

Calculations have been made of the activities, activity coefficients, free energies of formation, and partial molal free energies of lead and zinc bromides.

Density measurements have been made upon zinc bromide and a fifty mole per cent. solution of zinc bromide and lead bromide which may be expressed by the equations: $d^t = 3.776 - 0.000913t$ for the salt, and $d^t = 5.086 - 0.001248t$ for the solution.

The positive deviation of the results from Raoult's law has been briefly discussed.

CAMBRIDGE, MASSACHUSETTS

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The Photochemical Polymerization of Methylacetylene and Allene

BY S. C. LIND AND ROBERT LIVINGSTON

The photochemical polymerization of acetylene has been studied quantitatively by Lind and Livingston,¹ who compared the quantum yield with the ion pair yield² of the radiochemical reaction. The radiochemical work has been extended by Heisig³ to include the polymerization of a number of the simpler unsaturated hydrocarbons. The following deals with the photochemical polymerization of two of the compounds studied by Heisig, methylacetylene and its double-bonded isomer, allene.

Rate of Polymerization as a Function of Pressure

Apparatus.—In these experiments a hot mercury arc was used, and particular care was taken to prevent the contamination of the reactants by mercury vapor. The details of the reaction system and the method of operation are described in an earlier paper.⁴

The gases used were highly purified samples,³ kindly furnished by Dr. G. B. Heisig. They were further purified by low temperature distillation before use.

Reaction Products.—All of the gases studied (except ethylene) were polymerized by the action of ultraviolet light to solid (or viscous liquid) products of low vapor pressure.

The allene polymer precipitated on the walls as a smooth white film, which was either a solid or a very viscous liquid. In one experiment allene at 685 mm. pressure was radiated until the pressure had been reduced by 15.5 mm. The remaining allene was then frozen in a side tube with the aid of liquid air, and the residual pressure was found to be less than 0.2 mm. (the limit of accuracy of the manometer). This may be taken as evidence that the reaction consists of simple polymerization and that not more than 1% of the reaction involves the formation of hydrogen or methane. The polymer apparently has a higher vapor pressure than cuprene, since it can be sublimed in high vacuum by heating the reaction vessel with a direct flame (probably between 200 and

(1) Lind and Livingston, *THIS JOURNAL*, **54**, 94 (1932).

(2) Lind and Bardwell, *ibid.*, **48**, 1556 (1926); Mund and Koch, *J. Phys. Chem.*, **30**, 292 (1926).

(3) Heisig, *THIS JOURNAL*, **53**, 3245 (1931).

(4) Ref. 1, pp. 95-96 and Fig. 1.

300°). In one experiment about 90% of the polymer produced from 15.5 mm. of allene was sublimed rapidly in vacuum to one end of the reaction flask. The sublimate was yellowish in color, and, after cooling, it was found that the pressure had been increased from less than 0.2 mm. to 4.5 mm.; approximately one mole of gas was formed by heating the polymer for each three moles of allene polymerized. In another experiment 13.2 mm. of allene was polymerized, and the remaining gas pumped off. A vessel connected to the reaction system by a stopcock was filled with oxygen at a pressure of 30.0 cm. This gas was allowed to distribute itself between the vessel and the evacuated reaction system; the resulting pressure was 146.9 mm. The stopcock was closed and the pressure was observed for forty-five minutes. During that time there was no detectable change in pressure. To make sure that no oxygen had been absorbed instantaneously, the reaction system was again evacuated and the side vessel filled to the same pressure as before. The gas was allowed to distribute itself as before; the final pressure was 147.2 mm. These experiments demonstrate that if there is any reaction between the allene polymer and oxygen it is slow at room temperature.

Methylacetylene polymerized to a white substance, which appeared to be a solid. Tests for a permanent gas (methane or hydrogen) gave negative results.

Isoprene was used in a few experiments. It likewise formed a white film when irradiated by a hot mercury arc. The polymer (or condensate) of isoprene burned in air readily and was sublimed in vacuum by heating with a direct flame. The polymerization (or condensation) of isoprene was too slow,⁵ to permit the accumulation of a quantity of the reaction product sufficient for other tests.

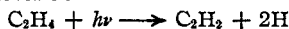
Although ethylene was not studied quantitatively it may be worth while to report at this time the results of certain qualitative experiments on its photochemical decomposition. In agreement with the results of Bates and Taylor and of Olson and Meyers,⁶ we were unable to obtain any indication of reaction when ethylene, at room temperature, was exposed to the complete radiation of a hot quartz mercury arc. However, when ethylene at 27° and at a pressure of 75 cm. was exposed, in a fused quartz vessel, to the radiation from a hydrogen arc (operating at 0.2 ampere), for one hundred and fifty minutes, the pressure decreased by 2.9 mm. and a faint white film was deposited on the walls of the reaction vessel. This film sublimed (or distilled) in vacuum when heated with a free flame. The irradiated gas was tested for acetylene with ammoniacal cuprous chloride, and gave the characteristic red precipitate. The same reagent indicated that the original ethylene contained no detectable quantity of acetylene. The observed formation of acetylene is in agreement with the results of Mooney and Ludlam,⁷ who obtained acetylene when they exposed ethylene, in a flow system, to the radiation from an aluminum spark.

Effect of Pressure.—Several experiments were performed at pressures ranging from 3.5 to 68.5 mm. but under conditions which were otherwise similar. These experiments are summarized in Table I. The values of the initial pressures are given in the second

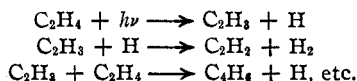
(5) It is possible that isoprene may undergo a more rapid photochemical reaction which does not involve a change in pressure or the formation of a solid or non-volatile liquid.

(6) (a) Bates and Taylor, *THIS JOURNAL*, **49**, 2458 (1927); (b) Olson and Meyers, *ibid.*, **48**, 389 (1926); (c) see, however, Berthelot and Gaudechon, *Compt. rend.*, **159**, 1169 (1910).

(7) Mooney and Ludlam, *Trans. Faraday Soc.*, **25**, 442 (1929). These authors suggest that the formation of acetylene is due to the reaction



The following mechanism seems somewhat more probable, and is consistent with the formation of compounds of higher molecular weight (which action was indicated by the precipitation of the film and the decrease in pressure).



column. The average temperatures are given in the third column. Since the temperature coefficients of these reactions were not determined, no attempt has been made to reduce the measurements to a single temperature. The observed values of the initial rate, in centimeters per minute, are given in the last column. To eliminate uncertainties introduced by the absorption of light by the film of polymer, the values of the initial rate are based upon the first 2 mm. change in pressure (except where the total change was less than this amount).

TABLE I

RATE OF POLYMERIZATION OF ALLENE			
No.	P_0 , cm.	t , °C.	V , cm./min.
1	68.5	10.5	0.029
2	36.5	9.0	.024
3	28.8	10.5	.027
4	26.9	11.6	.024
5	8.3	9.2	.017
6	3.6	9.0	.0115
Rate of Polymerization of Methylacetylene			
7	35.3	18.8	0.0120
8	20.0	20.9	.0085
9	7.0	22.1	.0060
10	3.7	18.0	.0068
11	3.6	19.1	.0082
Rate of Polymerization of Isoprene			
12	19.0	29.2	0.0021
13	11.8	26.2	.0016

To illustrate the type of pressure-time curves obtained, the detailed results of several experiments from Table I are plotted in Fig. 1. The numbers attached to the curves are the experiment numbers listed in the first column of the table. Since the temperature of the flowing water-bath sometimes varied by as much as 1.5° , it was necessary to correct the observed pressures to a constant (average) temperature, by means of the perfect gas laws. The volume of the quartz spiral manometer and the capillary connections was sufficiently small to render the effect of fluctuations in room temperature negligible.

The data of Table I are plotted in Fig. 2; the data of Table I, Ref. 1, on the polymerization of acetylene, are also represented on the plot. The form of these rate-pressure curves suggests strongly that the only effect of pressure is to change the percentage absorption and that the rate is directly proportional to the intensity of the absorbed light. This conclusion may be tested more definitely by combining the data of Table I with the results of absorption measurements (which are presented in Fig. 4). If the distribution of the energy of the absorbable light produced by the optical system used in the absorption measurements is the same as that from the horizontal arc used in the rate measurements, the assumption that the rate is

directly proportional to the intensity of the absorbed light but is otherwise independent of the pressure, leads directly to the following relation⁸

$$V = k(I_{\text{abs.}}/I_0)$$

where V is the rate, k is a factor which is a constant for each gas, and $(I_{\text{abs.}}/I_0)$ is the ratio of the intensity of the absorbed light to that of the incident light, in the absorption measurements. In Fig. 2, $k(I_{\text{abs.}}/I_0)$ is represented by a solid line, which (by adjusting k) has been made to coincide with the average value of V at a pressure of 30 cm. The agreement between the slopes of the dotted and solid lines is, in each case, close enough to afford strong support for the correctness of the assumption. The small departures may be due either to experimental error or to a difference in the energy distributions of the two sources.

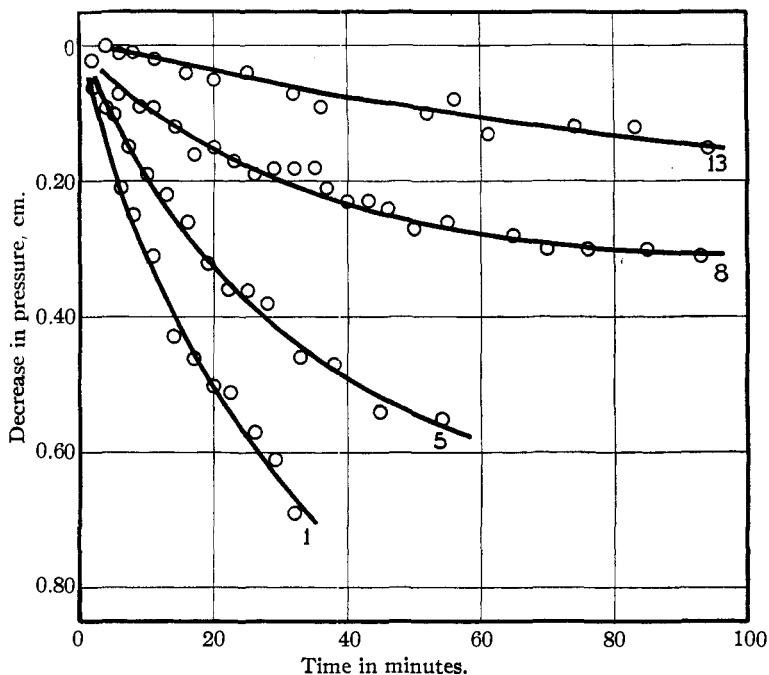


Fig. 1.—Rate of polymerization.

Determination of the Quantum Yield.—The apparatus used in these measurements was similar to that used in the determination of the quantum yield of the polymerization of acetylene, and has been described by Lind and Livingston.⁹

A few minor adjustments of the focal isolation monochromator were made in an attempt to reduce the amount of stray light of longer wave

(8) See Ref. 1, p. 98.

(9) Ref. 1, pp. 100-103.

length, but the character of the light source was essentially the same as that used in the earlier measurements.

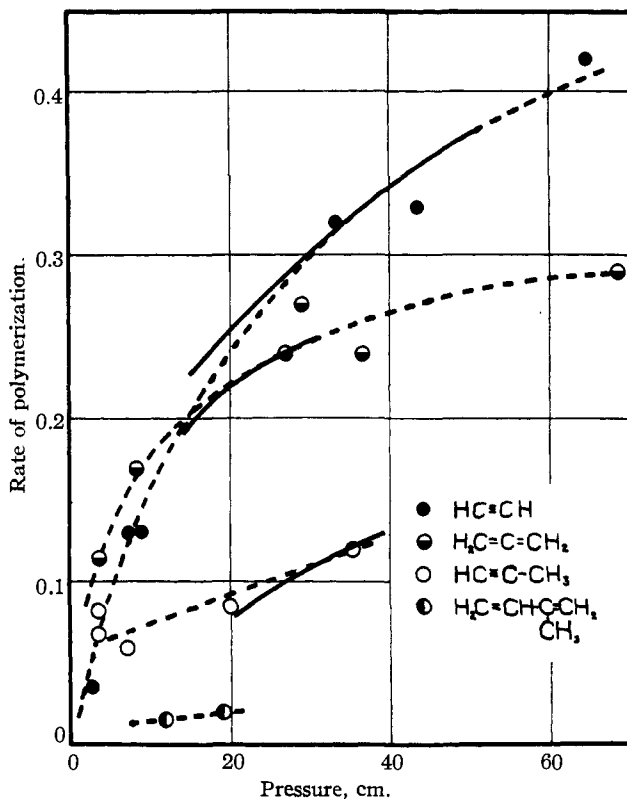


Fig. 2.—Rate of polymerization as a function of pressure.

The energy measurements were made with the same galvanometer and thermopile. The results of the calibrations, which were made during the course of the experiments, are summarized in Table II.

TABLE II
CALIBRATION OF THE THERMOPILE AND GALVANOMETER

Amperes through filaments ^a	Ergs/sq. mm. sec. ^b	Average deflection, mm.	Ergs/sq. mm. sec. per mm. deflection
0.250	4.26	264	0.01614
.300	6.27	390	.01609
.350	8.67	532	.01611

^a The current was measured with an accurate ammeter kindly furnished by the Department of Electrical Engineering of the University of Minnesota.

^b Calibration of the Bureau of Standards for flux at two meters distance from the standard lamp.

When proper allowance is made for the shunt (which was used to reduce the sensitivity during the calibrations) and for the area of the thermopile,

and corrections are applied for absorption and reflection, both by the fluorite window of the thermopile and the second window of the quartz reaction vessel, the working value of the sensitivity is 3.82 ergs/sec. per mm. deflection.¹⁰

Except for a few minor improvements in the electrical circuit the differential manometer was identical with that used in the earlier measurements. To reduce the effect of temperature fluctuations the reaction vessel and manometer were enclosed in a small box, which in turn was placed in a large air thermostat. No attempt was made to regulate the temperature during the experiments with allene, the thermostat consisting simply of a large box containing a small electric fan. While the temperature was approximately constant during each experiment, the several experiments were performed at temperatures ranging from 25 to 29°. During the experiments with methylacetylene a simple, electrically shielded thermostat was used, which kept the temperature at 25°. The differential manometer was compared, before and during the progress of the experiments, to an accurately calibrated McLeod gage, at pressures ranging from 0.7 to 0.1 mm. All of these results fitted the following semi-empirical equation within 1 or 2%.

$$\Delta P(\text{mm.}) = 3.23 \times 10^3 \frac{\Delta C}{C_2 \cdot C_1} \quad 11$$

where C_1 and C_2 are, respectively, the initial and final readings of the variable condenser.

To determine the number of quanta corresponding to the energy absorbed, it is necessary to know the average wave length of the absorbed light. This was determined approximately by comparing a spectrogram of the light emerging from the focal isolation apparatus with absorption spectrograms of allene and methylacetylene.¹² A hydrogen arc, operating at 3000 volts and 0.3 ampere, was used as a source of light. The cell used in the absorption measurements was 10 cm. long, was of fused quartz, and was provided with plane ends. Oiled process plates were used.

The following results were obtained with a small quartz spectrograph. At room temperature and at 60 cm. pressure allene completely absorbed

(10) The correction for reflection and absorption is probably uncertain by about 10%. It seems quite probable that the value, 4.40 ergs/sec. per mm., of the sensitivity used in the acetylene measurements is too high and that a better value would be 4.00 ergs/sec. per mm. This change would increase the average value of the quantum yield for acetylene polymerization from 9.2 to 10.1, but would not affect any conclusions which have been presented.

(11) Due to a misprint, the constant of the corresponding equation of Ref. 1, p. 102, reads 10^4 instead of 10^3 .

(12) Absorption spectrograms of vinylacetylene were also taken, although rate measurements were not made with this gas. At 35 cm. pressure absorption was complete at 2480 Å. and appreciable at 2540 Å. When a side tube was immersed in a solid carbon dioxide-acetone bath [see Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, **53**, 4200 (1931) for vapor pressure data] the absorption was complete at 2280 and was still appreciable at 2400 Å. The absorption was definitely banded. The sample of vinylacetylene used in these experiments was prepared from a solution of pure vinylacetylene in toluene, kindly furnished by Dr. H. W. Elly, Director of the Chemical Section, E. I. du Pont de Nemours and Company.

light of wave length shorter than 2340 Å. and showed some absorption to 2380 Å. At a pressure of 12.5 cm. the absorption was complete at 2290 Å. and was appreciable at 2370 Å. Methylacetylene at a pressure of 44 cm. showed complete absorption at 2190 Å. and appreciable absorption at 2240 Å. We have, somewhat arbitrarily, taken the average wave length of the light absorbed in the quantum yield experiments as 2200 Å. for methylacetylene and 2300 Å. for allene. The value of the energy of a quantum based on these estimates is not likely to be in error by as much as 5%.

After the completion of the rate and quantum yield measurements, a Steinheil spectrograph with two quartz prisms became available for our use. This instrument was adjusted for minimum deviation of λ 2200 Å. An iron arc was used as a reference spectrum.

Absorption spectrograms of acetylene were taken at a pressure of 45 cm., with a side tube immersed in a mixture of solid carbon dioxide and acetone. A series of sharply defined bands were obtained between 2230 and 2100 Å. These bands occur between the regions photographed by Herzberg¹³ and by Kistiakowsky.¹⁴ This is in agreement with the fact that the pressure of acetylene was intermediate to the pressures used by these investigators. Since the absorption of the fused quartz cell used in these experiments set in at about 2100 Å. it was impossible to observe bands at shorter wave lengths or to determine whether any continuous absorption was present.

No banded structure could be detected in the spectra of either allene or methylacetylene. The apparent transmission limits, while varying somewhat with the time of exposure, are in agreement with those determined with the small spectrograph. Allene was photographed at a pressure of 51 cm. and also with a side tube immersed in a mixture of solid carbon dioxide and acetone (corresponding to a pressure of about 6 cm.). The limit of transmission was about 2330 Å. for the higher pressure, about 2200 Å. for the lower. Methylacetylene was photographed at 44 cm. pressure. Cooling the side tube to -23° , which is above the boiling point of methylacetylene, had no effect whatever on its absorption spectra.

These results throw some doubt on the interpretation of the quantum yield measurements for allene and methylacetylene. The existence of a continuous absorption for allene and methylacetylene would not have been predicted, and the observation of a continuous (or quasi-continuous) absorption suggests that the observed absorption may be due to the presence of (less volatile) impurities. However, the following facts may be cited as evidence against the hypothesis that the continuous absorption is due to impurities. 1. The gases were very carefully prepared and purified³ and neither vapor pressure measurements¹⁵ nor molecular weight

(13) Herzberg, *Trans. Faraday Soc.*, **27**, 378 (1931).

(14) Kistiakowsky, *Phys. Rev.*, **37**, 276 (1931).

(15) Livingston and Heisig, *THIS JOURNAL*, **52**, 2409 (1930); also Heisig, unpublished work.

determinations gave any indication of the presence of impurities. 2. An impurity if present was apparently not light sensitive, since there was no change in rate of polymerization during the course of an exposure (other than that observed in the preliminary experiments due to the formation of an opaque film of polymer on the window.) 3. The products of polymerization of the two compounds were apparently identical, and there was never (in either preliminary or final measurement) any detectable quantity of bromine formed.¹⁶ 4. The observed absorption limits and the total absorption of methylacetylene and acetylene differ by only 10%. 5. Immersing a side tube of the absorption cell in a low temperature bath did not affect the absorption spectra of methylacetylene at all, and only shifted the absorption limit of allene to an extent comparable with its reduction in pressure.

The answers to the questions raised here must await the development of new methods of preparation of these gases or of more certain methods for their purification. A comparison of the ion pair and quantum yields of acetylene with those of methylacetylene and allene indicates that if an impurity were present (in the latter two) and if it had any effect on the results, it must have been acting as an internal filter, not as a sensitizing agent.

The procedure followed and the precautions observed in the final series of rate measurements were similar to those discussed by Lind and Livingston.¹⁷ To illustrate the type of pressure variations obtained, the detailed

TABLE III
DETERMINATION OF THE QUANTUM YIELD OF ALLENE

No.	<i>P</i> , mm.	Δp , mm.	<i>t</i> , min.	Ergs/sec. absorbed	Quanta absorbed $\times 10^{-17}$	Molecules reacted $\times 10^{-17}$	<i>M/Q</i>
1	316	0.270	33	980	2.25	6.4	2.8
2	313	.380	60	935	3.9	9.0	2.3
3	285	.481	50	990	3.5	11.3	3.2
4	216	.305	60	830	3.5	7.2	2.1
5	209	.294	50	775	2.7	6.9	2.6
6	204	.278	60	830	3.5	6.6	1.9
Average							2.5

Determination of the Quantum Yield of Methylacetylene

7	386	0.131	60	245	0.99	3.35	3.4
8	371	.141	100	150	1.03	3.6	3.5
9	371	.096	100	140	0.92	2.5	2.7
10	233	.130	72	175	.84	3.3	3.9
11	162	.129	70	175	.82	3.3	4.0

Average 3.5

(16) The method of preparation of allene (3) would suggest that the most probable impurity would be dibromopropene. It should be noted, however, that a halide was not used in the preparation of methylacetylene.

(17) Ref. 1, pp. 104-105.

results of several experiments are plotted in Fig. 3. The readings of the variable condenser are plotted against time in minutes. The numbers on the curves are the experiment numbers of Table III.

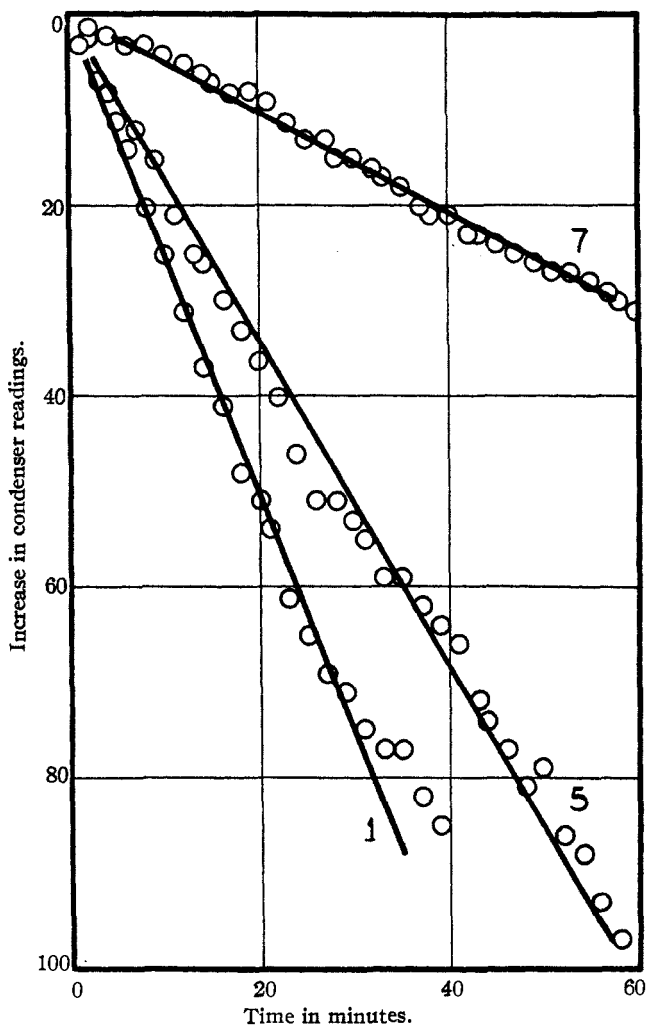


Fig. 3.—Rate of polymerization.

The percentage absorption of light by allene and by methylacetylene, in the reaction vessel and at the pressures used in the rate measurements, was determined in separate series of measurements. These experiments are summarized in Fig. 4. The percentage of the transmitted light absorbed is plotted against the pressure of the gas. The corresponding results for acetylene¹⁸ are also represented in this figure. It is interesting to note that

(18) Ref. 1, Fig. 6.

both in the total absorption of the light from the focal isolation apparatus, and in the limits of absorption indicated by the spectrograms, methylacetylene is similar to the structurally related acetylene, but differs widely from its (double-bonded) isomer, allene.

The results of six determinations of the quantum yield of the polymerization of allene and five of that of methylacetylene are summarized in Table III.

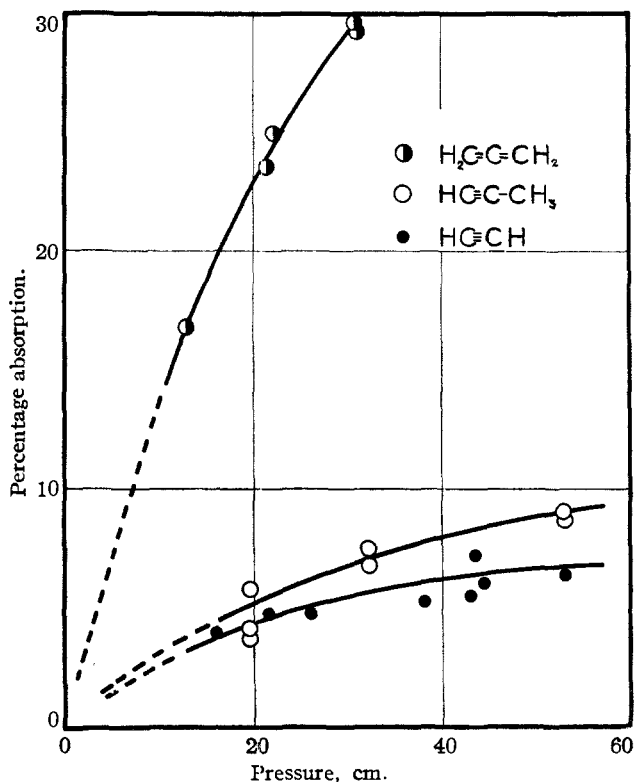


Fig. 4.—Absorption as a function of pressure.

The pressures listed in column two are the initial pressures of the reacting gas. The total change in pressure in millimeters is given in column three, and the corresponding decrease in number of gas molecules ($\times 10^{-17}$) is given in column seven. The duration of the experiments in minutes is given in column four. The average energy of the absorbed light in ergs per second is given in column five. These values are based upon measurements of the energy of the transmitted light, made at fifteen-minute intervals during the course of each experiment, and upon the percentage absorption data recorded in Fig. 4. The total number of quanta absorbed ($\times 10^{-17}$) is given in column six. The quantum yield is given in the last column.

It is apparent that, within the limits of experimental error, the quantum yield is not dependent either upon the pressure of the gas or upon the intensity of the absorbed light.

In Table IV the average values of the quantum yields are compared to the ion pair yields for the four polymerization reactions which have been studied, with both forms of activation. The formula of the gas polymerized is given in the first column. The quantity listed in the last column is the ratio of the ion pair yield to the quantum yield.

TABLE IV

COMPARISON OF ION PAIR YIELD TO QUANTUM YIELD FOR POLYMERIZATION REACTIONS

Gas polymerized	M/N	M/Q	$(M/N)/(M/Q)$
$\text{HC}\equiv\text{CH}$	18 ⁸	10.1 ¹⁹	1.8
$\text{HC}\equiv\text{CCH}_3$	8.3 ⁹	3.5	2.4
$\text{H}_2\text{C}=\text{C}=\text{CH}_2$	10.4 ⁸	2.5	4.2
$(\text{CN})_2$	7.4 ²⁰	3 ²¹	2.5

The only regularity which is apparent from these data is that the quantum yield is never greater than the ion pair yield. This same relation has been found to hold for all other reactions which have been studied both radiochemically and photochemically. It would not be justifiable to place too much emphasis on the exact value of the ratio $(M/N)/(M/Q)$. It is difficult to estimate the probable error of the absolute value of M/N , but it is probably about 10%. Due to possible uncertainties in the energy measurements,²¹ the probable error of the absolute value of M/Q may be as great as 20 or 30%. In addition to the uncertainty in the values of the ratios, it must be remembered that in the cases of allene and methylacetylene the products of reaction are apparently different for the photo and radiochemical reactions. It is also quite probable that the values of the ratio are functions of temperature. The effect of temperature has been studied only in the case of acetylene, but in that case the ion pair yield is independent of temperature, from 0 to 100°,² while the photochemical reaction has a ten degree temperature coefficient of 1.25.²²

While this paper was in proof, it came to our attention that Berthelot ("Notice sur les travaux scientifiques de M. Daniel Berthelot," Paris, 1917, p. 130) had previously reported that methylacetylene polymerized under the influence of light to a white solid. This reference is quoted by Dahr ("The Chemical Action of Light," London, 1931, p. 303); we have not yet obtained access to the original.

In conclusion we wish to express our appreciation of the assistance of Savetta L. Livingston in the performance of the quantum yield measure-

(19) Lind, Bardwell and Perry. *THIS JOURNAL*, **48**, 1556 (1926).(20) Hogness and Liu-Sheng Ts'ai, *ibid.*, **54**, 123 (1932).(21) See Leighton, *J. Phys. Chem.*, **36**, 1882 (1932).

(22) Ref. 1, pp. 98-99.

ments, and of Henry M. Davis and Dr. George Glockler in the adjustment of the Steinheil spectrograph.

Summary

1. Both allene and methylacetylene are polymerized to white solids when they are exposed (separately) to ultraviolet light.
2. The results of Mooney and Ludlam on the photolysis of ethylene have been confirmed.
3. Qualitative determinations of the long wave length limit of absorption for allene, methylacetylene and vinylacetylene have been made.
4. The quantum yield for the polymerization of allene is 2.5; for methylacetylene, 3.5. For both reactions the quantum yield is independent of the pressure and of the intensity of the absorbed light.
5. A comparison of quantum yields to ion pair yields has been made for four polymerization reactions.

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Extra Specific Heat in Cuprous Sulfide; Specific Heat of Ferrous Oxide

BY WALTER P. WHITE

Determinations of the specific heat of cuprous sulfide up to 900° have shown a region of abnormally high specific heat at 300° and above, where there is no corresponding crystallographic change of state. Since such variations in specific heat are of recent discovery and are now being studied in various substances, it seems desirable to publish the data. Along with them are given two specific heats of ferrous oxide, determined, apparently, for the first time.

Method and Apparatus

The method is the "dropping" method, with a water calorimeter. The furnace was practically the same as reported on in 1921,¹ platinum wound on a thin-walled alundum tube of 28 mm. inner diameter, and 30 cm. high. At that time there were vertical gradients of 30° in 12 cm. at 900° and a difference of 8° between the specimen and the thermocouple junction immediately beside it. In the present case similar differences were reduced to 2°.

The chief agent in this improvement was a separately heated plug in the furnace bottom, which was disconnected just before being dropped out to make way for the specimen. Since the maximum temperature was only 900° this plug could be more easily made and preserved than in some previous work, where 1400° was reached. A description of this plug will be published elsewhere.

(1) Latent heats of melting of nickel and monel metal, White, *Chem. Met. Eng.*, **25**, 17 (1921).