

The Chain Photolysis of Acetaldehyde in Intermittent Light

W. L. Haden Jr. and O. K. Rice

Citation: [The Journal of Chemical Physics](#) **10**, 445 (1942); doi: 10.1063/1.1723746

View online: <http://dx.doi.org/10.1063/1.1723746>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/10/7?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[The Photolysis of Acetaldehyde](#)

J. Chem. Phys. **21**, 748 (1953); 10.1063/1.1699002

[The ChainBreaking Process in Acetaldehyde Photolysis](#)

J. Chem. Phys. **18**, 993 (1950); 10.1063/1.1747831

[Erratum: The Chain Photolysis of Acetaldehyde in Intermittent Light](#)

J. Chem. Phys. **12**, 521 (1944); 10.1063/1.1723904

[Note on the Chain Photolysis of Acetaldehyde in Intermittent Light](#)

J. Chem. Phys. **9**, 377 (1941); 10.1063/1.1750912

[Note on the Chain Photolysis of Acetaldehyde in Intermittent Light](#)

J. Chem. Phys. **8**, 998 (1940); 10.1063/1.1750616



The Chain Photolysis of Acetaldehyde in Intermittent Light¹

W. L. HADEN, JR.,² AND O. K. RICE

University of North Carolina, Chapel Hill, North Carolina

(Received April 6, 1942)

(1) By comparison of the data on the photochemical decomposition and the azomethane-induced decomposition of acetaldehyde vapor, it has been concluded that the chain-carrying steps in the two cases are different. For the photolysis the following mechanism is suggested:

- (1) $\text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_3 + \text{CHO}$,
- (2) $\text{CHO} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO} + \text{CHO}$,
- (3) $\text{CHO} + \text{CH}_3 \rightarrow \text{stable products (chain-ending)}$,
- (4) $\text{CHO} \rightarrow \text{stable products (chain-ending)}$.

(There are possibly other chain-ending steps similar to reaction (3)). (2) Experiments have been performed using intermittent light at 200° and 300°. As a result of these

experiments, estimates have been made for the individual rate constants, k_2 , k_3 , and k_4 , and it has been found that the activation energies are 2.6, 11.3, and 7.8 kcal., respectively.

(3) It has been found that k_2 and k_3 check closely with the collision number multiplied by the appropriate Arrhenius factor. There is little or no evidence of necessity for mutual orientation of the molecules. The significance of this has been discussed. Reaction (4) probably takes place at the walls, and the value of k_4 is of the same order of magnitude as the fraction of the molecules hitting the walls per second, times the appropriate Arrhenius factor. (4) The extent of and effect of diffusion of radicals beyond the illuminated region have been considered.

SOME years ago it was suggested to one of us by Dr. D. V. Sickman that the use of intermittent light, obtained by means of a rotating sector, would yield valuable additional information on the photolysis of acetaldehyde.³ It is the purpose of the present paper to present some results of this sort, the continuation of experiments recently reported in a preliminary note.⁴ The theory of the effect of intermittent light, which it will be necessary to apply, has been fully set forth in the preceding article.⁵

1. MECHANISM OF THE PHOTOLYSIS

It has been found that at elevated temperatures (between about 150° and 300°C) the rate of photolysis of acetaldehyde is proportional to

the square root of the light absorbed per unit volume per unit time, I_{abs} , and to the pressure of acetaldehyde.⁶ Grahame and Rollefson^{6b} have noted that at low light intensities there appear to be deviations from the square root law, and we shall later see that such deviations are of some importance, but as a rough approximation to the experimental facts the above statement will suffice for the present. A number of mechanisms can be, and have been, written down which reproduce this rate law. Some of them, however, can be eliminated by other considerations. It seems to be necessary to go into these matters in some detail, in order to be able to interpret the experimental results we have to present.

All the mechanisms which have been proposed conform to the general type represented by reactions (1)–(3) of the preceding article.⁵ One of the most commonly suggested mechanisms is the following:

- (1) $\text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_3 + \text{CHO}$,
- (2) $\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}$,
- (2') $\text{CH}_3\text{CO} \rightarrow \text{CH}_3 + \text{CO}$,
- (3) $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$.

The CHO radical is supposed to break up as

¹ Presented in part at the Symposium on Elementary Reactions, Division of Physical and Inorganic Chemistry, American Chemical Society, Atlantic City meeting, September, 1941. We wish to acknowledge the contribution of E. P. H. Meibohm, who constructed a considerable portion of the apparatus (Master's Thesis, University of North Carolina, 1938), and G. W. Murphy, who made some of the runs at 300° and assisted in other ways.

² Eastman Kodak Company Fellow, 1939–1940. Present address: Columbia Chemical Division, Pittsburgh Plate Glass Company, Barberton, Ohio.

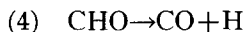
³ For other examples of the use of the rotating sector or other methods to measure lifetimes of atoms or radicals see F. Briers and D. L. Chapman, *J. Chem. Soc.*, p. 1802 (1928); H. W. Melville, *Proc. Roy. Soc. A* **163**, 511 (1937); E. A. B. Birse and H. W. Melville, *ibid.*, **A175**, 164, 187 (1940); T. T. Jones and H. W. Melville, *ibid.*, **175**, 392 (1940).

⁴ W. L. Haden, Jr., E. P. H. Meibohm, and O. K. Rice, *J. Chem. Phys.* **8**, 998 (1940).

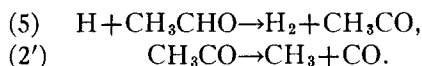
⁵ O. K. Rice, *J. Chem. Phys.* **10**, 440 (1942).

⁶ (a) J. A. Leermakers, *J. Am. Chem. Soc.* **56**, 1537 (1934); (b) D. C. Grahame and G. K. Rollefson, *J. Chem. Phys.* **8**, 98 (1940). References 6a and 6b, though agreeing in outline, disagree in detail. The latter gives faster rates and lower activation energy. See also (c) E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, p. 890 (1936).

follows:



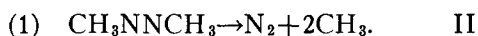
followed by



Thus each CHO becomes effectively converted into CH₃, which is the chain carrier. Reaction (2) is the rate determining step, but the CH₃ concentration is determined by reactions (1) and (3). The rate is given by Eq. (2) of the preceding article, B now being CH₃CHO.

The above mechanism is essentially the same as that proposed for the decomposition of acetaldehyde as induced by the admixture of a small amount of azomethane, at temperatures at which azomethane decomposes but acetaldehyde alone does not.⁷

Reaction (1) is replaced by the following:



Reactions II (2), (2'), and (3) are the same as the corresponding reactions in scheme I, and reactions (4) and (5) are, of course, missing, since no CHO radical ever appears. This leads to the rate law

$$-d(\text{CH}_3\text{CHO})/dt = (k_2 k_1^{1/2}/k_3^{1/2})(\text{CH}_3\text{CHO})(\text{CH}_3\text{NNCH}_3)^{1/2},$$

which agrees with the observations. If we are correct, as is almost certainly the case,⁸ in assuming that the decomposition of azomethane produces methyl radicals, then it is difficult to imagine any other mechanism which will conform to a rate law of this type and at the same time give CO and CH₄ as the principal products of the decomposition.

If we accept this conclusion, however, it at once becomes apparent from a comparison of Leermakers' data on the photochemical decomposition and Allen and Sickman's on the azomethane-induced decomposition, that mechanism I for the photochemical decomposition is hardly tenable.

Before attempting to discuss this matter, however, it will be well to consider the value of

⁷ A. O. Allen and D. V. Sickman, *J. Am. Chem. Soc.* **56**, 2031 (1934).

⁸ T. W. Davis, F. P. Jahn, and M. Burton, *J. Am. Chem. Soc.* **60**, 10 (1938).

k_1 for the photochemical reaction. Experiments by Gorin⁹ showed that it is possible to remove radicals formed by light if a small pressure of iodine vapor is present. Methyl radicals combine with iodine to give CH₃I, and formyl radicals apparently react with each other to give H₂CO and CO. The iodine atoms released apparently recombine without further action. From analyses of the products formed in such experiments, Gorin found that about 0.7 of the molecules which absorbed light at 3130Å, formed radicals (i.e., $k_1=0.7$). These experiments have been repeated by Blacet, Heldman, and Loeffler,¹⁰ who found $k_1=0.20$, which does not agree well with the value of Gorin. Their results also disagree in some other respects from those of Gorin.* We shall, however, use Gorin's value. For k_1 for the azomethane-induced reaction we take Ramsperger's¹¹ value for the rate constant of azomethane at 300°, namely, 3×10^{-4} sec.⁻¹. The data of Leermakers and Allen and Sickman, then, indicate that $k_2/k_3^{1/2}$ is almost 3 times as great for the photochemical reaction as for the induced reaction. This means that, if the acetaldehyde pressure and the rates of production of free radicals are the same in the two cases, the photochemical reaction goes almost 3 times as fast, and this factor is about doubled at 200°. It appears probable from Grahame and Rollefson's and Gorin's data that the results would be practically unchanged for the photochemical decomposition at shorter wave-lengths (2500–2700Å). If Grahame and Rollefson's data had been used throughout instead of Leermakers' data, however, the photochemical reaction would have appeared relatively even faster; use of Blacet, Heldman, and Loeffler's data to determine k_1 would also have made the value of $k_2/k_3^{1/2}$ for the photochemical reaction relatively still larger both at 3130Å and 2650Å, though if we use their values of k_1 the resulting values of $k_2/k_3^{1/2}$ show considerable discrepancy as between

⁹ E. Gorin, *Acta Physicochimica* **9**, 681 (1938).

¹⁰ F. E. Blacet, J. Heldman, and D. Loeffler, paper presented to Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City, September 1941 (*J. Am. Chem. Soc.* **64**, 889, 893 (1942)).

* In particular they believe CHO to react with I₂. In view of our conclusions below, and the fact that I₂ seems to stop any chain, this may seem to be a more probable disposition of the formyl radicals.

¹¹ H. C. Ramsperger, *J. Am. Chem. Soc.* **49**, 912 (1927).

the two wave-lengths, a situation which is difficult to understand. In any event, it seems fairly certain that, under similar conditions, the photochemical reaction goes considerably faster than the azomethane-induced reaction, which is the point which we wish to establish at this time, and from which we shall shortly draw certain conclusions concerning the reaction mechanism.¹²

The values of $E_2 - \frac{1}{2}E_3$ [where E_2 and E_3 are the energies of activation for reactions (2) and (3)] are, for the photochemical reaction and induced reaction, approximately 10 and 14 kcal. per mole, respectively. The slower reaction thus has the higher activation energy, as is to be expected. The Arrhenius factor $\exp [-(E_2 - \frac{1}{2}E_3)/RT]$ is about 30 times as small at 300°C for the induced reaction as for the photochemical reaction, so that the difference in the reaction rates is considerably less than would be expected from the activation energies.

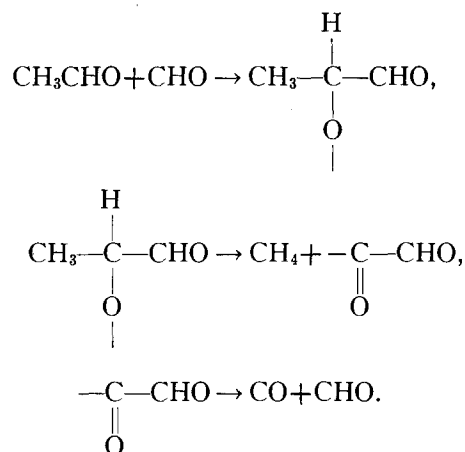
It has been recognized that the difference in activation energies indicates that the two chain mechanisms must differ in some respect. It has been suggested that the presence of the formyl radicals in the photochemical reaction gives a chain-breaking step involving the reaction or recombination of a methyl radical with a formyl radical, which cannot occur in the induced reaction. That this happens is altogether probable, but it is clear that the introduction of a new chain-breaking step can hardly make the photochemical reaction go *faster*. This can be explained only by a new chain-carrying mechanism.

Although it has been frequently supposed that reaction I (4) takes place very readily, evidence has been presented by Burton¹³ that CHO radicals are stable up to 100°, and it seems quite likely that they will be stable up to higher temperatures. This suggests the possibility that the new chain-carrying step in the photochemical reaction involves the formyl radicals. If they react with the acetaldehyde faster than the CH₃'s, then, as has already been suggested by one of us,¹⁴ the CHO radical will be the principal

chain carrier when it is present. The following mechanism appears probable:

- (1) $\text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_3 + \text{CHO}$,
- (2) $\text{CHO} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO} + \text{CHO}$,
- (3) $\text{CHO} + \text{CH}_3 \rightarrow \text{stable products}$, III
- (3') $2\text{CHO} \rightarrow \text{stable products}$,
- (3'') $2\text{CH}_3 \rightarrow \text{stable products}$.

The exact method by which reaction (2) proceeds is not important for the kinetic analysis of this mechanism, as long as a new CHO is always produced. It may occur in steps, and the following sequence is a possibility:



It may also be possible, as suggested in a private communication by Dr. M. Burton, that the CHO radical, because of its magnetic moment, induces a predissociation in an excited acetaldehyde molecule. He believes that this may be an example of a rather large class of reactions, in which the chain carrier may be a free radical or other molecule with a magnetic moment (e.g., NO or O₂).¹⁵

We shall assume in dealing with the photolysis of acetaldehyde that the mechanism is represented in its essential features by III, though it is not possible to assert unequivocally that all other conceivable mechanisms are excluded. It has been suggested, for example, that hydrogen atoms may take part in the chain. But if this is the case, it is difficult to find a suitable chain-

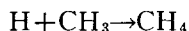
¹² Our calculation may be compared with the calculation of M. Burton, H. A. Taylor, and T. W. Davis, J. Chem. Phys. **10**, 146 (1942), which is for 2650Å, is based on earlier work of G. K. Rollefson and D. C. Grahame, J. Chem. Phys. **7**, 775 (1939), and is for a value of $k_1 = 0.184$.

¹³ M. Burton, J. Am. Chem. Soc. **60**, 212 (1938).

¹⁴ See p. 1540 of reference 6a.

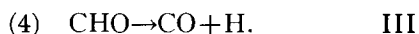
¹⁵ See H. A. Taylor and M. Burton, J. Chem. Phys. **7**, 417 (1939).

breaking step. Such a chain-breaking step as



would be allowable in this case, but it appears most likely that this would require a third body. If this third body is an acetaldehyde molecule, as it would have to be, the rate of reaction would be proportional to $I_{\text{abs}}^{\frac{1}{2}}(\text{CH}_3\text{CHO})^{\frac{1}{2}}$ instead of $I_{\text{abs}}^{\frac{1}{2}}(\text{CH}_3\text{CHO})$ as observed. Burton¹³ has given evidence that hydrogen atoms do not appear in the primary step.

There thus seem to be reasons to consider that mechanism III is the actual mechanism in the photochemical case. We may, however, anticipate at this point, and note that the results of our experiments indicate that this mechanism does still need some modification, which is unimportant at 200°C and high light intensities, but fairly appreciable at low light intensities and at 300°. What is indicated is the presence, also, of an unimolecular chain-breaking step. This is anticipated by the remark of Grahame and Rollefson to the effect that at low light intensities the rate appears to fall below the expected value. They attributed this effect to a chain-ending process at the walls, and the considerations of Section 6 below make it appear quite probable that this interpretation is correct. Though the CHO radical may be fairly stable, it would not be at all surprising if, to a limited extent and especially at the walls, it did undergo direct decomposition according to the reaction



This was postulated in mechanism I. There it was supposed that the hydrogen atoms reacted in such a way as to produce eventually a methyl radical. Since it appears that CH_3 reacts much more slowly with acetaldehyde than CHO, this would mean that reaction (4) would be essentially a chain-breaking step. However, if reaction (4) takes place at the walls, it is more than likely that the hydrogen atoms are adsorbed, later to appear as hydrogen molecules.

It is, of course, not possible to decide definitely between the various chain-breaking steps suggested in mechanism III. For the purpose of discussion, we shall assume reaction III (3) to be the principal one, with reaction III (4) playing a subsidiary but rather important role. We shall

also assume that the concentrations of CH_3 and CHO are equal, which can only be strictly true, of course, under conditions such that III (4) is negligible, unless the methyls also disappear at the wall to the same extent as the formyls. Otherwise, there would be a tendency for CH_3 to accumulate until finally reaction III (3'') occurred to a sufficient extent to stop further accumulation. An increase in concentration of CH_3 , if neglected in the calculations, would show up in an apparent increase in k_3 . The extent and accuracy of our results, however, do not warrant the attempt to iron out all minor inconsistencies in the mechanism, and the assumptions we choose apparently make up a reasonably good working hypothesis.

It is to be noted that reaction III (1) produces but one CHO radical and reaction III (3) destroys but one. In this way they differ from reactions (1) and (3) of the preceding paper. This will be corrected for if in all formulas we substitute $k_1/2$ for k_1 and $k_3/2$ for k_3 . In particular we have

$$b = t_i(K_s + k_2\gamma)(k_3^{\frac{1}{2}}/k_2)k_3^{\frac{1}{2}} \quad (1a)$$

and

$$\gamma = k_4/2k_3. \quad (1b)$$

2. EXPERIMENTAL PART

Preparation of Acetaldehyde

The acetaldehyde used was prepared from Eastman paraldehyde which had been fractionated through a long vacuum jacketed silver column. The paraldehyde was depolymerized by the addition of a few drops of dilute sulfuric acid, and the operation was carried out in the kettle of the same fractionating column. Thus the acetaldehyde was fractionated as it was formed. Because of the low boiling point (20.2°) of acetaldehyde, it was necessary to run ice water through the condenser, and to cool the portion of the reflux system not enclosed in the vacuum jacket to prevent superheating of the vapor. The latter operation was satisfactorily done by wrapping with cloth and saturating the cloth occasionally with acetone, thus cooling by evaporation.

The acetaldehyde was collected in a reservoir, which was sealed to a vacuum line after cooling the acetaldehyde to a safe point. It was then distilled back and forth between traps on the line, in order to remove any dissolved air and was occasionally distilled later to remove any polymer which might have formed.

According to Letort¹⁶ the thermal decomposition of acetaldehyde is very sensitive to traces of air. It is probable

¹⁶ M. Letort, J. Chim. Phys. **34**, 265 (1937).

that this is true of the photochemical reaction, also. We believe, however, that in the experiments reported any effect of traces of air has been eliminated. Our procedure was to make several runs with the same sample of acetaldehyde, and the total amount of decomposition was never over a few percent. Between runs the acetaldehyde was frozen out in a liquid-air trap and all permanent gases were pumped off. The results obtained in such a series of experiments were generally quite consistent, except for the first one, which was likely to be high. We attributed this to a trace of air remaining in the acetaldehyde and always discarded this preliminary run, at least in the later series of experiments.

The Reaction System

The reaction system consisted of a quartz cell 9.9 cm long and 2.43 cm in diameter, which was connected to the rest of the system by a Pyrex quartz seal. The acetaldehyde reservoir was connected to the reaction cell through a mercury cut-off. On the other side of the reaction cell was a manometer, a trap for freezing out the acetaldehyde, and another mercury cut-off. Beyond the second cut-off was the analytical apparatus, which has been described elsewhere.¹⁷ The cell was placed in the center of a fairly large furnace, the temperature of which was controlled by automatic regulation. The temperature was measured by an iron-constantan thermocouple which was calibrated from the cooling curve of tin. The temperatures given are probably correct to within $\pm 2^\circ$, but the variation of temperature during a run, or between runs made close together, was almost always considerably less than 1° .

The Optical System

The source of ultraviolet light was a capillary high pressure mercury arc of the type described by Daniels and Heidt.¹⁸ This was enclosed in a water-cooling jacket made of Pyrex tubing, and the leads from the arc were passed through a rubber stopper at the top of the tube. The water was introduced at the bottom of the tube, and there was a large outlet near the top. A small heating coil, consisting of about six turns of No. 24 Chromel wire was placed at the lower end of the arc to heat the mercury and start the arc, and the cooling water was turned on as soon as the arc flashed. In order to allow free transmission of the 3130 Å line, a small hemisphere about 1 cm in diameter was blown on the Pyrex jacket opposite the arc. This acts both as a thin glass window and as a lens when the water is run through, focusing the light to a considerable extent. The light was further collimated by a fused quartz lens which rendered it nearly parallel or only slightly divergent at the reaction cell. The light was then passed through 1.55 cm of a 0.001 *M* solution of K_2CrO_4 in 0.05 *M* KOH and a Correx red-purple A filter 3 mm in thickness. This combination gives fairly good purity of radiation near 3130 Å, but

transmits a small amount of visible light, which does not affect the acetaldehyde.

The light then entered the reaction cell, which had plane fused quartz windows. Over the window near the light source was placed a diaphragm with an opening 1.35 cm in diameter to prevent light striking the sides of the cell.

The measurement of light intensity was carried out by means of a Weston photronic cell, type 2, with a quartz window. The photo-cell was used only as a qualitative indicator of light intensity, and to maintain the intensity constant over a series of runs. Absolute intensities were calculated, by comparison with Grahame and Rollefson's results, from the rate of reaction in continuous light.

The rotating sector consisted of a cardboard disk from which a section of 90° was cut. From another sector four symmetrical sections of 22.5° each were cut. The disk was mounted on a ball-bearing shaft and was driven by a belt from a friction drive stirring motor. The speed could be varied by adjusting the friction disk on the motor, or by use of a rheostat in series with the motor. The speed was measured stroboscopically.¹⁹

Experimental Procedure and Errors

After the lamp had been lit and had come to a steady condition, and the optical system had been adjusted, a photo-cell reading was made, the light beam was intercepted by a shutter, and the acetaldehyde was admitted to the reaction cell. When the acetaldehyde was in the cell, the shutter was removed from the light path, and the cell was illuminated. Generally this illumination lasted between one and ten minutes. At the end of the run the light beam was interrupted, liquid air was placed on the trap, and the gas drawn through the trap to the analytical apparatus,¹⁷ after which another photo-cell reading was made. The gas was first brought into contact with a pellet of moist KOH to remove any traces of acetaldehyde which might have escaped through the liquid-air trap. The pressure of the remaining permanent gas, consisting chiefly of CO and CH_4 , was then measured in a previously calibrated volume, and the room temperature was noted.

The runs were always made in pairs, and a run with intermittent illumination was compared with an immediately following or preceding run with continuous light (or the average of both), performed under conditions as nearly similar as possible. In any given series of runs in which the optical set-up remained unchanged, the results were generally very reproducible. When it became necessary to replace a lamp, necessitating refocusing, the same deflection on the galvanometer attached to the photo-cell as previously used resulted frequently in a different rate of reaction. The reproducibility in this respect seemed less good at 300° than at 200° , and at 300° variations in rate amounting in the extreme to 25 or 30 percent were found. On one occasion at 300° , when the experiments were running quite smoothly, it was found that a new sample of acetaldehyde gave a 25 percent increase in rate without any change in the optical system, but, unfortunately, the lamp stopped

¹⁷ W. L. Haden, Jr., and E. S. Luttrupp, *Ind. Eng. Chem., Anal. Ed.*, **13**, 571 (1941).

¹⁸ F. Daniels and L. J. Heidt, *J. Am. Chem. Soc.* **54**, 2381 (1932).

¹⁹ See A. Farkas and H. W. Melville, *Experimental Methods in Gas Reactions* (Macmillan, 1939), p. 241.

after one preliminary (discarded) run, one continuous run, and one intermittent run were made, so this could not be further checked. In spite of these variations in individual rates, the ratio of the rate in intermittent light to that in continuous light was extremely reproducible.

If one seeks possible causes for the lack of reproducibility observed, he finds it rather difficult to understand. It is true that if the light is somewhat differently focused from time to time the illuminated volume will vary. If a given total amount of light falls on the system, an increase in the illuminated volume will decrease the light intensity as much as it increases the amount of gas illuminated. However, with the rate depending approximately on the square root of the light intensity, it is seen that the decrease in intensity is not as important as the increase in volume of gas reached. Now our optical system was by no means ideal as regards the matter of having a known and constant illuminated volume, but an increase in rate of 25 percent would require an effective increase in illuminated volume of more than 50 percent, and this amount of variation we believe to be considerably larger than could have occurred. Furthermore, our results indicate that the chain lasted long enough for free radicals to diffuse to an appreciable extent toward the wall, which effect would tend to equalize the effective volumes. If the cell were completely filled with radicals it would not matter where they were formed, and the situation would be equivalent to illuminating the entire cell with light of lower intensity. Unfortunately, this ideal condition could not be realized, either, in the most important series of experiments.

On the other hand, if we are to refer the observed error to the photo-cell, it must be noted that to explain a 25 percent variation in rate, again a 50 percent variation in intensity is necessary. That the photo-cell should vary in sensitivity by such a factor because of slight changes in the position of the light beam also seems unlikely.

In general, resetting of the optical system was accompanied by the introduction of a new sample of acetaldehyde. It seems difficult to believe that our acetaldehyde could have varied sufficiently to give 25 percent difference in rates, although it may be sensitive to such things as small amounts of polymer which might be present. As stated before, we believe we eliminated any oxygen.

In handling the results, our procedure has been to assume that the observed rate is a better measure of the intensity than the photo-cell readings. Whether or not this is justifiable, it leads to excellent correlation of the data.

3. RESULTS AT HIGH SECTOR SPEEDS WITH VARYING LIGHT INTENSITY

We shall first consider results obtained with very fast sector speeds (60 light flashes per sec. is sufficient—see Section 4), at 200° and an acetaldehyde pressure of 10 cm. Towards the end of the preceding paper⁵ it was suggested that we should plot $\log K_s$ against ρ_∞ and compare with the theoretical curve. (Here

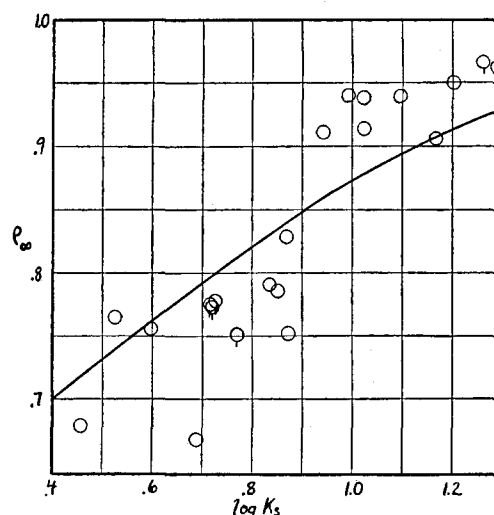


FIG. 1. Experiments at high sector speed.

$K = -(\text{CH}_3\text{CHO})^{-1}d(\text{CH}_3\text{CHO})/dt$ with the subscript s referring to the case of continuous illumination, and ρ is defined by Eq. (14) of the preceding article. ρ_∞ refers to rapid sector speed.) Essentially this has been done in Fig. 1. However, on account of the possible doubt expressed above, as to the effective volume of the reaction cell, we have preferred to use a special set of units for K_s , so that it may be closely related to the experimental data. We have, therefore, used the pressure in cm of non-condensable product gases, (essentially $\text{CO} + \text{CH}_4$) measured dry at 25°C, in a calibrated volume of 0.100 cc, (or corrected to the equivalent thereof) produced by 1 minute of continuous irradiation of acetaldehyde at 10.0 cm pressure and 200°C. This, of course, assumes that the illuminated volume is constant, though unknown, and does not eliminate errors caused by variation in the illuminated volume. The gases were actually measured wet, so a correction was made for water vapor pressure, as well as corrections for slight changes in conditions, as room temperature and pressure of acetaldehyde (which was always within 2 or 3 percent of 10.0 cm). Most of these runs (plain circles) are from a single series which was performed within a limited time using 120 flashes per second and varying the light intensity. The circles with tails represent runs done at various times in the course of the research—some of these were at 60 flashes per second. All runs performed after December 1,

1940, at 10 cm and 60 or 120 flashes per second are included, except a few which were spoiled.

The theoretical curve, from Fig. 3 of the preceding paper, is shown in Fig. 1 for comparison with the experimental points. Only the shape of it is important; since the actual rate constants are not yet known, the theoretical curve may, for comparison, be shifted arbitrarily along the axis of abscissas, thus determining $k_2\gamma$ (see Eq. (12b) of the preceding article). The curve shown corresponds to a value of $k_2\gamma = 1.58$, in the units described above.

It is probably true that the experimental points fit the theoretical curve within the limits of accuracy; however, there seems to be a trend in the experimental points toward a more rapid decrease than is anticipated theoretically in ρ_∞ as K_s decreases, and this may well be real. If K_s were proportional to $I_{\text{abs}}^{1/2}$ throughout the range, ρ_∞ would remain at 1. The fact that ρ_∞ falls off from 1 indicates that at low values of K_s , i.e., at low I_{abs} values, K_s is beginning to deviate in the direction of proportionality to I_{abs} instead of $I_{\text{abs}}^{1/2}$; this means that at these low intensities K_s decreases more rapidly than $I_{\text{abs}}^{1/2}$. The trend in the experimental results means that the onset of this effect comes in more suddenly than mechanism III would lead one to expect. A probable explanation of this is that reaction (4), which probably occurs at the walls, increases in importance at the lower light intensities. The chain time, of course, increases as the light intensity decreases. From the calculation in the Appendix, it may be inferred that the rate of diffusion of radicals is such that probably only a moderate number of them get to the wall at the highest intensities used by us, but that they begin to reach the walls in large numbers at only slightly lower intensities. The result is an effective increase in k_4 at the low intensities. If the choice of chain-breaking step, made at the end of Section 1, is correct, we might also expect an apparent increase in k_3 under these conditions, which would also contribute to the discrepancy observed. On the other hand, the greater diffusion which takes place at low light intensities has a tendency to lower the concentration of free radicals, which would then be expected to have a relatively longer life period, thus causing K_s to decrease abnormally slowly rather than ab-

normally rapidly. However, this would probably only partially counterbalance the effect of the changes in k_4 and k_3 .

4. RESULTS WITH VARYING SECTOR SPEEDS

A large number of runs were made at 10 cm and 200°C, with varying sector speeds and at a number of different light intensities. With the exception of a few which were done at odd light intensities and those known to be spoiled, all done after December 1, 1940 are presented in Table I. K_s is expressed as described in the preceding section. The value of K_s is always taken from a continuous run just preceding or just following the intermittent run (or it is the average of such runs). The conditions for the continuous run were always kept as near as possible to those of the intermittent run. Slight variations in conditions were corrected for; in particular, slight variations in light intensity, as recorded by the photo-cell, were corrected for by assuming the rate to be proportional to the square root of the intensity, and this was sufficiently good for the small corrections involved. The corrections were always applied to the continuous run. The value of δ , which is the parameter determining the relative importance of the chain-breaking steps III (3) and III (4), was obtained from K_s by means of Eq. (12b) of

TABLE I. Experiments at 200° and 10 cm. $k_2\gamma = 1.585$.

K_s	Flashes per sec.	ρ	δ	$\delta(\text{corr.})$	$\rho(\text{corr.})$	$t(K_s + k_2\gamma)$
3.30	$\frac{1}{2}$	0.540	0.325	0.35	0.537	2.44
3.30	1	.570	.325		.563	1.220
2.78	2	.668	.3635		.675	.545
2.97	$\frac{1}{2}$.535	.348		.534	2.275
2.86	1	.592	.356		.595	1.110
2.74	2	.612	.366		.619	.540
2.69	4	.682	.370		.694	.267
2.72	8	.666	.368		.675	.1343
7.96	1	.652	.1659	.17	.650	2.385
7.41	4	.804	.1760		.809	.562
7.59	15	.766	.1730		.768	.1528
19.52	120	.962	.0750	.075	.962	.0440
18.28	60	.966	.0799		.970	.0828
18.54	32	.901	.0788		.904	.1572
18.75	16	.953	.0779		.955	.318
20.20	32	.945	.0728		.943	.1702
20.24	2	.710	.0725		.708	2.73
20.32	4	.787	.0723		.785	1.369
21.00	8	.886	.0702		.882	.706
20.73	1	.601	.0710		.598	5.58
19.95	$\frac{1}{2}$.576	.0736		.575	10.76
28.47	8	.884	.0527	.050	.886	.939
30.20	4	.773	.0498		.773	1.986

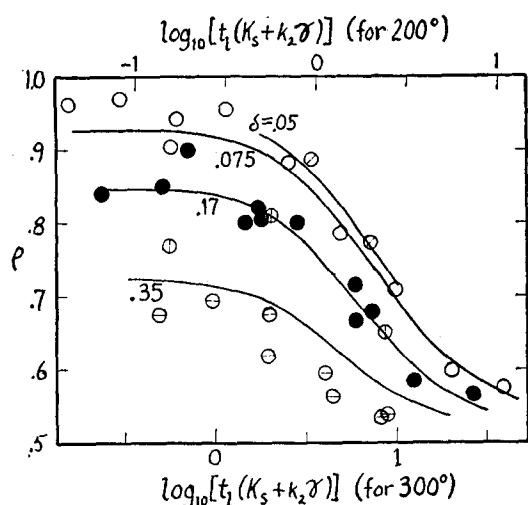


FIG. 2. Experiments at 10 cm, varying sector speeds. Open circles, 200°, with values of δ as follows: \circ , 0.05; \odot , 0.075; \oplus , 0.17; \ominus , 0.35. Black circles, 300°, $\delta=0.17$.

the preceding article,⁵ using $k_2\gamma=1.58$, as determined in Section 3. It will be noted that in Table I the runs occur in groups, clustering around certain values of δ . To get a basis of comparison all the runs in a group were corrected to a definite value of δ , as shown in the table. These corrections were made holding $t_1(K_s+k_2\gamma)$ constant (which is equivalent to holding b , of the preceding article, constant) and determining from Fig. 2 of the preceding article, how much ρ should be changed to correspond to the indicated change in δ .

A similar set of results at 300° and 12.1-cm pressure (same concentration as 10-cm pressure at 200°) is shown in Table II. The value of $k_2\gamma=16.9$ was obtained directly from the runs at 60 and 120 flashes per second. It was assumed that in these runs $\rho=\rho_\infty$, the value of δ then being obtained from the uppermost curve of Fig. 2 of the preceding article. $k_2\gamma$ was then obtained directly from Eq. (12b) of the preceding article, and the average taken for the two runs noted. The non-condensable gas produced was measured in a larger calibrated volume, but the results are corrected to 0.100 cc, so the units are the same as in Table I. The last five runs of Table II were made by Mr. G. W. Murphy; they were the last five made by him. Some runs made before these, which were very erratic, were discarded on the grounds that this operator

had not yet become familiar with the technique.

Since the selection of the value of k_2/k_3 from the data of previous investigators needs some discussion, and since K_s is in special units, it seemed advisable to plot ρ against $\log [t_1(K_s+k_2\gamma)]$ in this instance, a slight deviation from the procedure recommended in the preceding article. $t_1(K_s+k_2\gamma)$ is proportional to b at any temperature, and results at different temperatures can be compared on the same graph by displacing the origins of abscissas with respect to each other. This has been done in Fig. 2, where a comparison of all the data with theoretical curves is given. It is seen that the agreement is as good throughout as could be expected from Fig. 1.

Since the deviation in Fig. 1 is probably real, however, it seems more reasonable, when attempting to calculate rate constants and consider temperature coefficients, to use the value of $k_2\gamma$ actually corresponding to the curve for the particular value of δ . Thus if we calculate $k_2\gamma$ for the set of runs with $\delta=0.075$ in Table I in a way similar to that used to calculate $k_2\gamma$ for Table II, we find, approximately, $k_2\gamma=0.79$. If now we recalculate δ on this basis, we find the values cluster about 0.04 rather than 0.075. The results thus obtained were corrected as before and are shown in Fig. 3, which includes, also, the results at 300°, but only the one set of results at 200°. The latter were (save for two runs) the most recent runs made at 200°, and are, we believe, the most reliable. Furthermore, the conditions as to light intensity were closely comparable to those at 300°. We shall, therefore, use Fig. 3 as a basis for the calculation of rate constants and temperature coefficients.

TABLE II. Experiments at 300° and 12.1 cm. $k_2\gamma=16.9$, $\delta(\text{corr.})=0.17$.

K_s	Flashes per sec.	ρ	δ	$\rho(\text{corr.})$	$t_1(K_s+k_2\gamma)$
74.0	8	0.788	0.186	0.800	2.84
76.8	4	.708	.180	.715	5.86
75.8	16	.791	.182	.801	1.449
69.0	30	.879	.197	.900	.715
83.6	2	.586	.168	.585	12.58
78.7	4	.662	.177	.666	5.97
99.4	16	.826	.146	.805	1.819
100.0	4	.696	.145	.678	7.30
104.2	60	.875	.140	.850	.505
97.9	120	.859	.148	.840	.239
92.0	16	.831	.155	.820	1.701
89.1	1	.570	.159	.566	26.5

5. CALCULATION OF THE RATE CONSTANTS

In order to evaluate K_s in absolute terms, it is necessary to know the effective volume in which the reaction occurs. This will necessarily depend upon the diffusion of the free radicals, for if the radicals can diffuse out of the light path to any appreciable extent, the effect becomes that of a less intense beam illuminating a larger volume. An approximate treatment is given in the Appendix. The effective volume in our experimental set-up is estimated to be 35 cc, which enables us to convert K_s to sec.^{-1} . The conversion factor for 200°C is

$$0.100/35 \times 0.50 \times 473/298 \times 1/60 \times 1/10 \\ = 3.78 \times 10^{-6}.$$

The first fraction converts from the calibrated volume to 35 cc, the second term relates the number of molecules of acetaldehyde decomposed to the number of permanent gas molecules formed, the third factor corrects the temperature to the furnace temperature, the fourth converts min.^{-1} to sec.^{-1} , and the denominator of the last factor is the pressure of the acetaldehyde. For 300°C the conversion factor is the same, since the pressure is 12.1 cm, which compensates the change in temperature.

Since we made no determination of the absolute intensity of our light source, it is necessary to evaluate $k_2/k_3^{1/2}$ from the work of previous investigators. On account of the wide light beam used, it may be shown that the diffusion in Grahaime and Rollefson's experiments⁶ at high intensities is not important. Since they based their calculations on the actual illuminated volumes, and since their intensity was high at 200° and 3130Å, it seems reasonable to use their value of $k_1^{1/2}k_2/k_3^{1/2}$ of 40 Einsteins^{-1/2} cc^{1/2} sec.^{-1/2}. With a value of k_1 of 0.7, following Gorin,⁹ we then get $k_2/k_3^{1/2} = 48$.

However, because their light intensity at 300° was considerably lower, and since the unimolecular chain-breaking step seems to be much more important at 300°, we do not believe we should use their temperature coefficient. Rather, for this purpose, we turn to the work of Leermakers,⁶ since his light intensity was considerably higher. The difference between Grahaime and Rollefson's and Leermakers' results at 200°

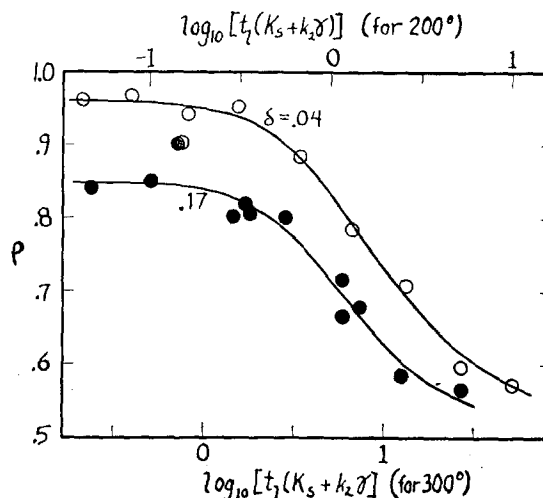


FIG. 3. Experiments at 10 cm, varying sector speeds. Open circles, 200°, $\delta = 0.04$. Black circles, 300°, $\delta = 0.17$.

undoubtedly rests largely on the fact that the former based their calculations on the actual illuminated volume, while Leermakers assumed his radicals diffused uniformly through the cell. In this assumption, Leermakers was, with his high light intensities, undoubtedly wrong. If we assume Grahaime and Rollefson's constants to be correct, we find that Leermakers' effective volume must have been 15 cc. With a cell of 41-cc capacity, and his set-up, this is not unreasonable, though perhaps slightly low. Using 15 cc, the value of I_{abs} in most of Leermakers' experiments at about 10-cm pressure was about 10^{-10} Einstein per cc per sec., while for their highest intensity, at around 10 cm, Grahaime and Rollefson's I_{abs} was about 10^{-11} Einstein per cc per sec. Leermakers' very high light intensity should make the diffusion fairly small, and should assure that a correct value of the activation energy $E_2 - \frac{1}{2}E_3$ of $k_2/k_3^{1/2}$ will be obtained from the results. We, therefore, adopt his value of 10 kcal. per mole.²⁰ We feel that this is a very

²⁰ If we compared runs at equal deflections of the galvanometer, we found a temperature coefficient not higher than Grahaime and Rollefson's. As stated, however, we do not believe our intensity measurements are comparable unless the optical system is left practically unchanged. A few runs, made later by Mr. G. W. Murphy, during which the optical system was kept as constant as possible, gave a very consistent set of results, though their absolute rates appeared much higher than we expected for the galvanometer deflections obtained. These checked Leermakers' temperature coefficient almost exactly.

TABLE III. Summary of rate constants.

Symbol	Units	Expt. rate constants		Act. energies Cal. per mole reaction	Collision numbers	
		At 200°	At 300°		At 200°	At 300°
$k_2/k_3^{1/2}$	mole ⁻¹ cc ^{1/2} sec. ^{-1/2}	48	306	10,000		
k_3	mole ⁻¹ cc sec. ⁻¹	4.0×10^{14}	6.6×10^{14}	2,600	$\left\{ \begin{array}{l} 1.9 \times 10^{14} \\ 0.21 \times 10^{14*} \end{array} \right\}$	$\left\{ \begin{array}{l} 2.1 \times 10^{14} \\ 0.34 \times 10^{14*} \end{array} \right\}$
k_2	mole ⁻¹ cc sec. ⁻¹	9.7×10^8	7.8×10^9	11,300	$1.5 \times 10^9*$	$1.2 \times 10^{10*}$
k_4	sec. ⁻¹	2.5	10.8	7,800	12*	49*

* These collision numbers have been multiplied by the appropriate Arrhenius factor.

reasonable solution of the difficulty regarding the temperature coefficients, though the fact that in our experiments the reproducibility as regards the rate of reaction observed for a given current from the photo-cell appears to be less good at 300° than at 200°, together with the fact that the unimolecular chain-breaking reaction appears to be more important at 300°, suggests the possibility that an unreproducible wall reaction at 300° may affect the results. This matter obviously needs further investigation.

With K_s known in absolute units, and with $k_3^{1/2}/k_2$ evaluated, it is a simple matter to find k_3 itself. Comparison of Fig. 3, in which the abscissa is given in terms of the experimental value $t_i(K_s + k_2\gamma)$, with the theoretical curve in which the abscissa is the log of the defined quantity $b = t_i(K_s + k_2\gamma)(k_3^{1/2}/k_2)k_3^{1/2}$ (see Eq. (1a)) tells us what value of $t_i(K_s + k_2\gamma)$ corresponds to a given value of b , thus enabling us to solve for k_3 . Knowing k_3 and $k_3^{1/2}/k_2$ we find k_2 ; knowing k_2 , k_3 , and $k_2\gamma = k_2k_4/2k_3$ (see Eq. (1b)) we find k_4 . The results are given for 200° and 300° in Table III. The corresponding activation energies are also given. Included also, for comparison, are certain theoretically calculated quantities, which will be discussed below.

The values in Table III are not to be considered as highly accurate, but the orders of magnitude are undoubtedly correct. An idea of the possible errors involved may be obtained by calculating k_3 for 200° from Fig. 2 instead of Fig. 3, using the same set of runs. If we do this we find $k_3 = 2.1 \times 10^{14}$, differing by an almost twofold factor from the value tabulated. Further, there is some uncertainty in $k_2/k_3^{1/2}$ itself, due in greatest measure to uncertainty in k_1 . The value of k_3 given is, then, certainly a rough approximation; but it is of great interest, nevertheless, and is correct to within the same order of ac-

curacy as it is generally possible to determine the frequency factor of the rate constant of a chemical reaction. k_2 is probably about twice as accurate as k_3 (outside of possible error from k_1) since it is calculated from a relation involving $k_3^{1/2}$. k_4 at 200°, calculated from Fig. 2, is about 50 percent greater than calculated from Fig. 3. It is quite possible, however, that the errors in k_4 are larger than this would indicate. Since, as seen from Fig. 1, the theoretical equation for the rapidly moving sector is not exactly obeyed, the significance of k_4 , found by applying this equation, is in some doubt, and the number of runs at 300° is small. We do not believe that these same doubts apply with anything like equal force to k_2 and k_3 , at least at high intensities where the importance of the unimolecular chain-breaking step is not great. On account of the greater importance of the unimolecular reaction at 300°, they may affect the temperature coefficient of k_2 and k_3 somewhat. For example, if we should neglect the unimolecular chain-breaking reaction at both temperatures, we would get an energy of activation E_3 of over 13 kcal. This is so large as to be utterly impossible, as will be clear from the discussion in the next section. Therefore, the fact that the value of E_3 in Table III is quite reasonable lends some confidence in the validity of our calculation of k_4 .

6. INTERPRETATION OF THE RESULTS

It is, of course, not absolutely certain which of the chain-breaking steps in mechanism III is the principal one. However, as a matter of fact, it is not very important for the purpose of interpreting the numerical results given in Table III, and we shall simply assume, as at the end of Section 1, that reaction III (3) is the correct one. It is then indicated that we should

compare k_3 with the collision number for CHO and CH₃ (by collision number we mean the number of collisions per cc per sec. with both substances at unit concentration). This calculated collision number (based on an effective σ^2 of 10^{-15} cm², σ being the collisional diameter) is given in the last columns of Table III. The effective collision number, i.e., the collision number multiplied by the Arrhenius factor $e^{-2100/RT}$ is also given.²¹ It is seen that k_3 is of the same order of magnitude as the collision number. The Arrhenius factor reduces the effective collision number to the point where it is one-twentieth of k_3 . In view of the various uncertainties involved, both in k_3 itself and its temperature coefficient, as well as in σ , such a factor is probably within the expectations. It would appear to indicate, however, that the value of E_3 is probably somewhat less than 2600 cal., and that we may reasonably say that E_3 lies between 2600 cal. and $\frac{1}{2}RT \sim 500$ cal.

Since reaction occurs at practically every available collision, it is seen that the reaction is not slowed down to any appreciable extent by the necessity of mutual orientation of the reactants. The reaction is, therefore, a case in which the "hypothesis of exact orientation"²² does not hold. This would be unexpected if the reaction involved transfer of an atom and formation of CH₄ and CO. It would, perhaps, seem less surprising if the collision of CH₃ and CHO resulted in the formation of a molecule of acetaldehyde.²³ There are other cases in which methyl radicals do not seem to need to be completely oriented;²² we have had, of course, little experience with CHO radicals.

The theoretical value of k_2 is calculated in essentially the same way as k_3 . k_2 is compared with the collision number for CHO with CH₃CHO (again calculated using $\sigma^2 = 10^{-15}$ cm²) multiplied by $e^{-10,800/RT}$. It again appears that reaction occurs at practically every collision in which the necessary energy is available, showing little or

no effect of orientation. This is certainly surprising if an ordinary chemical reaction, such as addition of the CHO to acetaldehyde, as suggested in Section 1 is involved. It may, perhaps, be taken as evidence in favor of the suggestion of Burton that the CHO induces a predissociation in the acetaldehyde, provided some certain degree of freedom in the latter is already at the proper energy, presumably corresponding to the crossing of a repulsive potential energy curve with an attractive one, though the predissociation must be induced with extremely high efficiency. The energy at which the crossing occurs is close to $E_2 - \frac{1}{2}RT + RT \cong 11.8$ kcal., or about half a volt, above the lowest point of the potential-energy curve of the ground state.

Although this interpretation seems most reasonable on the basis of the photochemical reaction alone, it is not entirely satisfying when one considers the azomethane-induced reaction. If the chain-carrying step of this reaction differs merely in that a methyl radical, instead of a formyl radical, induces the predissociation, one could, indeed, suppose that reaction I (2) would be slower, but one would hardly surmise that it would have a higher activation energy, since this quantity should depend entirely on the properties of the acetaldehyde. Yet Allen and Sickman's experiments on the induced reaction indicate that E_2 must be appreciably higher than is the case with the photochemical reaction. The explanation of this apparent anomaly is not clear.

In the case of k_4 , the values in Table III offer rather good evidence that the unimolecular chain-breaking step does not occur in the gas phase. If it did occur in the gas phase it certainly could not be a strictly first-order reaction, but, rather, it would be an unimolecular reaction in the low pressure, second-order stage. CHO is such a small molecule that one would expect that once it attained the necessary activation energy it would decompose before the next collision. It ought to react, therefore, after every collision with acetaldehyde in which it obtains the necessary energy, and this would be the total number of collisions multiplied by the Arrhenius factor $e^{-7300/RT}$. However, it will be noted that CHO reacts with acetaldehyde in a chain-carrying step only if there is available a

²¹ The energy of activation, 2600 cal., given in Table III, includes the intrinsic collisional activation, $\frac{1}{2}RT$ of collision. (See H. Gershinowitz and O. K. Rice, J. Chem. Phys. 5, 275 (1934). The collisional activation energy has been subtracted out in calculating all Arrhenius factors.

²² O. K. Rice and H. Gershinowitz, J. Chem. Phys. 3, 479 (1935).

²³ See E. Gorin, Acta Physicochimica 9, 692 (1938).

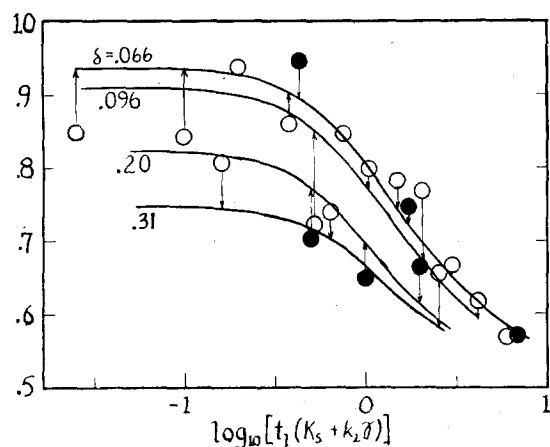


FIG. 4. Experiments at higher pressures and 200°. Open circles, 20 cm. Black circles, 40 cm. Arrows indicate the curve on which point should lie.

higher excess energy than 7300 cal. If the chain-breaking step did, therefore, go in the gas phase, it ought to go faster than the chain-carrying step, which does not happen, and would, indeed, be an impossibility. Therefore, we believe that reaction III (4) must be a wall reaction. Accordingly, we have calculated the number of collisions with the walls. The figure given in Table III is the total number of collisions with the walls, taking into account the whole surface of the reaction vessel, divided by the total number of CHO's in the reaction vessel, assuming them uniformly distributed throughout the whole vessel, multiplied by $e^{-7300/RT}$. Since the total number of collisions and the total number of radicals are both proportional to the concentration, the quantity given is independent of the concentration, and is directly comparable to k_4 . Since the assumption of uniform distribution is not correct, it is certainly not surprising that the calculated values are larger than the observed.

It should be noted that the experimental k_4 's given are apparent values for high light intensities. At low intensities k_4 does actually appear to increase, as we have already noted, corresponding to the expectation for a more uniform distribution of radicals. It should be emphasized, however, that in view of the uncertainties involved in the determination of k_4 , no exact correspondence between experi-

mental and calculated values could be looked for. The check in order of magnitude does seem likely to be significant.

7. RUNS AT HIGHER PRESSURES

A number of runs were made at 200° at pressures of 20 cm, and 40 cm, especially in the earlier stages of the research. The accuracy of these runs is considerably lower than that of the runs at 10 cm, and they suffer further from the rather great variation in light intensity through the reaction vessel, because of absorption of the beam as it goes through the cell. Nevertheless, it seemed worthwhile to present these runs, and they are given in Table IV and Fig. 4. Since their accuracy was not high, small corrections for room temperature, slight variations in pressure, etc., amounting to only a few percent, were not made. Furthermore, in the various series of runs, only an average K_s is given, the variation in $t_1(K_s + k_2\gamma)$ being assumed to come solely from t_1 . This was a reasonably good approximation. Some of the runs listed in Table IV are really averages of several runs, the number so averaged being indicated.

We have compared these runs with the curves in Fig. 4 on the basis of the assumption that reaction III (4) occurs at the walls. If reaction III (4) occurred in the gas phase, k_4 , and hence $k_2\gamma$, would be proportional to the acetaldehyde pressure. If the reaction occurs at the walls, k_4 will be unchanged provided the amount of diffusion is the same. Examination of Fig. 1 indicates that at the higher light intensities the points pretty well parallel the theoretical curve, indicating a nearly constant apparent k_4 , undoubtedly caused by compensating factors already mentioned. At higher pressures, this region of constant apparent k_4 should extend to considerably lower light intensities, because the amount of diffusion is decreased. We have, accordingly, in constructing Fig. 4, used the same value of $k_2\gamma$ which was used in Fig. 3, except in one case of very low light intensity, where the value used for Fig. 2 was assumed. It is to be remembered that Figs. 2 and 3 give different values of $(k_3^{1/2}/k_2)k_3^{1/2}$, and in getting the relation between $t_1(K_s + k_2\gamma)$ and b , which is necessary in setting up the curves in Fig. 4, we

have in each case used the appropriate value of $(k_3^{\frac{1}{2}}/k_2)k_3^{\frac{1}{2}}$. Thus the position of each curve in Fig. 4 is definitely fixed by previously discussed data, and is not specially adjusted to fit the data of Table IV.

It will be observed that the experiments fit the curves in Fig. 4 about as well as could be expected, and it may also be stated that they fit better than would be the case if k_4 were assumed to be proportional to the acetaldehyde pressure. A set of such experiments of higher accuracy, and performed in a shorter reaction vessel, would be highly desirable, as would also experiments in the presence of an excess of inert gas. Similarly, experiments at 300° would also be desirable. It is barely possible that decomposition of HCO could occur in the gas phase at 300°, and that we are actually observing a surface reaction at 200°, but that this surface reaction is overwhelmed at 300° by a gas-phase reaction. If the surface reaction had an activation energy considerably less than 7800 cal. and the gas-phase reaction an activation energy considerably higher, this could produce the results we have obtained, though the correspondence between our experimental and calculated results makes it seem somewhat improbable. Experiments at high pressures or in the presence of inert gases at 300° could settle this question definitely, and experiments at higher temperatures would likewise be of interest.

We should like to close with a word of propaganda in favor of the rotating sector. We feel that the above results make it clear that the use of intermittent light is a powerful instrument for the study of the individual steps in a chain reaction, giving an insight into the mechanism which would not otherwise be possible. The rotating sector has been much exploited in the study of photosynthesis; in the study of gas-phase reactions, though some interesting work has been done,³ its possibilities have scarcely been touched. Yet, aside from the fact that more runs are required, it adds little in the way of technical difficulties which are not already present in ordinary photochemical experiments. The use of the rotating sector should become a routine procedure in the study of chain photolyses.

APPENDIX—THE DIFFUSION OF THE FREE RADICALS

The problem of the diffusion of radicals through acetaldehyde can be handled approximately by a relatively simple application of the diffusion equation. Since our reaction vessel is a fairly long cylinder, the equation may be written in the form

$$\frac{dA}{dt} = \frac{D}{r} \frac{d}{dr} \left(r \frac{dA}{dr} \right) + k_1 I_{\text{abs}} - k_3 A^2 - k_4 A, \quad (2)$$

where t is the time, A the concentration of free radicals, r the distance from the axis of the cylinder, and D the diffusion constant. The first term on the right-hand side of the equation is the rate of increase in concentration at any point due to diffusion; the second term is the rate of formation of radicals per cc by absorption of light (this term is zero where the cell is dark), and the last two terms give the rate of destruction of radicals by chemical action.

In the case of continuous illumination a steady state is reached in which $dA/dt = 0$, and theoretically it should be possible to handle the resulting equation in r . Even if the first term on the right is replaced by the term $D d^2 A / dr^2$, appropriate to a one-dimensional problem, and the term $k_4 A$ is neglected, the result eventually involves an elliptic integral. Further, the boundary conditions at the point at which I_{abs} becomes zero are complicated, involving parameters whose numerical values can only be found after the equation is solved. Under these circumstances, it seems desirable to use a rougher but considerably easier method of approximation.

In the presence of an overwhelming excess of acetaldehyde, the diffusion of any given radical will depend only on the acetaldehyde, and be entirely independent of the other radicals. Since this is the case, we may consider that the light shining at any moment into the reaction

TABLE IV. Experiments at 200° and higher pressures.

Flashes per sec.	ρ	Number runs	Flashes per sec.	ρ	Number runs
$p = 20 \text{ cm}$ $k_2\gamma = 0.8$			$p = 20 \text{ cm}$ $k_2\gamma = 0.8$		
	$K_s = 11.3$ $\delta = 0.066$			$K_s = 7.5$ $\delta = 0.096$	
120	0.849	1	4	0.722	1
30	.843	1	2	.799	1
15	.938	2	1	.767	1
8	.860	4	$\frac{1}{2}$.616	1
4	.846	4			
2	.781	4	$p = 20 \text{ cm}$ $k_2\gamma = 1.6$		
1	.666	3		$K_s = 3.55$ $\delta = 0.31$	
$\frac{1}{2}$.568	3	8	0.806	1
			2	.739	2
			$\frac{1}{2}$.655	1
$p = 40 \text{ cm}$ $k_2\gamma = 0.8$			$p = 40 \text{ cm}$ $k_2\gamma = 0.8$		
	$K_s = 13.0$ $\delta = 0.058$			$K_s = 3.2$ $\delta = 0.20$	
8	0.945	1	2	.702	1
2	.745	1	1	.648	1
$\frac{1}{2}$.570	1	$\frac{1}{2}$.664	1

The pressure has been so handled that K_s is in the same units as in Tables I and II and strictly comparable thereto.

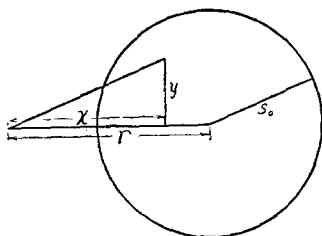


FIG. 5. Notation for Eq. (8). The circle outlines cross section of the illuminated cylinder.

vessel produces, in the case of a system with approximate cylindrical symmetry, a set of instantaneous line sources, each of which will diffuse independently of the others according to the differential equation

$$\frac{dA'}{dt} = \frac{D}{\rho} \frac{d}{d\rho} \left(\rho \frac{dA'}{d\rho} \right), \quad (3)$$

where now ρ is the radial distance to the source, and A' is the concentration due to the source. As is well known, the following solution of the equation gives A' at a distance ρ after elapse of the time t :

$$A' = at^{-1} \exp(-\rho^2/4Dt). \quad (4)$$

If the strength of the instantaneous line source is 1 radical produced per length of source, then we have

$$\int_0^\infty 2\pi\rho A' d\rho = 1,$$

which gives

$$a = (4\pi D)^{-1}. \quad (5)$$

The above treatment does not consider the destruction of the radical, but is adequate to take care of the average diffusion of any radical until it is destroyed. The radical, it should be noted, may take part in the chain without being effectively destroyed, since it is almost immediately replaced by another radical.

Now the rate of destruction of radicals is, if we neglect the unimolecular term, $k_3 A^2$. Therefore, the probability of destruction of any radical in unit time is $k_3 A = 1/\tau$. If A were a constant for all points in space and time (the usual steady-state assumption), out of any n_0 radicals produced at any given instant, a number n would survive after time t , given by

$$n = n_0 e^{-t/\tau}. \quad (6)$$

If we have n_0 sources per unit volume produced by the light per unit time, then, if there were no diffusion, the total concentration at any point would be the sum of the concentrations left from all previous times. We should then have

$$A = \int_0^\infty n dt = n_0 \tau. \quad (7)$$

We shall now make the assumption that τ is the same for all radicals. This is certainly not by any means true for the region outside the illuminated cylinder, which is just the region we are interested in; it obviously tends to underemphasize the diffusion. However, the chance that any radical will survive to reach a point outside the region

of illumination depends not only on the concentration at that point, but also on the greater concentrations through which it had to travel to reach the point. Also τ is actually obtained directly from the experimental data, so that it represents an average in which the effect of diffusion is already included, though, of course, this does not completely correct for the greater lifetimes of radicals which have wandered outside the beam. As will be shown later, however, the approximations to be made in the integrations will be in the direction to nullify the error.

With the assumption of constant τ , the total concentration at any point outside the illuminated cylinder will be given by adding up the effects of all sources which have been produced in past time. The concentration due to any given source is given by Eqs. (4) and (5), so the steady state concentration is given by (for notation see Fig. 5)

$$A_s = n_0 (4\pi D)^{-1} \int_0^\infty dt \int_{r-s_0}^{r+s_0} dx \int_{-y_0}^{y_0} dy \left(t^{-1} \exp\left(-\frac{x^2+y^2}{4Dt}\right) \exp\left(-\frac{t}{\tau}\right) \right), \quad (8)$$

where $y_0 = (s_0^2 - (r-x)^2)^{1/2}$. Integrating first with respect to y , we note that if y_0 is quite large we have what is essentially a complete probability integral. As y_0 decreases, corresponding to regions of x near the edge of the cylinder, the integral with respect to y also decreases, and when

$$y_0 = 0.5(4Dt)^{1/2} = (Dt)^{1/2} \quad (9)$$

the value of the integral is about half the value of the complete integral.²⁴ The complete result of integration with respect to y is a rather complex function of x , which makes integration with respect to x impossible. We shall handle this situation approximately by setting²⁵

$$\int_{-y_0}^{y_0} \exp\left(-\frac{y^2}{4Dt}\right) dy = (4\pi Dt)^{1/2} \quad (10)$$

if $y_0 \geq (Dt)^{1/2}$ and 0 if $y_0 < (Dt)^{1/2}$. This is equivalent to replacing the integral with respect to y by $(4\pi Dt)^{1/2}$ in Eq. (8) and restricting the integration with respect to x to limits between $x = r \pm (s_0^2 - Dt)^{1/2}$. At the upper limit $\exp(-x^2/4Dt)$ will, in the cases involving a moderate amount of diffusion which we shall encounter in practice, be so low that we may set $x = \infty$. If we replace x by $v = x/(4Dt)^{1/2}$ in the integral, and set $v_0 = [r - (s_0^2 - Dt)^{1/2}]/(4Dt)^{1/2}$ Eq. (8) becomes

$$A_s = n_0 \pi^{-1/2} \int_0^\infty dt e^{-t/\tau} \left[\int_{v_0}^\infty \exp(-v^2) dv - \int_0^{v_0} \exp(-v^2) dv \right] = \frac{n_0}{2} \int_0^\infty dt e^{-t/\tau} \left[1 - P\left(\frac{r - (s_0^2 - Dt)^{1/2}}{(4Dt)^{1/2}}\right) \right], \quad (11)$$

where P as a function of the argument written is to be read directly out of Peirce's table of the probability integral previously referred to.

Finally, we have to consider the integration with respect to t . Since the quantity in brackets does not vary very greatly with t , it seems reasonable, as an approxima-

²⁴ See B. O. Peirce, *A Short Table of Integrals* (Ginn and Company), 1910, p. 116.

²⁵ B. O. Peirce, reference 24, p. 63.

tion, to consider the bracket a constant, with $t = \tau$. Our final result, then, is

$$A_s = (n_0\tau/2) \left[1 - P \left(\frac{r - (s_0^2 - D\tau)^{1/2}}{(4D\tau)^{1/2}} \right) \right]. \quad (12)$$

This expression is approximately valid for any point *outside* the illuminated cylinder in the reaction cell. We shall now find the concentration $A_s(0)$ at the *center* of the reaction cell, and this will be sufficient to enable us to plot a reasonably good curve. n_0 sources at any point at a distance ρ from the center of the cell would contribute a concentration $n_0(4\pi D t)^{-1} \exp(-\rho^2/4Dt)$ after a time t , if no recombination took place. We thus have

$$\begin{aligned} A_s(0) &= n_0(4\pi D)^{-1} \int_0^\infty dt \int_0^{s_0} t^{-1} e^{-t/\tau} \exp(-\rho^2/4Dt) 2\pi \rho d\rho \\ &= n_0 \int_0^\infty (1 - \exp(-s_0^2/4Dt)) e^{-t/\tau} dt \\ &= n_0\tau(1 - \exp(-s_0^2/4D\tau)). \end{aligned} \quad (13)$$

The approximation involved in the last step is legitimate in the cases to which it will be applied, since $\exp(-s_0^2/4Dt)$ is still not very different from zero when $t = \tau$.

Once we have a value of A_s as a function of r , we can find an effective volume V_e in which the reaction occurs. This is best done by comparing the number of radicals R_e destroyed per second, with the number R_i which would be destroyed if the same radicals were confined within the illuminated volume V_i . Since the number destroyed per unit volume depends upon the square of the concentration of radicals, and since R_e and R_i are taken over the whole volume, we see that

$$R_e/R_i = (A_e^2/A_i^2) V_e/V_i = V_e/V_i,$$

where $A_i V_i = A_e V_e$ = total number of radicals present. But

$$R_i = k_3 A_i^2 V_i$$

and

$$R_e = 2\pi k_3 l \int_0^\infty A_s^2 r dr$$

where l is the length of the reaction cell. Therefore

$$V_e = \frac{A_i^2 V_i^2}{2\pi l \int_0^\infty A_s^2 r dr}.$$

However, since the total number of radicals is to be equal to $A_i V_i$ we have

$$A_i V_i = 2\pi l \int_0^\infty A_s r dr. \quad (14)$$

Hence

$$V_e = \frac{2\pi l \left(\int_0^\infty A_s r dr \right)^2}{\int_0^\infty A_s^2 r dr} \quad (15)$$

and if A_s can be obtained as a function of r from Eqs. (12) and (13), V_e can be evaluated.

In order to obtain A_s it is necessary to evaluate numerically the quantities in Eqs. (12) and (13). s_0 will be taken as the average radius of the beam of light in the reaction cell, which was not exactly cylindrical. This, in our experiments, was about 0.75 cm. τ and D we will evaluate specifically for the set of experiments at 200° included in Fig. 3.

τ may be evaluated directly from the experimental data. We have seen in the preceding paper that, when $b=1$, t_i is equal to the value τ_0 which the chain time would have if k_4 were zero.²⁶ For experiments at 200°, which are recorded in Fig. 3, we will make no great error in setting $\tau = \tau_0$. Then by direct comparison with the experimentally determined values of t_i we find $\tau = 0.03$ sec.²⁷ This, of course, is an average value, which, as mentioned above, already includes the effect of diffusion. It is further to be noted that, both on account of the appreciable absorption of light by the acetaldehyde in the length of our cell (about 45 percent absorbed), and the spreading of the beam, τ must actually vary considerably along the cell. Our procedure, however, certainly gives a reasonably good average. The fact that the light intensity varies along the reaction cell might also be expected to affect the effective value of l to be set into Eq. (15). However, it is $I_{\text{abs}}^{1/2}$ which determines the amount of reaction, and the value of $I_{\text{abs}}^{1/2}$ near the middle of the cell is sufficiently close to the mean of its values at the two ends, so that the correction which might be expected is probably small compared to the correction due to diffusion.

D may only be estimated indirectly. It seems reasonable to suppose that the diffusion coefficient of CHO radicals in acetaldehyde will be close to the diffusion coefficient of air into ethyl alcohol, or, what is the same thing, the diffusion coefficient of ethyl alcohol into air. The latter is given as 0.1088 cm²/sec. at 9.5° and 1 atmos. by Landolt-Börnstein.²⁸ The diffusion coefficient varies inversely as the pressure and directly as about the 1.75 power of the absolute temperature.²⁹ From this we calculate $D = 2.0$ at 200° and 10-cm pressure. This completes the necessary evaluation of the numerical quantities. Rather than

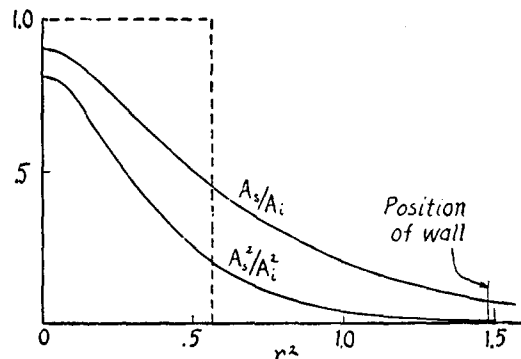


FIG. 6. Diffusion of the radicals.

²⁶ This is not altered in the modified mechanism we have assumed at the end of Section I.

²⁷ This may be compared with the value of 0.5 sec. reported in the preliminary note (reference 4). The preliminary note referred to an experiment in which the concentration of radicals was less and the chain time consequently longer, but the chief difference was due to a much rougher method of interpreting the data.

²⁸ Landolt-Börnstein, *Physik.-Chemische Tabellen*, Vol. 5, second edition, Supplement, p. 201.

²⁹ E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, New York, 1938), p. 198.

attempt to evaluate n , it is convenient to assume A_i to be given by Eq. (7), and calculate A_s/A_i . This quantity is given as a function of r^2 in Fig. 6 as is also $(A_s/A_i)^2$. From these curves it is easy to evaluate V_s , which turns out to be 35 cc. This corresponds to a radius of 1.06 cm, as compared to the value of s_0 of 0.75 cm.

At 300° the value of V_s may be taken as the same. D , of course, will be larger. The experiments indicate essentially the same value of τ_0 , but on account of the appreciable value of k_i in this case, τ will be smaller, and this will be almost sufficient to offset the increase in D . $D\tau$ will thus be sufficiently close, so that it is not worthwhile to make a separate calculation for 300°.

The value of V_s is, of course, extremely rough, but it may be remarked that the curves in Fig. 6 look very reasonable. The calculation of the concentration of radicals at the center of the cell should be fairly reliable, and it fits in well with the other points. By comparison of the area under the curve for A_s/A_i with that under the broken lines (which indicate the extent of the beam) it is observed

that Eq. (14) does not hold exactly, since the right-hand side appears to be about 10 percent larger than the left-hand side. This is undoubtedly due to the approximate integration used to obtain Eqs. (11) and (12). In obtaining Eq. (11) we overestimated the amount of diffusion, because the true contribution of the integration with respect to y goes to zero for $x < r - (s_0^2 - Dt)^{1/2}$ faster than it goes to 1 for $x > r - (s_0^2 - Dt)^{1/2}$. Also, setting $t = \tau$ in the argument of the probability function in Eq. (11) in order to get Eq. (12) was probably an overestimate for the average of t , and would result in an overestimate of A_s . It is difficult to say off-hand, whether these errors would more than compensate the underestimate of the amount of diffusion arising from the assumption that τ is constant throughout the volume. The discrepancy between the right- and left-hand sides of Eq. (14) is in the direction to be expected from a decrease in τ as the radical gets outside the illuminated cylinder; that it is not more than 10 percent suggests that the errors in integration have not overcompensated the error due to calling τ constant.

The Effect of Electrical Forces on the Stability of Colloidal Sols

W. G. EVERSOLE AND ALLEN L. HANSON

Division of Physical Chemistry, State University of Iowa, Iowa City, Iowa

(Received April 4, 1942)

It is assumed that the stabilizing potential in a sol is not the potential at a distance l from the surface of the particle, (ζ), but the potential at a distance λ , (λ). l is the distance from the solid surface at which a maximum in the potential energy curve determines the rate of coagulation, and λ is a constant for a given sol in states of equal stability. The quantities l and λ are evaluated from experimental data.

THE original concept of the relation of the ζ potential to the stability of a slightly hydrated sol was that in the stable sol the ζ potential of the particles was sufficiently high to prevent the close approach and adhesion of the particles. The addition of salt to the sol was supposed to lower the ζ potential to the critical potential, (ζ^*), and at this point coagulation of the sol would begin. It was assumed, at least by implication, that ζ^* was a constant for each sol.

However, it was soon demonstrated by data such as that of Ghosh,¹ which is given in Table I, that ζ^* was not a constant for a given sol, but in general was higher for salts having higher flocculation values. It was even observed by Kruyt and van der Willigen² that the addition of KCl

or $K_4Fe(CN)_6$ to an arsenous sulfide sol caused the ζ potential to *increase* until ζ^* was reached and coagulation began.

Nearly all modern attempts to interpret the significance of electrostatic forces in colloidal sols involve the use of the Debye-Hückel theory. The approximations involved in this theory introduce quantitative errors into calculations re-

TABLE I. Data of Ghosh (reference 1) for isostable states of the arsenous sulfide sol. (Coagulation time = 25–30 min.)

Salt	$C \times 10^3$ of moles +ion/l	ζ^* mv	$\lambda^* (= \psi_{l+16})$ mv
KNO ₃	70	45.8	10.8
KCl	68	43.2	10.4
MgCl ₂	1.02	15.0	10.6
SrCl ₂	0.98	14.6	10.6
BaCl ₂	0.92	14.2	10.2
AlCl ₃	0.3	15.1	11.2
Th(NO ₃) ₄	0.125	13.9	10.6

¹ B. N. Ghosh, J. Chem. Soc. p. 2693 (1929).

² H. R. Kruyt and P. C. Van der Willigen, Zeits. f. physik. Chemie **130**, 170 (1927).