

## The Photochemical Polymerization of Butadiene

David H. Volman

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## The Photochemical Polymerization of Butadiene<sup>1</sup>

DAVID H. VOLMAN

*Noyes Chemical Laboratory, University of Illinois*

and

*Division of Chemistry, College of Agriculture, University of California, Davis, California*

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The mercury photo-sensitized polymerization of butadiene and butadiene-acetone mixtures in the gas phase, and the photochemical reactions in solutions of butadiene and acetone in hexane, were studied. Metal mirror experiments demonstrated the absence of hydrogen atoms and the presence of alkyl radicals at low pressures. The mechanism proposed for butadiene vapor postulates an activated butadiene molecule produced by collision with activated mercury and competition between deactivation by collision, predissociation into free radicals, and a collisional process to give hydrogen gas. The polymerization chain proceeds by a mechanism involving either free radicals or hydrogen atoms. In the presence of acetone vapor, the rate is increased and the increase is directly proportional to the number of free radicals coming from acetone, indicating

that polymerization chains are not broken by bimolecular gas phase reaction between free radicals. The quantum yield for butadiene alone at 53-mm pressure and 43°C was 0.24. The average number of molecules reacting per free radical formed was calculated to be between 3 and 8. The liquid solution results are explained on the basis of a modified Frank-Rabinowitch hypothesis for the primary photochemical process. Activated acetone molecules are deactivated by collision with hexane, and react with acetone to yield unsaturated compounds and with butadiene to initiate polymerization. The following kinetic equation is developed for the rate of polymerization,  $dP/dt = (kI_{abs}/I_0)(n[C_4H_6] - [(CH_3)_2CO])$ , where  $n$  is the average number of molecules reacting per free radical.  $n$  is taken equal to 4.

### INTRODUCTION

THE polymerization of alkadienes in the presence of free radicals in the liquid phase is a well-known reaction leading to the production of polymers. Since photochemical methods may be used to introduce free radicals into a system, it was thought that it would be of interest to investigate the polymerization of butadiene induced by free radicals obtained from decomposing acetone in ultraviolet light. The

fact that butadiene is transparent at wavelengths greater than  $2300\text{\AA}^2$  and that aliphatic ketones absorb light and yield free radicals in the wave-length region greater than  $2300\text{\AA}^3$  permits such an experiment.

In general photochemical reactions in the liquid state are complicated in comparison to reactions in the gas state because of solvent effects. Therefore it was considered valuable to study the vapor phase reaction involving butadiene as a preliminary to work in liquid solutions.

<sup>1</sup> The experimental work reported herein was carried out at the University of Illinois under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government's synthetic rubber program.

<sup>2</sup> G. Scheibe and H. Grieneisen, *Zeits. f. physik. Chemie* **B25**, 52 (1934).

<sup>3</sup> R. G. W. Norrish, *Trans. Faraday Soc.* **33**, 1521 (1937).

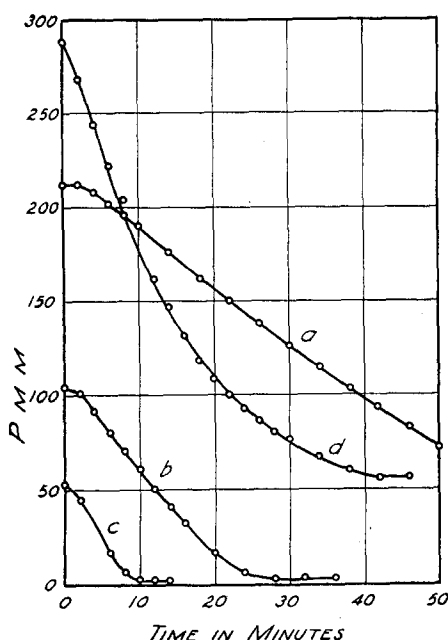


FIG. 1. Pressure vs. time for some typical experiments. *a*, *b*, and *c* are for butadiene alone. *d* is for 106-mm acetone and 182-mm butadiene initially present.

#### PART I. THE MERCURY SENSITIZED VAPOR PHASE REACTION OF BUTADIENE AND BUTADIENE-ACETONE MIXTURES

Gee<sup>4</sup> and later Gunning and Steacie<sup>5</sup> have carried out investigations on the mercury photo-sensitized polymerization and hydrogenation of butadiene. Gunning and Steacie were apparently unaware of the earlier work, and their paper contains no evaluation of the findings of Gee. In the present study some further experiments on the mercury sensitized reaction of butadiene are reported. In addition, experiments on the mercury sensitized reaction of butadiene-acetone mixture were carried out.

#### Experimental

Glass tubes containing butadiene and acetone were attached to the irradiation system by ground glass joints and stopcocks. No precautions to eliminate the use of stopcock grease were taken since, with the intense lamp used, the rates of reaction were great enough so that the absorption of butadiene by lubricant was negligible.

<sup>4</sup> G. Gee, *Trans. Faraday Soc.* **34**, 712 (1938).

<sup>5</sup> H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **12**, 484 (1944).

The reaction tube was a quartz cylinder, 30 mm  $\times$  200 mm, ending in Pyrex seals at either end. Provision for evacuating the system by a mercury diffusion pump was made. The remainder of the apparatus consisted of suitable traps, a McLeod gauge, and a mercury manometer for following the pressure changes. In practice some liquid mercury was always placed inside the reaction tube in order to insure constant mercury vapor pressure.

At the start of an experiment, previously outgassed butadiene or acetone was allowed to enter the outgassed reaction tube until the proper pressure was established. The vapors were then frozen out with liquid air and any residual uncondensed gas was pumped off. The mercury resonance lamp, in the shape of a helix around the reaction tube, was allowed to warm up for fifteen minutes, sufficient time for the lamp to become constant and thermal equilibrium to be established. The light shields were then removed and the pressure of the system followed by the manometer. The temperature of the system was  $43 \pm 1^\circ\text{C}$ .

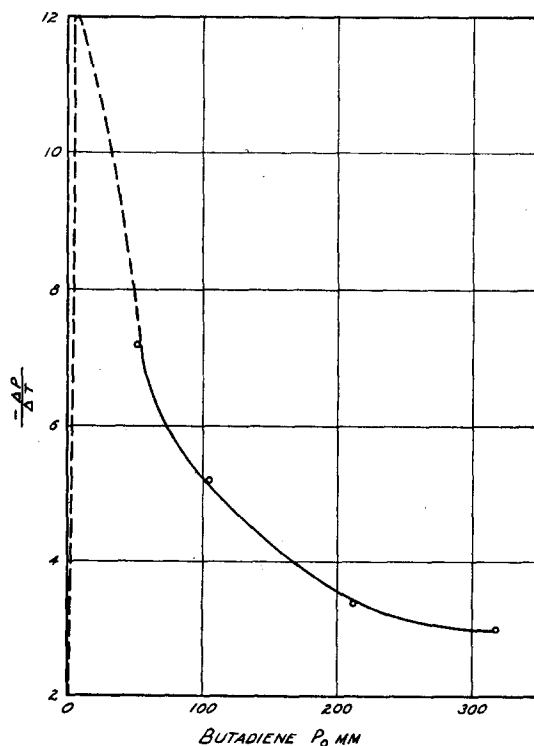


FIG. 2. The initial rate vs. the initial butadiene pressure in the absence of acetone.

The light source was of the rare gas mercury vapor type supplied by the Hanovia Company, which emits most of its radiation as the mercury resonance wave-length, 2537Å.

### Rate of the Reaction

The rate of the reaction at various butadiene pressures in the absence of acetone, and the rate of the reaction for various acetone pressures and a fixed butadiene pressure, were followed. Figure 1 shows typical curves obtained when total pressure in the system is plotted against time of illumination for experiments carried out at 43°C. It may be seen that for butadiene alone the reaction starts slowly at the highest pressure and more rapidly at the lower pressures. The rate then reaches a maximum and diminishes slowly until, near the end of the reaction when it tapers off rapidly. The experiment represented by curve *a* was carried to completion, but only the first 50 minutes are shown. The course of the reaction was not substantially different from the experiments represented by curves *b* and *c*. In each case a few mm of gas uncondensable at liquid-air temperature remains. When acetone is added, curve *d*, the reaction starts out rapidly but slows up gradually and stops while considerable pressure remains.

After a preliminary adjustment period the course of the reaction proceeds smoothly, the maximum rate being reached a few minutes after irradiation begins. In Fig. 2 this initial reaction rate or slope of the  $P$  vs.  $t$  curve, Fig. 1, is plotted as a function of butadiene pressure for experiments in which butadiene was the sole reactant and in Fig. 3 against acetone pressure for experiments in which the initial butadiene pressure was constant and the initial concentration of acetone was varied. The broken portion of Fig. 2 was extrapolated from the data of Gunning and Steacie<sup>5</sup> since they covered the pressure region below 50 mm while the present work was carried out at higher pressures. In the extrapolation allowance was made for the differences in intensity of illumination used.

### The Quantum Yield

Since the absorption of resonance radiation by Hg vapor is so great, the number of quanta absorbed in any of the experiments may be taken

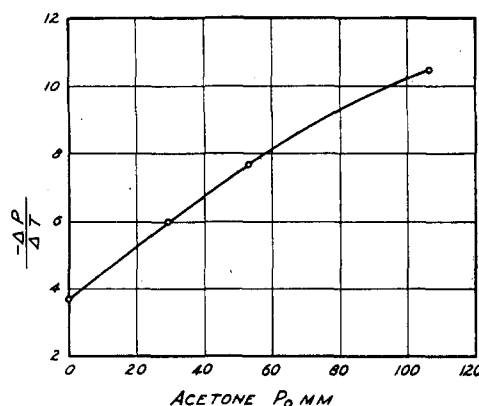


FIG. 3. The initial rate vs. the initial acetone pressure for an initial butadiene pressure of 190 mm.

as equal to the number of quanta entering the reaction vessel. If the intensity may be considered constant, then the quantum yield may be known for any experiment provided a determination of the incident quanta has once been made.

A determination of the incident quanta was made using uranyl oxalate as an actinometer.<sup>6</sup> The reaction vessel was filled with a solution containing 0.01 mole per liter uranyl oxalate and 0.05 mole per liter oxalic acid. After a known period of irradiation an aliquot of the solution was titrated with standard 0.1*N* potassium permanganate. The intensity of light entering the reaction cell was found to be  $4.2 \times 10^{-4}$  einstein per minute. From the total volume of the system, 243 ml, and the rate of polymerization one obtains the expression for the quantum yield,  $\Phi = -\Delta P / \Delta t \times 0.034$ .

For the lowest pressure studied, 53 mm, this leads to a quantum yield of 0.24. Gee<sup>4</sup> has obtained a value of 0.2 for a pressure of 10 mm and a temperature of 15°C and Gunning and Steacie report  $0.8 \pm 5$  for a pressure of 25 mm and a temperature of 30°C.

### The Reaction Products

The principal reaction product has the appearance of a light yellow oil. This is somewhat soluble in benzene. In addition some white solid polymer insoluble in benzene is also formed. This polymer was removable only when heated in an oxygen stream. When there is no pressure change in the system on two successive readings, there is

<sup>6</sup> W. G. Leighton and G. S. Forbes, *J. Am. Chem. Soc.* **52**, 3139 (1930).

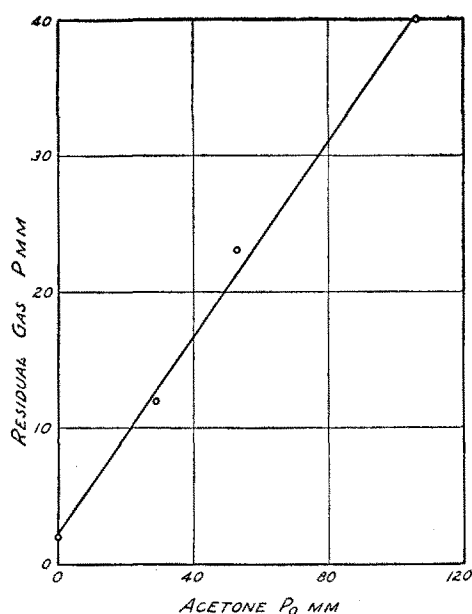


FIG. 4. Yield of gaseous products for experiments with constant initial butadiene pressure.

a residual gas which is not condensed at liquid-air temperature. For butadiene alone it has been shown that this gas is hydrogen.<sup>4,5</sup> For mixtures of butadiene and acetone, the uncondensable residue is much larger than for butadiene alone. In Fig. 4 the connection between this final residual pressure and the acetone concentration is shown. The linear relationship points to acetone as the source of this uncondensable residue. Carbon monoxide is formed when acetone is photolyzed,<sup>7</sup> and it is very probable that this is the gas formed in these experiments when acetone is present.

#### Detection of Free Radicals by the Metal Mirror Method

To determine whether free radicals are formed in the system  $C_4H_6$ , Hg, 2537Å, the metallic mirror technique was used. Butadiene saturated with mercury vapor at room temperature was irradiated at a pressure of about 2.5 mm. The products passed over antimony mirrors which were readily removed. When acetone was substituted for butadiene, the same results were obtained. By measuring the time of mirror removal as a function of distance of irradiation zone from

mirror, it was found that the half-life of free radicals from butadiene was about the same as for acetone.

Using the guard mirror methods developed by Burton<sup>8</sup> a search was made for H atoms in the irradiation products. The fragments were first passed over lead mirrors and then over antimony mirrors. Since lead will react with free radicals containing carbon but not with H atoms, the removal of antimony mirrors which will react with either is a criterion for the presence of H atoms if carbon containing radicals are first removed by lead mirrors. With these experimental conditions no evidence for the presence of H atoms was found.

#### Discussion

The findings of this study are in good agreement with the results obtained by Gunning and Steacie.<sup>5</sup> For butadiene alone, the existence of an apparent inhibition at the start of the run, the lessening of this inhibition, and an increased rate at lower pressures have been confirmed. The effect of adding acetone in this work has been found to be analogous to the addition of hydrogen in the work of Gunning and Steacie. However, the result of our mirror experiments demonstrating the absence of H atoms at low pressures leads to a modified interpretation of the mechanism. The results of Gunning and Steacie and the results reported herein are not in agreement with the work presented by Gee on the effect of pressure on the rate, the effect of hydrogen on the rate, and the interpretation of the inhibition. For this reason the discussion of the mechanism will be based on the suggestions already made by Gunning and Steacie.

The initial absorption act may be represented by

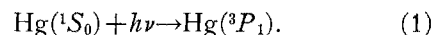


TABLE I. Polymerization rate initiated by acetone.

Initial pressures Bu	Acetone	Mole fractions Bu      Acetone		Reaction rates, (mm/min.)		
				Total	buta- diene only	Acetone initiated
212	0	1	0	3.38	3.38	0
203	29	0.875	0.125	6.02	2.96	3.06
183	54	0.772	0.228	7.70	2.61	5.09
182	106	0.634	0.368	10.53	2.14	8.39

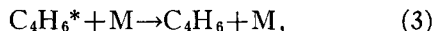
<sup>7</sup> G. H. Damon and F. Daniels, J. Am. Chem. Soc. **55**, 2363 (1933).

<sup>8</sup> M. Burton, J. Am. Chem. Soc. **58**, 1656 (1936).

The low quantum yield of the reaction and the effect of pressure on the rate indicate that the next step is the formation of an activated molecule,

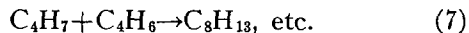
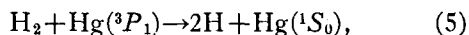
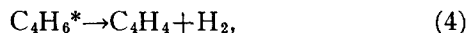


and that deactivation by collisional processes play an important role,

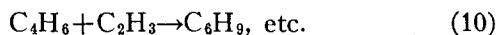
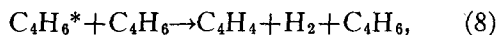


where M represents another molecule or the walls of the reaction vessel.

To explain the inhibition at the start of the reaction, the effect of pressure on the inhibition period, and the effect of added hydrogen on the rate, Gunning and Steacie have proposed the following sequence,



Reactions (5), (6), and (7) explain the effect of adding hydrogen on the rate very satisfactorily. However reaction (4) indicates that hydrogen formation is favored by low pressures and that the polymerization at low pressures occurs by an H-atom mechanism. In the mirror experiments, the presence of alkyl radicals and the absence of H atoms have been demonstrated. This leads to the conclusions that at low pressures the polymerization is induced by alkyl radicals and that hydrogen formation is favored by increasing the pressure. The following sequence is in accord with these conclusions:



Reaction (9) may be considered to be a type of predissociation which would be favored by low pressures since it is in competition with reactions (3) and (8) which are favored by high pressures. Reaction (4) is now eliminated from consideration. Although reactions (5)–(10) may be going on at all pressures, the predominant mechanism at high pressures would be through the series (8),

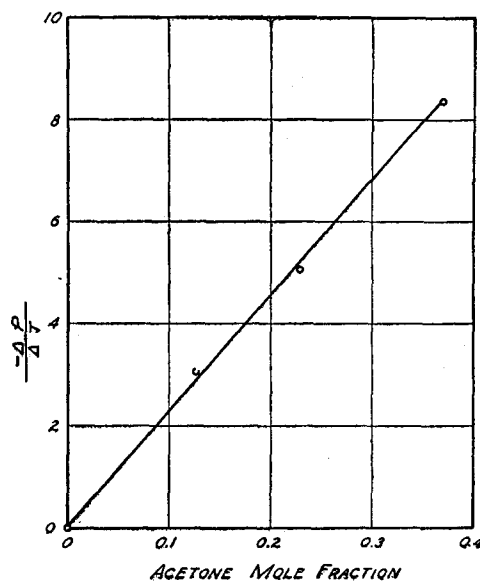
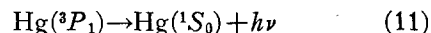


FIG. 5. Rate of polymerization induced by acetone.

(5), (6), (7) while at low pressures the sequence (9), (10) would predominate. The evidence for  $\text{C}_4\text{H}_4$  which is shown in reaction (8) is given in the paper by Gunning and Steacie.

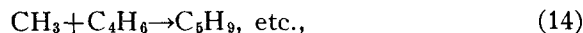
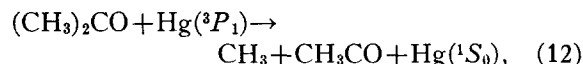
A consideration of the sequence involving hydrogen indicates that until the hydrogen pressure is built up to the point where reaction (5) can take place to an appreciable extent, the apparent polymerization rate will be low because of the formation of hydrogen gas.

Gunning and Steacie have already explained the falling off of the rate at pressures below 2 mm as caused by incomplete quenching of activated mercury atoms. Thus the reaction



can occur at low enough pressures. This appears to be an adequate explanation.

The results obtained for added acetone are comparable to those obtained by Gunning and Steacie for added hydrogen. The equations necessary are,



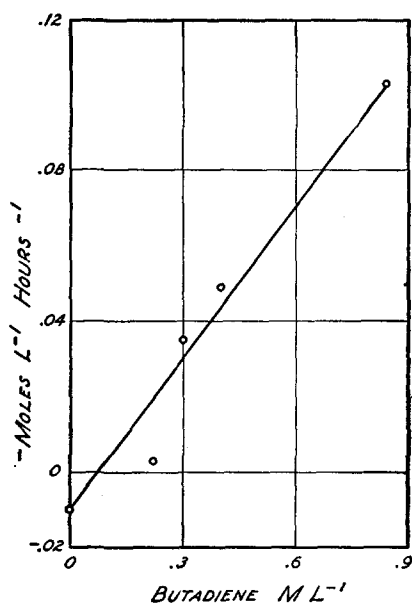


FIG. 6. The initial rate vs. the initial butadiene concentration for an initial acetone concentration of 0.23M.

Reactions (12) and (13) may be deduced from what is already known of the radicals formed from acetone.<sup>9</sup> Since only about 40 percent of the possible CO is accounted for by the uncondensed gas formed, CO may enter the polymer through such a reaction as (15). In addition to these reactions, it is quite probable that alkylation of the polymer can occur after the butadiene concentration is reduced sufficiently. The shape of curve *d*, Fig. 1, suggests such a reaction, the steepest linear portion being attributed to polymerization while the curved portion represents an alkylation of the polymer. This curved portion is much more marked than may be attributed to a reduction of incident light intensity by the deposition of polymers on the quartz surface.

Although no data on the quenching of activated mercury by acetone or butadiene are known, it might be expected that they would have comparable quenching diameter. Since their molecular weights are very close together, 54 and 58, the amount of energy transferred from mercury to either molecule would be proportional to its mole fraction. If it is further assumed that the process for the mixture may be separated into two parts, one initiated by energy transferred to butadiene

and the other initiated by energy transferred to acetone, then it is possible to calculate the part due to acetone. Table I and Fig. 5 show the results obtained.

The straight line obtained in Fig. 5 indicates that the rate of polymerization induced by acetone is directly proportional to the number of free radicals formed from acetone. This is a very interesting result as it suggests that the termination of the polymerization chain is not caused by the interaction between free radicals and that the termination step is first order with regard to free radicals. It may be observed that a similar suggestion with regard to butadiene alone has been made.<sup>4</sup>

A crude estimate of the average polymer chain length may be made from the above data. From the values of quantum yield given for acetone photolysis,<sup>7</sup> the quantum yield of free radical production from acetone may be taken as  $0.2 \pm 0.1$  for the conditions of these experiments. From the actinometric determination and from the data of Table I, the quantum yield of the acetone induced part of the reaction is calculated to be 0.8. This gives, as the number of molecules reacting per free radical, the value  $0.8/(0.2 \pm 0.1)$ , or between 3 and 8 molecules per chain as the average length.

## PART II. THE REACTION OF BUTADIENE-ACETONE MIXTURES IN HEXANE SOLUTION

Solutions of butadiene and acetone in hexane were irradiated in a quartz tube  $20 \times 250$  mm. The tube was quartz jacketed and thermostated water at  $25^\circ$  circulated through the jacket. The entire assembly fitted inside the helical mercury resonance lamp. Irradiation was carried out for 10-minute periods.

The butadiene content of the solution was determined by removing 1.00-ml aliquots and adding an excess of ICl solution in carbon tetrachloride. The solution was allowed to stand 30 minutes in the dark; an excess of 10 percent KI solution was added and the liberated iodine was titrated with 0.1N sodium thiosulfate until the  $CCl_4$  layer became colorless. It was assumed that addition occurred on all of the double bonds and that each butadiene molecule which entered into a polymerization reaction lost one double bond.

<sup>9</sup> H. H. Glazebrook and T. G. Pearson, J. Chem. Soc., 567 (1937).

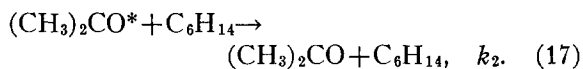
Figure 6 shows the results obtained when the initial polymerization rate is plotted against the initial butadiene concentration for a constant initial acetone concentration. The effect of varying the initial acetone concentration for a constant initial butadiene concentration is shown in Fig. 7. An apparent negative polymerization means an increase in the double bond character of the solution. This may be attributed to the fact that unsaturated molecules are formed when ketones alone are irradiated.<sup>3</sup>

### Discussion

To explain the low quantum yield of many photochemical reactions in liquid solution, Franck and Rabinowitch<sup>10</sup> have postulated that recombination of primary free radicals plays an important role. Thus when free radicals are formed in a cage of solvent molecules, if they cannot react with solvent molecules then, except for free radicals which have enough energy to escape the solvent cage, the principal reaction is a recombination of the radicals. Atwood and Rollefson<sup>11</sup> have pointed out that an equivalent concept is the formation of an activated molecule which can lose its energy by collision with solvent molecules until there is insufficient energy to break a bond, and hence free radicals are not formed. From this point of view, the initial absorption act for acetone is



The activated molecule formed may be considered to be in a state of collision with one of the 3 substances, acetone, butadiene, or hexane. Let it now be postulated that collision with hexane molecules results in deactivation,



Now when there is a possibility of reaction between the activated species and another molecule, then the collision may be considered to result in free radicals even though it is realized that at least one of the free radicals formed is instantaneously removed by reaction. If it is

<sup>10</sup> J. Franck and E. Rabinowitch, *Trans. Faraday Soc.* **30**, 120 (1934).

<sup>11</sup> K. Atwood and G. K. Rollefson, *J. Chem. Phys.* **9**, 506 (1941).

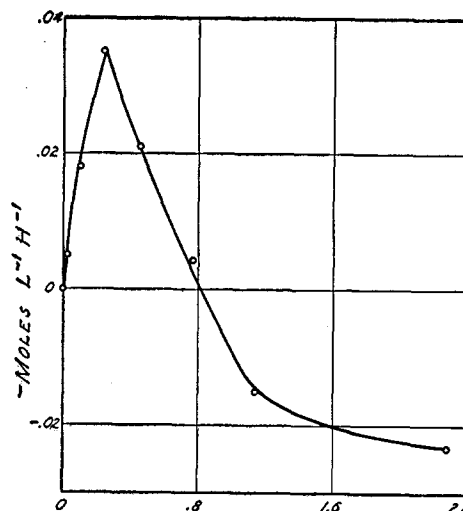
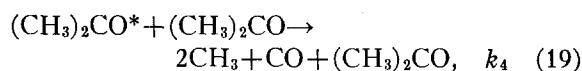
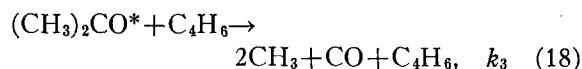
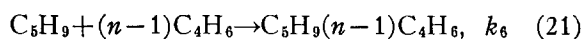
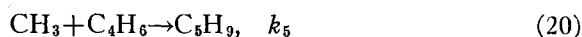


FIG. 7. The initial rate vs. the initial acetone concentration for an initial butadiene concentration of 0.30M.

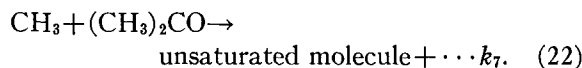
assumed that collision between activated acetone and either butadiene or another acetone molecule results in reaction, then the equations may be written



followed by,



and,



This sequence accounts for the main features of Fig. 7. The initial rise in polymerization rate with increasing acetone concentration is attributed to an increase in the amount of light absorbed. It may be calculated that a 1-cm layer of hexane solution 0.25M in acetone will absorb more than 95 percent of incident 2537Å radiation. The subsequent decrease and finally apparent negative polymerization with increasing acetone concentration can be accounted for by reaction (22) which is considered to yield unsaturated compounds. This differs from the interpre-



TABLE II. Calculated rates of polymerization.

Concentration, moles/liter		$I_{\text{abs}}/I_0$	Polymerization rate, moles/liter/hour	
Butadiene	Acetone		Experimental	Calculated
0.30	0.023	0.40	0.0052	0.016
0.30	0.091	0.86	0.018	0.028
0.30	0.23	1.00	0.035	0.035
0.30	0.45	1.00	0.021	0.026
0.30	0.68	1.00	0.0041	0.017
0.30	1.20	1.00	-0.015	0.004
0.30	2.20	1.00	-0.023	-0.035
0.00	0.23	1.00	-0.01	-0.008
0.21	0.23	1.00	+0.004	+0.021
0.30	0.23	1.00	+0.035	+0.035
0.40	0.23	1.00	+0.049	+0.049
0.84	0.23	1.00	+0.12	+0.11

tation of Norrish<sup>3</sup> that unsaturated molecules would result from interaction with hexane.

The apparent rate of polymer formation then becomes the rate at which C=C bonds are removed less the rate at which they are formed. Using the steady-state treatment for activated molecules and free radicals this becomes

$$dP/dt = nk_5[\text{CH}_3][\text{C}_4\text{H}_6] - k_7[\text{CH}_3][(\text{CH}_3)_2\text{CO}]. \quad (\text{a})$$

Let

$$[\text{C}_4\text{H}_6] = A, \quad [(\text{CH}_3)_2\text{CO}] = B, \quad [\text{C}_6\text{H}_{14}] = C.$$

Then

$$\frac{dP}{dt} = \frac{k_1 I_{\text{abs}}(nk_5 A - k_7 B)(2k_3 A + 2k_4 B)}{(k_5 A + k_7 B)(k_3 A + k_4 B + k_2 C)}. \quad (\text{b})$$

Assuming  $k_2 = k_3 = k_4$ ,  $k_5 = k_7$  and that the total concentration  $A + B + C$  is a constant, this may

be written

$$\frac{dP}{dt} = \frac{k I_{\text{abs}}}{I_0} (n[\text{C}_4\text{H}_6] - [(\text{CH}_3)_2\text{CO}]). \quad (\text{c})$$

$I_{\text{abs}}/I_0$  may be calculated from the law of Lambert and Beer,  $I_{\text{abs}}/I_0 = l - 10^{-\epsilon cl}$ . We may use for  $l$  the average length of light path or for a cylinder 20 mm in cross section take  $l = 12$  mm, the average chord length for a circle 20 mm in diameter. The value of  $\epsilon$  in hexane at 2537 Å is 8.0.<sup>12</sup> If values are assigned to  $k$  and  $n$  it is now possible to calculate the polymerization rate from Eq. (c). In Table II such a calculation has been made for the experimental points of Figs. 6 and 7. Here  $n$ , the average chain length, has been taken as equal to 4 and  $k$  has been assigned the value 0.035.

Considering the nature of the approximation involved in obtaining the final rate equation and the effective  $I_{\text{abs}}/I_0$  values, the extent of agreement obtained seems significant. It may be observed that the value of average chain length used, 4, is within the limits previously derived for the gas phase polymerization. Again no explanation for the chain breaking step is given but it is implied that it does not occur by interaction between free radicals.

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<sup>12</sup> *International Critical Tables* 5, 371 (1929).