene should not be very far from  $40 \times 10^{-16} \text{ cm}^2$ ,<sup>14</sup> by analogy with other unsaturated substances, although it has never been experimentally determined. Using these values in the standard kinetic theory expression for the collision number, we obtain

$$Z(\text{H}_2, \text{Hg}^*)/Z(\text{C}_4\text{H}_6, \text{Hg}^*) = [\text{H}_2]/[\text{C}_4\text{H}_6],$$

where  $[\text{H}_2]$  and  $[\text{C}_4\text{H}_6]$  are the molar concentrations of hydrogen and butadiene, respectively.

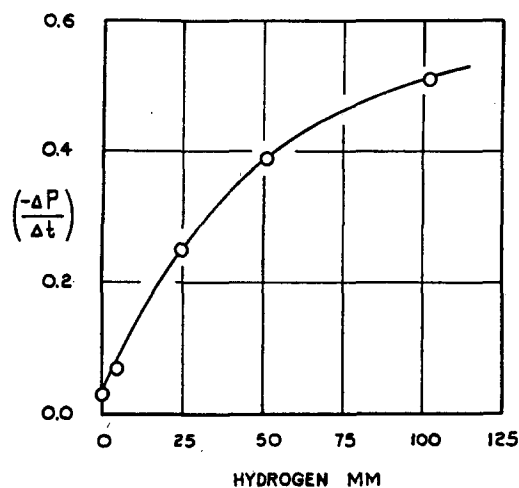
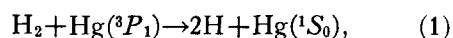


FIG. 7. The initial rate vs. mm of hydrogen added to 10 mm of butadiene.

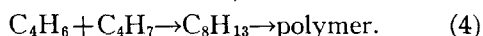
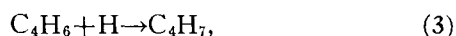
In other words, the extent of quenching of  $\text{Hg}(^3P_1)$  atoms done by butadiene and hydrogen in a mixture will be approximately proportional to the ratio of the molar concentration of the two substances in the mixture. It follows, then, that in a mixture of butadiene and hydrogen containing 90 mole-percent of hydrogen, the hydrogen will do about 90 percent of the quenching.

Bearing the above facts in mind, two primary steps seem likely; namely,

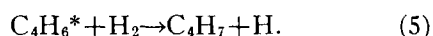


<sup>14</sup> A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, 1934), p. 224.

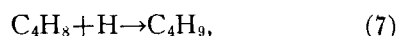
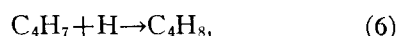
The large amounts of polymer formed in the hydrogenation runs lend weight to our previous conclusion that the polymerization occurs through the addition of an H atom—



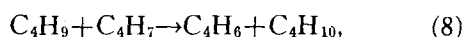
Another step which is energetically possible and may be important is,



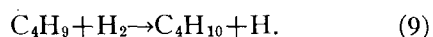
Certainly the fact that the main product formed is butane in a mixture containing 90 mole-percent of hydrogen would seem to indicate that there is a relatively high concentration of both  $C_4H_7$  radicals and H atoms. The butane formed, under these conditions, would likely arise from some such sequence as



followed by



and/or



Disproportionation is not considered important with normal radicals; however, the type of cross disproportionation represented in (8) may be quite important, owing perhaps to the C—H bond in the  $C_4H_7$  being slightly weaker than it is in  $C_4H_9$ .

Reactions of radicals with hydrogen molecules seem to possess rather high activation energies, probably of the order of 8 to 15 kcal., and therefore one would expect (9) to be relatively slow. However, a butyl radical formed by the successive addition of three H atoms to butadiene might conceivably have been able to retain some of this energy of hydrogenation, and, for this reason, we might be dealing in (9) with an activated radical. Of course, if butene is formed as an intermediate, and this seems to be the case, it would quench almost as strongly as butadiene, and consequently direct photosensitized hydro-

genation might occur. The octanes formed undoubtedly arise from radical recombination of butyl radicals. It is of interest to note here that Moore and Taylor<sup>15</sup> found that octanes were the main products in the mercury photosensitized hydrogenation of *n*-butene, while we obtained only a 10 percent conversion of butadiene to octanes, our yield of butane being correspondingly greater. This discrepancy could be explained if we assume that a large percentage of the butyl radicals formed from butadiene by hydrogenation remained in an activated state long enough to collide with a hydrogen molecule, forming butane as in (9).

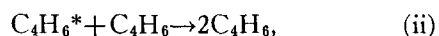
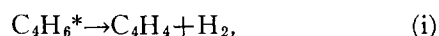
Presumably the methane and ethane formed could be accounted for by a series of "atomic cracking" reactions starting with the butyl radical. However, a detailed study of these secondary reactions is beyond the scope of the present investigation.

### Conclusions

The present investigation on the mercury photosensitized reactions of butadiene seems to suggest the following conclusions:

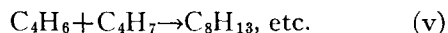
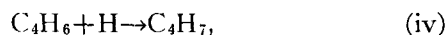
(a) Collisions of butadiene molecules with  $Hg(^3P_1)$  atoms result in the formation of activated molecules of relatively long life.

(b) These activated molecules are mainly used up by the following reactions:



(c) Hydrogen atoms are formed when the hydrogen formed by (i) reached a high enough concentration in the system to quench the  $Hg(^3P_1)$  atoms appreciably.

(d) Polymerization then occurs by the reactions:



<sup>15</sup> W. J. Moore and H. S. Taylor, J. Chem. Phys. **8**, 504 (1940).